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# Multi-Component Contaminants Transport of Heavy Metals in Clay Barriers

by

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**In the Name of God**
**The Compassionate, The Merciful**

To

Imam Mahdi and His Mother, Fatemeh

# Abstract

One major task facing the geoenvironmental engineering today is the development of methods to assess the long term changes, release and transport of contaminants from waste disposal sites, considering the hydrochemical interaction of the contaminants with the clay barrier. The prediction of the long-term leaching behaviour of heavy metals in multi-component contaminants, which represent a toxic threat to the local environment surrounding a landfill, is an increasingly important issue as awareness of the potential future pollution risks associated with landfills of such wastes grows.

Modelling of the leaching processes, which take place in a landfill, is an invaluable tool as it is often not possible to conduct experiments over sufficiently long timescales to observe the long term leaching behaviour of wastes. In this study the multi-component transport of heavy metals into a clay barrier has been investigated experimentally and theoretically by coupled solute transport and geo-chemical reaction. An experimental design for coupled solute transport and chemical reaction, based on the column leaching test in association with the batch equilibrium test for comparison, is proposed to examine the Cl and EDTA effects on the partitioning of Zn and Pb (dissolved, adsorbed, precipitated) into uncontaminated or; precontaminated kaolinite or; kaolinite mixtures with silica gel and calcium carbonate (K, KS, KC, KSC). The experimental results from the column leaching test were analysed in terms of adsorption, desorption and migration profiles of the each specific ion along the column depth and in the effluent at different pore volumes. It has been shown that the presence of other contaminants, especially inorganic and organic complexing agents, affect the distribution coefficient, Kd, which varies with time, space, soil constituents, cation exchange capacity (CEC), specific surface area (SSA) and pH of the soil solution. In most of the contaminant transport models Kd is often used as a constant parameter to describe the partitioning of a contaminant between the ground-water solution and the solid soil matrix.

A COupled Solute Transport and CHemical Equilibrium SPeciation (COSTCHESP) model was developed to simulate the transport of multiple thermodynamically reacting chemical substances through clay barrier systems. It consists of two main modules; a finite difference transport module

(COST), and an equilibrium geochemistry module (CHESP). This simplifies the coupling between the physical and chemical processes and leads to a simple and efficient model to simulate the simultaneous processes of advective-dispersive transport (advection; diffusion, osmotic and ion restriction effect) and geochemical reactions (complexation, exchange, precipitation, adsorption and desorption). The reliability of the model has been verified by laboratory experiments.The experimental results were used for the calibration of the proposed COupled Solute Transport Equilibrium Speciation (COSTCHESP) model and the heavy metals partitioning profiles at the different environmental conditions were predicted. The sensitivity of the parameters in the simulated model has been evaluated. It has been demonstrated that the model is a good tool for the prediction of multi-component transport of heavy metals into different clay soils under various environmental conditions.

The proposed model accounts for most of the hydro-geochemical interactions of the multi-components with the clay liner. The model will lead to proper identification of the form of specific ions ( i.e. adsorbed and precipitated on solid, and available in solution) and can be a useful tool for (i) assessing the importance of geochemical reactions on the transport of heavy metals in groundwater; (ii) predicting the forms by which the metals are partitioned in the clay barrier, and (iii) indicating the potential availability of the heavy metals from contaminated soil through the chemical processes, particularly, if one recognizes that the local equilibrium pH environment is neither stagnant nor uniform throughout the subsurface underlying the waste landfill.

# Sommaire

Le développement de méthodes d'évaluation du transport et du comportement à long terme des contaminants dans les sites d'entreposage avec parois d'argile, en tenant compte de l'interaction hydro-chimique entre ces contaminants et la barrière d'argile, reste l'un des défis majeurs du génie géo-environnemental actuel. En effet, on est de plus en plus conscient des risques de pollution par lessivage potentiel des métaux lourds contenus dans les contaminants à composants multiples, et une meilleure compréhension du phénomène est nécessaire.

La modélisation des processus de lessivage qui se produisent dans un site d'enfouissement est un outil essentiel puisqu'il est pratiquement impossible à l'heure actuelle de réaliser des études expérimentales à des échelles de temps assez longues pour pouvoir observer le comportement de lessivage des contaminants. Dans cette recherche, le transport de métaux lourds à travers une barrière d'argile est étudié expérimentalement et théoriquement par couplage du transport en solution et réaction géo-chimique. L'auteur propose un montage expérimental pour étudier le phénomène, en examinant les effets du chlore (Cl) et du EDTA sur le fractionnement du zinc (Zn) et du plomb (Pb) sous formes dissoute, adsorbée et précipitée, dans des échantillons non contaminés et pré-contaminés de kaolinite et d'un mélange de kaolinite avec gel de silice et carbonate de calcium (K, KS, KC,KSC). Le montage proposé est basé sur le test en colonne de lessivage avec mesures sur mélange en équilibre, comme essai témoin. Les résultats expérimentaux obtenus en colonne de lessivage ont été présentés sous forme de profils d'adsorption, de désorption et de migration spécifiques à chacun des ions étudiés en fonction de la profondeur de la colonne, et dans l'effluent, pour différents indices de vides (pore volumes). Les résultats indiquent que la présence d'autres contaminants, notamment les agents inorganiques et organiques "complexing", influence le coefficient de distribution, Kd, lequel varie avec le temps, la position, la composition du sol, la surface spécifique des particules, la capacité d'échange en cations, et le pH de la solution. Il est à noter que dans la plupart des modèles existants de transport de contaminants, Kd est considéré comme un paramètre constant pour décrire le fractionnement d'un contaminant entre la solution aqueuse et la matrice solide du sol.

En parallèle avec l'étude expérimentale, un modèle numérique (appelé COSTCHESP pour *COupled Solute Transport and CHemical Equilibrium SPeciation*) a été développé pour simuler le transport de substances chimiques à réactions thermodynamiques multiples à travers une barrière d'argile. Le modèle compte deux modules principaux: un module de transport basé sur les différences finies (COST) et un module d'équilibre géo-chimique (CHESP). Le modèle linéarise le couplage entre les processus physiques et chimiques et s'avère simple et efficace pour simuler les processus simultanés de transport par advection et dispersion (advection, diffusion, osmose et effet de restriction ionique) et les réactions géo-chimiques ("complexation", échange, précipitation, adsorption et désorption). La fiabilité du modèle numérique a été vérifiée par des essais en laboratoire. Les résultats du modèle expérimental ont été utlisés pour étalonner le modèle numérique (COSTCHESP), lequel a ensuite pu prédire les profils de fractionnement des métaux lourds correspondant aux différentes conditions environnementales étudiées. L'effet de la variabilité des paramètres du modèle numérique sur les prédictions a également été étudié, et le modèle s'est avéré très sensible, surtout.

Le modèle proposé tient compte de la plupart des interactions hydro-géomécaniques des multi-composants avec la couche d'argile. Il peut identifier la forme d'ions spécifiques (i.e. adsorbée, précipitée, et en solution) et peut servir à (i) évaluer l'importance des réactions géo-chimiques dans le transport des métaux lourds dans les eaux souterraines; (ii) prédire la forme que prendront les métaux fractionnés dans la barrière d'argile, et (iii) indiquer la disponibilité potentielle des métaux lourds de sol contaminé par les processus chimiques, en particulier si l'on note que le pH à l'équilibre dans l'environnement local n'est ni stagnant, ni uniforme dans le sol adjacent au site d'entreposage.

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## List of Principal Symbols

$a_{ij}^{aq}$ = stoichiometric coefficient of component j in species $c_i$
$a_{ij}^{s}$ = stoichiometric coefficient of component j in species $s_i$
$a_{ij}^{p}$ = stoichiometric coefficient of component j in species $p_i$
$c_i$ = concentration of species i in the aqueous phase ($M/L^3$ fluid)
$\dot{c}_i$ = concentration of species i in the solid phase (M/M solids)
$C_j$ = concentration of component j in the aqueous phase ($M/L^3$ fluid)
$\dot{C}_j$ = total concentration of component j on the solid phase (M/M solids)
D = dispersion coefficient ($L^2/T$)
$K_d$ = the ratio of the total amount of a component in the solid to the aqueous phase
$K_{ci}$ = equilibrium formation constant for species $c_i$
$K_{si}$ = equilibrium formation constant for species $s_i$
$n_{aq}$ = number of species in the aqueous phase
$n_s$ = number of species adsorbed on the solid phase
n = medium porosity ($L^3$ fluid/$L^3$ medium)
$n_p$ = number of species precipitated on the solid phase
$P_j$ = total concentration of component j precipitated on the solid phase ($M/L^3$)
$\rho$ = bulk density of medium (M solids/$L^3$ medium)
$s_i$ = concentration of species i in the solid phase ($M/L^3$ fluid)
$S_j$ = total concentration of component j adsorbed on the solid phase ($M/L^3$ fluid)
$S_j$ = $(\rho\dot{C}_j/n)$
$T_{ij}$ = total concentration of component j ($M/L^3$ fluid)
t = time (T)
V = average pore velocity (L/T)
$X_j$ = concentration of component j

## In the Name of God

# Multi-Component Contaminants Transport of Heavy Metals in Clay

## Chapter 1

## Introduction

### 1.1 Generalities

Enormous amounts of waste materials, potentially hazardous to groundwater, are stored or disposed of on, or beneath, the land surface. The municipal solid waste stream in Canada is among the largest in the world on a per capita basis. Canadians produce 1.9 kg of waste per capita per day (EPA, 1996). When water, coming from rainfall, snowmelt, and surface runoff, makes contact with waste in sanitary and hazardous landfills, it leaches material from the waste. This contact allows soluble organic or inorganic contaminants such as heavy metals to dissolve, producing what is called "leachate solution". Heavily contaminated leachate may migrate to the groundwater if it is not retained by the soil beneath the waste disposal sites. Its polluting potential can be 10 -100 times greater than that of solid waste.

Heavy metals wastes are an inevitable by-product of many industrial processes. Heavy metals are one of the contaminant groups of concern to environmentalists due to their toxic effects on human health. Copper (Cu), Cadmium (Cd), Chromium (Cr), Lead (Pb), Nickel (Ni), and Zinc (Zn) are often found in waste and, therefore, in leachate solutions. The concentration of heavy metals varies with the type and source of the waste, ranging from 0-200 ppm in municipal solid wastes to 200-10,000 ppm in sewage sludge, mining waste, and some industrial waste. Such wastes must be disposed so as to minimize the extent of leaching and the potential for contamination of the groundwater and surrounding environment.

Groundwater contamination by heavy metals and other pollutants is an important problem in Canada and other industrialized countries. Relatively high levels of soluble heavy metals may be naturally present in soils, or as a result of sewage sludge, sanitary land filling, mine tailings, industrial waste disposal, septic systems, and accidental spills of industrial products. It is therefore desirable to physico-chemically encapsulate and immobilize the waste before placing it in a landfill (Trussel and Batchelor, 1996).

Clay-rich geological materials are often used as barriers to retard the potential migration of contaminants from waste disposal sites because of their low hydraulic conductivity and high adsorption capacity. A prime requirement in proper waste management is to predict or determine the extent of transport of contaminants, as growth rates of contaminant plumes or concentrations of target pollutants at specific times and locations from the contaminant source. The schematic shown in Fig 1.1 for a solid waste landfill indicates the general problem (Yong *et al.* 1992). The main role of the barrier system is to minimize the rate of harmful substances migration and retard the mobility of various species of hazardous wastes (Yong, 1996). Modelling the movement of soluble metals in a underlying clay stratum would aid in selecting sites for new landfills, and assessing and monitoring the clean-up of facilities that release these harmful metals.

In Canada, over six million people, or 26% of the population, rely on groundwater for domestic use. In Ontario, Prince Edward Island, New Brunswick, and the Yukon, the largest users of groundwater are municipalities; in Alberta, Saskatchewan, and Manitoba, the agricultural industry for livestock watering; in British Columbia, Quebec and the Northwest Territories, industry; and in Newfoundland and Nova Scotia, rural domestic use. Prince Edward Island is almost totally dependent on groundwater for all its uses (Environment Canada, 1996).These statistics call for proper design of landfills and effective monitoring programs to evaluate the formation and migration of leachate. In Quebec, the natural presence of thick clay deposits at the surface makes clay barriers a desirable and economical means to limit and control leachate migration, including heavy metals. The design of a suitable clayey barrier requires an estimation of the physico-chemical interactions among the contaminants, soil and water, in order to predict the potential rate of contaminant transport and the impact on the surrounding groundwater systems.

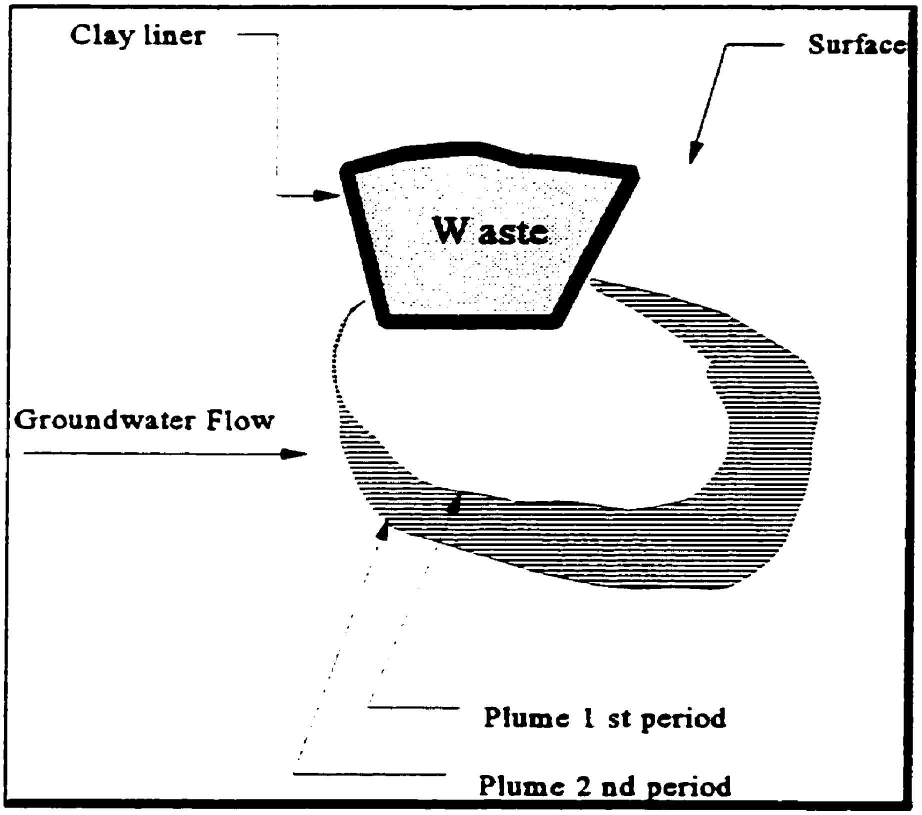

**Figure 1.1** Waste Landfill Showing Contaminant Migration.

Adequate techniques are needed to provide good estimates of the movement and attenuation of contaminants after they are released into the subsurface system to assess their environmental effects. Achievement of this objective requires careful prediction of the physico-chemical interaction of the heavy metals solution with the clay liner during the design period. This, of course, requires an appreciation of the mechanisms of contaminant transport through fine-grained materials and an ability to predict contaminant fluxes through the barrier.

A good way to gain some understanding of at least the most relevant of these complex processes and mechanism is through mathematical modelling. Modelling of the hydro-geochemical interactions, which take place in a landfill, is an invaluable tool as it is often not possible to conduct experiments over sufficiently long timescales in order to observe the long term transport processes of wastes. This is vital to the success of predictions of advance of contaminant plumes in the substrate, and/or distribution of concentrations of target pollutants at various points of concern and after specific time periods.

Questions with respect to how well the physical/chemical problem is characterized in most of the contaminant transport models is the central focus of this study. Regarding the role of soil-contaminant interaction upon transport of heavy metals in a clay barrier, the following questions may be asked:

- What is the interaction effect of multi-component solutions and soil fraction upon the attenuation potential of a clay barrier?
- To what extent do the multi-component solutions and soil constituents interactions affect the heavy metals transport in a clay barrier?
- How long does it take for the contaminant to reach the allowable limit?
- Which form of heavy metals speciesation is released into the subsurface?
- What is the partitioning of the contaminants in the soluble and solid phases ? (i.e. how much is dissolved, adsorbed and precipitated?)
- What fraction of the soil exhibits the greatest influence on heavy metals retention?

The above questions make obvious the necessity of an extensive study regarding the mechanics by which heavy metals are attenuated within clay liners in a multi component contaminant system at different environmental conditions.

## 1.2 Statement of the Problem

Heavy metal contaminants in landfills are some of the most problematic wastes especially when they are disposed of in an acidic environment, since this could increase both the mobility of heavy metals, and those contaminants already retained in the soil pores (Ray and Chan, 1986; Anonymous, 1988; and Al-Hashimi, 1995).

Borden and Yanoschak (1990) examined chemical data from monitoring wells at 71 municipal sanitary landfills in North Carolina, U.S.A. Groundwater-quality violations were found for Pb and Cr (18% of sites), and As, Cd and Zn (6% of sites). Several factors and processes combine to control the advance of heavy metals to groundwater. These include, in addition to the hydrogeology of the system, the multitude of complex interactions and reactions which occur between the contaminants and soils which will shed considerable light on the inter-relationships between two kinds of participants. The major hydrological and physical processes of interaction include advection, convection, diffusion, compaction and consolidation. The chemical reactions include aqueous complex, reduction/oxidation, acid/base reactions, sorption via surface reactions and precipitation/dissolution (Mangold and Tsang, 1991).

Technical understanding of the physical, chemical, and biological processes controlling the fate of heavy metals in the environment has increased in the past two decades. Many of the important advances are reflected in the quantitative mathematical models now being used to describe the influences of competing processes or reactions on the overall fate of heavy metals. Mathematical models, however, often provide the only means of gaining an insight into the mechanisms of the complex processes that occur in groundwater systems. Modelling is often the only way to take into account the effect of species types of chemical reactions in the simulation of solute transport for the purpose of a predictive analysis.

There is need for a model to capture all the physico-chemical interactions which occur between heavy metals, other contaminants and soil constituents along the flow path through the clay liner system. Any of the above mentioned physical and chemical processes will contribute to the distribution and redistribution of chemical components after they are introduced into clay barrier.

Existing knowledge of physical, chemical and biological interactions that take place between clay barriers and leachate solutions is quite limited due to the myriad of constituents and mechanisms involved. The biological processes involve uptake by biota and microorganisms that may transform a chemical species into another species or simply use the species as their nutrient diet. A discussion of the biological process will not be included in this research. The prediction of the long-term leaching behaviour of heavy metals and other inorganic wastes is an increasingly important issue as awareness of the potential future pollution risks associated with landfills of such wastes grows. Dissolution of the constituent mineral due to pH variation in the waste leads to the mobilisation of heavy metals which represent a toxic threat to the local environment surrounding a landfill. The long term safety of landfills is largely unknown and there is an ever growing need for the development of methods to assess the long term pollution risks associated with such deposits. It is now accepted that complete characterization of a disposal site is not feasible using experimental methods alone due to the long timescales involved. Processes which can be observed in a laboratory or in the field are, for all practical purposes, instantaneous from a geological time perspective. A waste landfill may be thought of as a large chemical reactor. Consequently, the use of models can be used to supplement experimental work where conditions do not permit direct economical measurement.

In most of the hydrological and hydro-chemical models the effects of hydrological and physical processes are incorporated rigorously but frequently simplify the chemical interactions among the contaminants and soil minerals with an empirical approach such as the linear isotherm ($K_d$ approach) and/or the Langmuir and Freundlich nonlinear isothermon , including the advective model (Wilson and Miller, 1978), advective-dispersive (McDonald and Harbaugh, 1988; Yong *et al.*, 1992; Diodata and Parizek, 1994; Harbaugh and McDonald, 1996), purely diffusive (Rowe and Booke, 1986), advective-diffusive (Miller and Benson, 1983), geochemical-dynamics (Barnes, 1989), temperature dependent (Kipp, 1986), density dependent (Zhang *et al.*, 1995), unsaturated soil advective-dispersive (Manshel *et al.*, 1993), and fractured porous media (Mackay, 1991).

The above mentioned models assume that the solutes being modelled act independently of the bulk solution composition. The adsorption characterization is also calculated using a constant retardation factor (i.e.,distribution coefficient), $K_d$. The migration of the heavy metals is highly dependent on the physico-chemical interaction of the heavy metals with the clay particles and groundwater composition and properties; thus $K_d$ in such systems may be a strong function of pH and solution composition and properties (Yong *et al.*, 1995).

However, most contaminants are in multi-component solutions and component interactions affect transport and attenuation potentials. On the other hand, there are sophisticated chemical equilibrium models that have incorporated the complete suite of the aforementioned chemical processes but which completely ignore the hydrological and physical processes (Parkhurst *et al.*, 1980; Sposito and Mattigold, 1988). In other words, these chemical equilibrium models can only be applied to beaker systems.

Recently, attempts have been made to account for the complex physical and chemical processes in the hydrological transport modelling of subsurface systems (Miller, 1983; Cederberg, 1985; Yeh and Tripathi, 1989; and Walter *et al.*, 1994). Although the modelling activity, in coupling the hydrological transport and chemical equilibrium of reactive multi-components through porous media systems, has been expanding rapidly, few of these models can really deal with practical problems. None of these models is applicable to the transport of the multi-components into a clay barrier which acts as a membrane in which chemico-osmotic, ion restriction and charge of clay surface effects on the transport of heavy metals must be considered (Yong and Samani, 1988).

For proper design of the clay barrier, the models must incorporate all the significant chemical interactions and physical processes. In addition, a strategy for simulating the long-term transport of heavy metals through clay barriers and the adsorption/desorption potential of heavy metals under different environmental conditions (leachate and soil characteristics) is needed. Adequate techniques are needed to provide good estimates of the movement and attenuation of contaminants after they are released into the subsurface system to assess their environmental effects. Thus, there is a great need to model heavy metals transport of chemical species incorporating chemical reactions along the flow path. The problem can be approached through a system of coupled solute transport equations, and chemical reaction equations (Darban *et al.*, 1995).

This study is aimed at developing a COupled Solute Transport and Chemical Equilibrium Speciation (COSTCHESP) model which accounts for most of the hydro-geochemical interactions of the multi-components with the clay liner, through the coupling of the geochemical and transport models. In order to determine the reliability of the model, some laboratory experiments are carried out and the simulated model will be compared with experimental results. Coupled solute transport and chemical reaction will be simulated through the column leaching test. Then, using the experimental data, long-term migration and retention behaviour of the heavy metals will be predicted by calibration of the proposed model. The sensitivity of the parameters in the simulated model will also be evaluated.

Through theoretical, laboratory and mathematical modelling we can make important contributions to the development of an improved predictive capability. The proposed geochemical transport model will lead to proper identification of the form of specific ions (i.e., adsorbed or precipitated into soils and remaining in the solution). This type of model provides a useful tool for geo-environmental engineers because of the advantages it provides when it comes to the following:

(1) assessing the importance of geochemical reactions on the transport of heavy metals in groundwater, considering contaminant interaction and soil composition;

(2) providing the means for existing models to account for some of the fundamental chemical processes that occur among transported solutes;

(3) predicting the forms of metals that are partitioned in the clay barrier; and

(4) indicating the potential availability of the heavy metals, particularly, if one recognizes that the local equilibrium pH environment is neither stagnant nor uniform throughout the subsurface beneath the waste landfill.

## 1.3 Restrictions of the Existing Solute Transport Models

The existing transport models (Cederberg, 1985; Yong and Samani, 1988) may not be applied for the transport of heavy metals in clay barriers. These models have the following limitations:

(i) Dissolved concentration of each component is predicted, regardless of the speciation effects of the other contaminants along the flow path.

(ii) Physico-chemical interactions among the heavy metals solutions, other contaminants and soil-surface properties (such as cation exchange capacity, surface area) cannot be simulated.

(iii) Profiles of the heavy metals partitioning ( dissolved in aqueous phase and adsorbed or precipitated on the clay surface) cannot be predicted.

(iv) The forces acting between clay surface, solute and solvent cannot be simulated. These forces are themselves dependent on the properties of solutes and surface of the clays that are involved in the adsorption processes.

(v) Chemico-osmotic forces acting between the compacted clay surface and the solute are not considered since clay soil, which is often used as a barrier, behaves as a leaky semi-permeable membrane (Yong *et al.* 1992) and hence, the flow of heavy metals of an electrolyte solution through clay soils is restricted relative to that of fluid. The lower the porosity and permeability of the clay mineral, the more important is the chemico-osmotic effect.

(vi) The diffusion/dispersion coefficient of the various contaminant ions cannot be assumed constant since the driving force for ionic movement is not only affected by the molecular diffusion due to the concentration gradient, but also by the seepage velocity due to the hydraulic gradient of the flow and pH of the solution. These factors are, to a very large extent, functions of concentrations of the solute components (Darban *et al.* 1997).

On the other hand, geochemical models (Parkhurst *et al.*, 1980; Sposito and Mattigold, 1988) provide the equilibrium distribution (dissolved, adsorbed and precipitated) of multi-components of heavy metals in a batch test. It considers all chemical reactions including aqueous complex, reduction/oxidation, acid/base reactions, sorption via surface reactions and precipitation/ dissolution. It does not provide the partitioning of multi-components with time and space unless coupled to a suitable transport model, as conducted in this study.

## 1.4 Scope and Objectives of the Study

Although clay soil sealing has been used for the construction of new waste disposal sites, in order to protect the groundwater from contamination by hazardous seepage waters, the total criteria which lead to the prediction of long term adsorption/desorption of heavy metals in a multi-component contaminant system have not been clearly defined. This lack of understanding is due to the limited consideration that has been given to the interaction between clay soil constituents and leachate composition at the different environmental conditions. This study is aimed at investigating, experimentally and theoretically, the COupled Solute Transport and Chemical Equlibrium Speciation (COSTCHESP) model of multi-components. This represents most of the hydrogeochemical interactions of multi-components of heavy metals in a clay liner. The main objectives of this research are as follows:

1. To develop a technique for incorporating multi-component equilibrium chemistry into the solute transport model for the prediction of heavy metals transport in clay soil.
2. To determine the role of multi-component contaminants to distribution of heavy metals (dissolved, adsorbed, precipitated) as a function of clay soil inorganic content (clay minerals, amorphous materials, and carbonate) along the depth of clay liner with time for an acidified leachate.
3. To predict long term migration and retention of a multi-component heavy metals solution into a clay barrier through the proposed model, suitably calibrated with column leaching test results.

To achieve these objectives and goals, various tasks were performed. These included model development and an experimental program.

(i) investigation of the migration behaviour (adsorption and desorption) of heavy metals through batch equilibrium and column leaching under different pH and soil inorganic constituents using complexing ligands, i.e. Cl and metal-ethylene- diamine-tetra acetic acid EDTA.

(ii) review of existing geochemical/transport models in order to evaluate their capability for coupling.

(iii) modifying the existing codes for development of a predictive model capable of explaining the hydro-geochemical transport processes into natural soil, considering the ion restriction, chemico/osmotic and diffusion/dispersion coefficient effects.

Once the coupled model is developed, the following tasks can be identified:

(iv) computing the required parameters (such as diffusion coefficient, osmotic and ion restriction effects coefficients, adsorption characteristics) through matching of model predictions and experimental results, using an optimization technique.

(v) validating the model by using experimental results from the column leaching tests, accompanied by sequential extraction techniques to establish possible partitioning of the heavy metals into the inorganic part of the soil.

(vi) comparing the $K_d$ approach to the proposed hydro-geochemical transport modelling.

(vii) discussing possible applications of the proposed hydrogeochemical transport model in the field (e.g. immobilization of heavy metals on site, and availability of heavy metals). The general scheme of the present study is shown in Fig. 1.2.

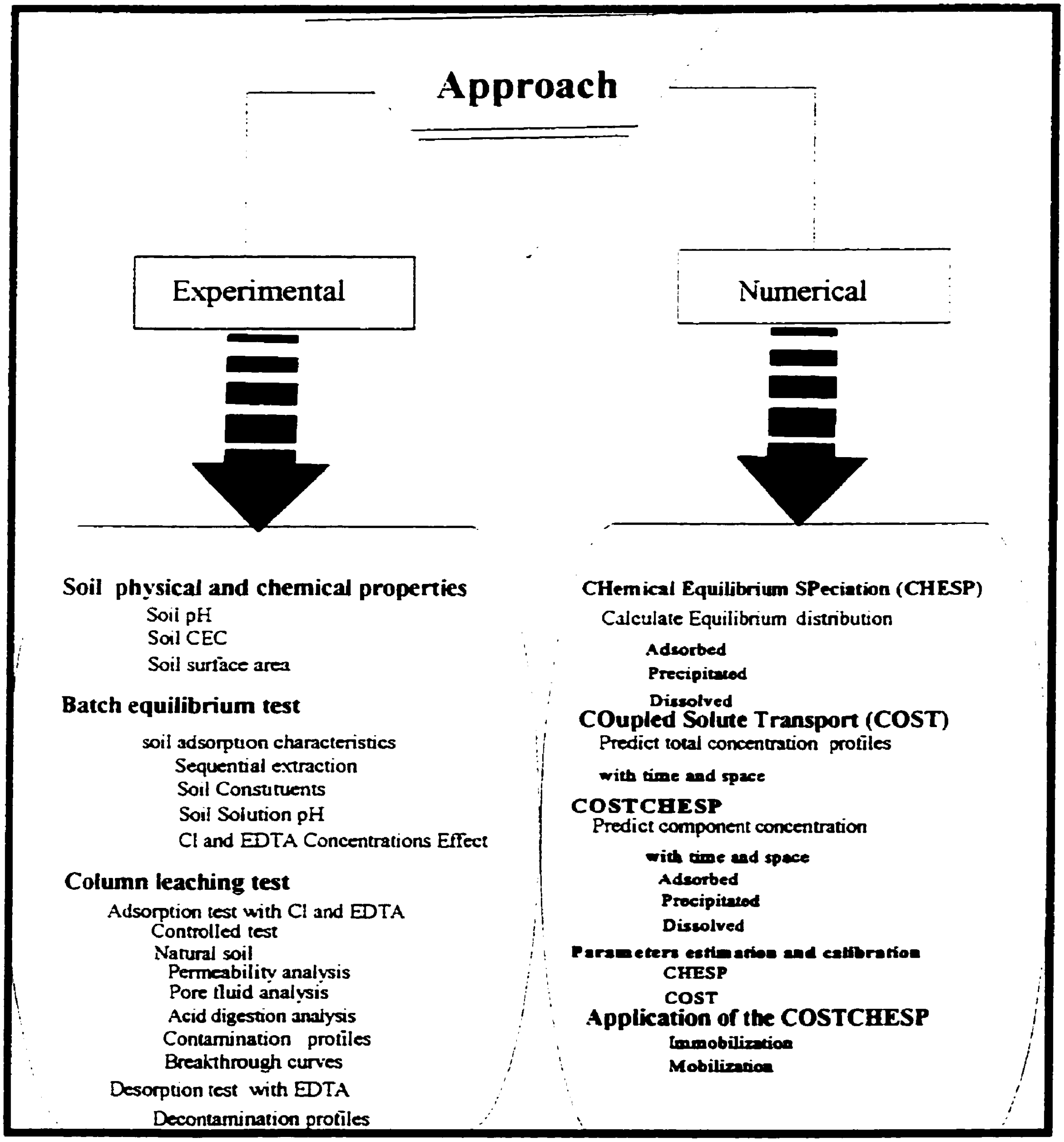

**Figure 1.2** General Scheme of the Present Study.

## 1.5 Innovative Aspect

The partitioning of heavy metals between the solid and liquid phases is an important issue in the control of heavy metals migration through porous media. Prior to the last decade, the possibility of managing pH was used as a strategy for controlling migration of heavy metals. In general, it was suggested that the pH should be kept at values higher than 6.5, by the addition of chemicals such sodium hydroxide or calcium carbonate (lime). Several studies have indicated the fragility of simple pH management on the determination of definitive metal attenuation. According to the literature (Walter *et al.*, 1994, Reddi *et al.*, 1997), there is no appropriate model which also predicts how the heavy metals are being partitioned (adsorbed or precipitated on solids or remaining in solution) into a clay barrier, and what physico-chemical interactions govern the partitioning of heavy metals at different environmental conditions (pH, soil constituents, leachate constituents).

The current design of clay barriers is based on the migration distribution coefficient or isotherm adsorption named $K_d$ approach (Freeze and Cherry, 1979; Melisson *et al.*, 1995). It is based on the general contaminant transport model in which the adsorption parameter is obtained for individual components through the batch equilibrium test at constant pH, regardless of the speciation effects of other contaminants in the solution and hydro-geochemical parameters (i.e. seepage velocity, surface properties of the soil).

In this research, the new model has been developed by coupling of the geochemical model and transport models which account for most of the hydro-chemical interactions between the contaminants and clay barrier materials. The model has the capability to simulate the simultaneous processes of advective-dispersive transport (advection, diffusion, osmotic and ion restriction effect) and geochemical reactions (cation exchange, precipitation, adsorption and desorption). The model will lead to a proper identification of the form of specific ions ( i.e. adsorbed and precipitated on solid, and available in solution).

## 1.6 Organization of the Thesis

The thesis consists of 10 chapters and 7 appendices, the contents of which are as follows:

| | |
|---|---|
| **Chapter 1** | is the introductory chapter in which the problem is presented together with the purposes and scope of the present study. Also, a note on the innovative aspect of this study is presented. This section is part of this chapter. |
| **Chapter 2** | summarizes the literature published to date on the known factors involved in the attenuation, which influence the mobility of the heavy metal within the soil systems. Based on these factors, a laboratory program is designed to simulate multi-component transport of heavy metals in clay. In addition, the materials and methods used in the performance of the tests are described. |
| **Chapter 3** | initially evaluates the state-of- the art of work with respect to geochemical and transport models. Next coupled models are considered with a detailed formulation of COupled Solute Transport and Chemical Equlibrium Speciation (COSTCHESP) in clay, and the proposed solution technique. |
| **Chapter 4** | presents the results of soil physical and chemical properties used in this study and renders the final results of the batch equilibrium test and the sequential extraction technique and discusses the effect of Cl and EDTA concentrations on heavy metals retention. |
| **Chapter 5** | describes the results of the column leaching test for artificial soil and leachate solution, the calibration of proposed model and prediction of long term retention and migration of heavy metals into the clay barrier. |
| **Chapter 6** | interprets the simulation of the proposed COupled Solute Transport and Chemical Reaction Model for leaching of actual leachate into natural soil and compares the results with the experimental leaching test. |
| **Chapter 7** | describes the results for leaching of heavy metals spiked with EDTA for different clays, and simulation by the proposed model. |
| **Chapter 8** | contains the results of the column leaching test for decontamination of different clay soils using EDTA as leachate, and simulation of proposed model |

| | |
|---|---|
| | for desorption of heavy metals. |
| **Chapter 9** | discusses the sensitivity of results to variations in chemical parameter, soil properties and pH of the solution. |
| **Chapter 10** | outlines a summary of the main conclusions of this research and contains recommendations for future work. |
| | |
| **Appendix A** | demonstrates the main subroutines in COSTCHESP program. |
| **Appendix B** | describes the COST derivation. |
| **Appendix C** | presents the adsorption model in CHESP program. |
| **Appendix D** | presents a sample of input of CHESP and COST for all cases. |
| **Appendix E** | summarizes a sample speciation result for CHESP and COSTCHESP for all cases. |
| **Appendix F** | presents program listing of the COSTCHESP. |
| **Appendix G** | presents program listing for PET. |

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# Chapter 2

# Experimental Investigation

## 2.1 General Remarks

Unquestionably, industrial practices are responsible for a high proportion of the heavy metals disposed in the environment. The general philosophy of waste disposal (industrial and/or domestic) is to ensure that substances that are considered toxic, such as heavy metals, do not pose a threat to the environment. Achievement of this objective requires proper understanding of the physico-chemical interaction of heavy metals solutions with a clay liner during the design period. To do so, the important factors that contribute to attenuation of heavy metals in a clay barrier should be identified.

In this chapter, previous research works are reviewed to determine the important factors that influence the retention of the heavy metals within soil systems. The tendency of heavy metals to reside in soils for a long time has been noted in this review; however , the factors controlling the mobility of heavy metals were only briefly mentioned. From this investigation, a laboratory model was designed to simulate the one dimensional contaminant transport of multi-component heavy metals through a clay liner.

## 2.2 Factors Affecting Heavy Metal Attenuation of Heavy Metals in Clayey Soil

The attenuation of heavy metals in the clay barrier in waste disposal landfills has already been an issue of great importance as far as the migration control of waste leachate into groundwater (Farah and Pickering, 1979; Yanful, 1986; Yong *et al.*, 1992; Cabral and Yong, 1993; and Mohamed *et al.*, 1994). Heavy metals may be retained in a clay barrier by adsorption or precipitation mechanisms. The term 'adsorption' in this thesis refers to any of the processes by which dissolved heavy metals, become attached to the surface of soil (solids) particles through mechanisms which seek to satisfy the forces of attraction from the soil solids (surfaces). This includes physical adsorption (physisorption), occurring principally as a result of ion-exchange reactions and van der Waals forces, and chemical adsorption (chemisorption) which involves short-range chemical valence bonds (Yong *et al.*, 1992). Such processes represent the means by which the forces of attraction existing at the surfaces are satisfied. Yonfiil (1986) notes that causes of adsorption, other than electrostatic attraction, include changes in the hydration state of adsorbent or adsorbate, interaction between the adsorbate molecules or ions themselves, covalent, van der Waals or hydrogen bonding between the adsorbate and adsorbent. These processes are governed by the surface properties of the soil solids (inorganic and organic), and the chemistry and physical-chemistry of the contaminant leachate and its constituents, e.g. cations, anions and nonionic molecules.

Specific adsorption arises from electrostatic attraction augmented by hydrogen bonding, coordinate bonding or van der Waals bonding. In specific cation adsorption, the adsorbed cations are held much more strongly by the adsorbent surface because they penetrate the coordination shell of the structural atom. Cation exchange or non-specific adsorption of heavy metals and most of alkali/ and alkaline earth cations occurs on clay minerals and other negatively charged soil surfaces (Sposito, 1990). The action of exchange adsorption is accompanied by a simultaneous desorption of an equivalent amount of other ionic species. These cations are held primarily by electrostatic or columbic forces near the negatively charged surfaces.

Precipitation of heavy metals as insoluble solids is likely to occur whenever the activity product of the ionic species in solution exceeds equilibrium solubility of the solid phase involving the ions (Sposito, 1984). Conversely, whenever the ionic concentrations drop below the equilibrium solubility of the solid phase, that phase begins to dissolve. The limited solubilities of heavy metals carbonates, sulphide and hydroxides suggest that high concentrations of dissolved metals in landfill leachates could result in their precipitation. The precipitation reaction will be governed by the amounts of total dissolved carbonate and sulphide in the leachate and the redox-pH regime. The partial pressure of carbon dioxide ($CO_2$) has been noted as the major chemical variable controlling the precipitation of heavy metal carbonates (Freeze and Cherry, 1979).

The factors governing the removal of solutes from solution are: (i) the concentration of dissolved metal species, other inorganic contaminants and their distribution, (ii) concentration of competing cations such as alkaline and alkaline earth, (iii) concentration of organic and inorganic ligand that can complex with the metal, (iv) electron availability as measured by oxidation-reduction potential, $E_h$ and ability of the clay barrier constituents to adsorb the heavy metal which is indirectly related to the pH of the soil solution, CEC, and surface area of the clay liner. In other words, the process of retention is governed by the surface properties of the clay (inorganic and organic), and the chemistry and physical-chemistry of the contaminant leachate and its constituents (Yong *et al.*, 1995). In the following section the contribution of soil composition and leachate constituents to heavy metals are briefly discussed.

### 2.2.1 Soil Composition

Most of the previous research has focused on the effect of organic content of clay soil on heavy metals retention (Davis, 1984; Yong *et al.*, 1995). However, several investigators have shown that the inorganic part of the soil has a great influence on the retention of heavy metals (Harter, 1983; Harsh and Donner, 1984; Zhan, 1986; Yanful *et al*, 1988a; Zahn, 1989; Oscarson and Heimann, 1990; Holm, and Zho, 1994; Warren and Zimmerman, 1994; Ohtsubo, 1994; and Boily and Fein, 1995). The partitioning of heavy metals in the inorganic part of the soil has been explored in terms of several mechanisms, such as cation exchange, precipitation of solid phase (as oxides, hydroxides, carbonates), and complexation reaction (Elliot *et al.*, 1986, and Yong *et al.*, 1995). In the inorganic fraction, clay minerals, carbonates and hydrous oxides of Fe, Al, Si, and Mn have a high affinity for contaminants. The mobility of heavy metals in several soils indicates that the least mobility was obtained in a mineral soil with a relatively high pH, Cation Exchange Capacity (CEC), and exchangeable base content (Phadungchewit, 1990). The CEC is the amount of cations that can be adsorbed exchangeably by a solid phase from solution at specified temperature, ionic strength and ionic species.

Less attention has been paid to the modelling of retention of heavy metals in the inorganic part of the clay barrier, particularly in a multi-component system for a leaching column test which closely simulates the field condition. This research deals with the effect of the inorganic constituents of the soil thus the contribution of each inorganic constituent mentioned above such as clay minerals, carbonate and amorphous content, and pH of the solution to the heavy metals transport/immobilization is investigated.

### 2.2.2 Clay Surface Charge

Surface charge of the clay plays an important role in the heavy metals retention or immobilization of heavy metals into the clay barrier, thus the effect of charge should be considered in the modelling of the heavy metals in soil. Surface charge can be classified into three types: (1) permanent structural charge, (2) coordinative surface charge, and (3) dissolved surface charge (Yong *et al.*, 1992). Permanent structural charge is associated with the charge due to isomorphous substitutions in minerals, such as that due to substitution of $Al^{3+}$ for $Si^{4+}$ in tetrahedral sites of the crystal lattice of silicate minerals. This charge is almost always negative among minerals commonly found in soils and sediments. Montmorillonite and bentonite can be considered as two permanent charge clay materials.

Positive adsorption of heavy metals cationic species such as $Zn^{2+}$, $Pb^{2+}$ and their hydrolysed species ($ZnOH^{+}$, $PbOH^{+}$) through electrostatic attraction is then possible. Kaolinite has a very low permanent charge. The pH-dependent charge of a clay soil such as kaolinite is considered to arise primarily from gain or loss of $H^{+}$ (Yong and Warkentin, 1975). The main inorganic functional group is [$OH^{-}$] and it becomes important when primary bonds are broken at the edges of clay minerals. The pH-dependency of charge is more important for kaolinite clay which is 1:1 minerals than for 2:1 type minerals such as smectites and vermiculites, because of the greater surface edge of 1:1 clay minerals (Yong *et al.*, 1992).

The coordinative surface charge is the charge associated with the reactions of potential-determining ions with surface functional groups. For oxides, such reactions include the adsorption of $H^{+}$ or $OH^{-}$ by the surface, but also include coordination reactions of other ions with surface functional groups. The charge on particles is usually expressed as a surface density $\sigma_p$, in units of charge per unit area (C $m^{-2}$). The net particle surface charge is defined as the sum of the surface densities of permanent structural charge, $\sigma_s$ and coordinative surface charge, $\sigma_0$ (Sposito, 1984).

$$\sigma_p=\sigma_s+\sigma_o$$

In general, this sum will not be equal to zero, and to preserve electro neutrality, a counterion charge must be accumulate near the particle surface, $\sigma_d$. The portion of the counterion charge that is presented as a dissociated charge in the diffuse layer is referred to as $\sigma_d$. The surface, compact, and diffuse layer charges are referred to collectively as an Electrical Double Layer (EDL). The theory which deals with attenuation of heavy metals based on EDL is called surface complexation which uses the formalism of ion association reactions in solution as a representative of surface reactions. This theory evolves from the Gouy (1910) and Chapman (1913) theory to Stern (1924) and Graham (1947) and Hunter, (1987) which considers asymmetrical electrolyte for charge potential. Detailed derivations and discussion of the governing equations are given in Sposito (1984) and Yong *et al.* (1992). Because of the complexity of natural systems, the empirical approach has been widely used in describing the partitioning of solutes between the mineral and water phases in geochemical applications, especially in transport models and engineering applications. Surface complexation models, on the other hand, have been used primarily by aquatic scientists interested in developing a thermodynamic understanding of the coordinative properties of mineral surface ligand groups via laboratory investigation.

A number of different surface complexation models have been proposed in the last two decades. Each model assumes a particular interfacial structure, resulting in the consideration of various kinds of surface reactions and electrostatic correction factors to mass law equations. While the models differ in their consideration of interfacial structure, all the models reduce to a set of simultaneous equations that can be solved numerically (Allison *et al.*, 1993). These equations include: (i) mass law equations for all surface reactions under consideration, (ii) a mole balance equation for surface sites, (iii) an equation for computation of surface charge, and (iv) a set of equations representing the constraints imposed by the model of interfacial structure.

All above mentioned models need experimental data to determine the required parameters.

### 2.2.3 The Mobility of Heavy Metals in Clay

According to Walsh *et al.* (1984), Yanful (1986) and Phadungchewit (1990), at acidic pH values, precipitated heavy metals re-dissolve and become mobile. This study indicated that heavy metals are not significantly removed from solutions at pH levels below 5. This is due to the increased solubility of the carbonates and hydroxides of heavy metals and the increased competition for exchange sites on clay offered by the hydrogen ion.

On the other hand, leachate constituents affect the heavy metals mobility in the clay barrier. Complexation of metal ions by ligands present in the leachate can significantly alter their adsorption by mineral surfaces (Bourg and Schnidler, 1978; Davis and Leckie, 1978; Schindler and Stumm , 1987). Chloride and sulfate complexes of Cd are weakly adsorbed by clay mineral surfaces in comparison to $Cd^{2+}$ (Benjamin and Leckie, 1982), and metal-ethylene-diamine-tetra acetic acid (EDTA) complexes are generally not adsorbed by the surfaces of silica, manganese oxides, calcite, or aluminosilicate minerals (van den Berg, 1982; Bowers and Haung, 1986; Davis 1984; Hunter, 1987). In these cases, the mineral surface sites and dissolved ligands compete thermodynamically for coordination of metal ions, and the net adsorption of the metal ion at equilibrium can be estimated from straightforward equilibrium calculations (Benjamin and Leckie, 1982; Fuller and Davis, 1987). Fein *et al.* (1995) studied the quantitative assessment of the importance of metal complexation with organic solution. Hahne and Kroontje (1973), Bowman (1981), Elliott *et al.* (1986), Sheremata (1990) found increased metal mobility with the presence of an inorganic solution such as chloride ($Cl^-$) ion, due apparently to complex formation. Thus, contaminant interaction plays a major role in the heavy metals mobility in soils.

The transport and immobilization processes of heavy metals are similar to those of other cations but some differences exist. The initial mobility, after addition to soils, will largely depend on the form in which the heavy metals are added, which in turn, will depend on the source. In landfill leachate heavy metals may be present as complexes with soluble organic, free uncomplexed cations and inorganic complexes such as $CuCl^+$, $CuCl^-_2$, $Pb(OH)^-$. Heavy metals leachate may be transported in a clay liner in any of the forms mentioned above, depending on the pH of the soil solution. At slightly high pH levels (6.5-8.5) heavy metals will exist mostly as hydroxy complexes if there are no other ligands in the soil solution with which the metals form more stable complexes. Thus, heavy metals in a clay liner may be transported in different forms such as i) simple uncomplexed dissolved cationic species; ii) dissolved organic and inorganic complexes; and iii) adsorbed or precipitated along the depth of the clay liner .

From the review of earlier described concepts, an illustrated diagram portraying the various parameters which contribute to mobilization of heavy metals with a clay liner can be structured as shown in Figure 2.1.

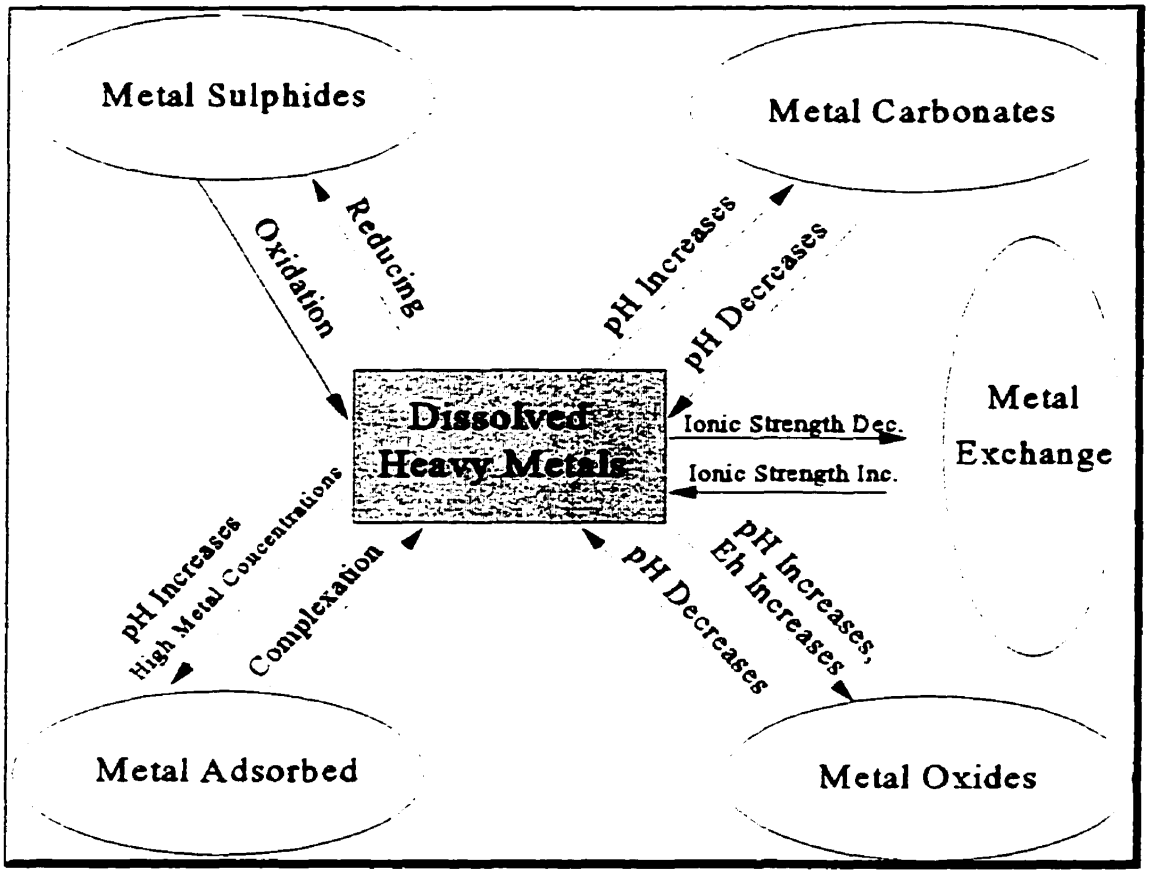

**Figure 2.1** Factors Affecting Mobility of Heavy Metals (After Galvez, 1995).

## 2.3 Experimental Program

The experimental program is designed to simulate the coupled solute transport and chemical reaction of the multi-components of heavy metals in clay and to present implementation of the following tasks:

1. To study migration and retention profiles of the contaminant solutes such as heavy metals (i.e. Pb, Zn), and their interactions in the bulk solution.
2. To use the results of the test for parameter estimation and calibration of the model.
3. To investigate the partitioning of the heavy metals (dissolved, adsorbed on

solid, and precipitated) in a multi-component system.

4. To verify the role of the inorganic fraction (carbonates, oxides and hydroxides) of soil in heavy metals retention.
5. To validate the proposed model for the transport of a multi-contaminant system with the experimental results.

The proposed program would be carried out in two parts. The first part involves investigation of the effect of inorganic ligands such as Cl and dissolved organic complexing component such as EDTA to heavy metals partitioning in different clay soil through batch equilibrium tests followed by sequential extraction techniques. The second part involves the experimental program to simulate the coupled solute transport and chemical reaction of heavy metals in multi-component system into different clay soil through the column leaching tests. Two types of the experiments were designed for coupled processes:

i) retention of heavy metals along the clay liner (immobilization), and

ii) mobilization of heavy metals from the contaminated clay liner (remediation/ mobilization).

For immobilization, the effects of Cl as an inorganic ligand and EDTA as a complexing agent on adsorption of heavy metals along the clay soil column at various times have been investigated. This part of the study is aimed at evaluating how multiple components affect the mobility of heavy metals into different clay soils, and how different functions of the soil material contribute to heavy metals retention.

For soil remediation, heavy metals that have already been adsorbed by clay, are mobilized by EDTA as leachate, to evaluate how effective EDTA is in removing heavy metals from the different clay soils. The basis of these two parts is described in the following sections.

### 2.3.1 Material

Generally, soil components include carbonates; silt; hydrous oxides of Fe, Al, Si, and Mn; clay minerals; and organic matter. Thus, in order to perform the test in a controlled environment, simple clay minerals such as kaolinite are used (characterized by low specific surface areas of 12 $m^2/g$, low CEC of about 15 meq/100g, maximum dry densities of 1.35 $mg/m^3$, and low hydraulic conductivity of 1.73 x $10^{-7}$ cm/sec for the compacted samples) mixed at a predetermined ratio with amorphous silica (silica gel) and carbonate to simulate the soil composition effect on heavy metals retention.

Kaolinite, Hydrate PX (Georgia Kaolin Co.) was selected as the clay mineral for a number of reasons; kaolinite is least reactive of clay minerals, it is very low in amorphous content and has no quartz, smectites, carbonate or organic matter. The absence of carbonate and amorphous will make it possible to study the effects of both the absence and the presence of the carbonate and amorphous materials.

Silica gel was chosen because it has a high affinity for adsorption of heavy metals at low pH and the potential of using fly ash as a treatment material for low buffer clay liner (calcium carbonate was selected as an additive because most of Quebec soil contains 10-15% carbonate and also because of the potential use of calcium carbonate (sandstone) instead of lime for immobilization of heavy metals in the Acid M ine Drainage (AMD) problem (Mohamed *et al.*, 1994).

Organic matter was not used in this stu +dy because the presence of organic matter requires consideration of the biological effect on transport of heavy metals which is not within the scope of this study. The prepared soils we re air dried and ground to pass a 2 mm sieve. They were subjected to a variety of chemical and physical tests including soil pH measurement, cation exchange capacity determin+ation and surface area measurement. Soil pH was measured in 1:2 soil-water solution ratio with a Beckman pH meter pH/ISE type. The surface areas were determined using Ethylene Glycol-Monoethyle Ether (EGME), according to the procedure described by Warren and Zimmerman (1994). The CEC of the soil was determined by the silver thiourea method (Chabra *et al.*, 1975). Because of the exclusion of the organic part of the soil, the clay, carbonate and hydrous oxides of the soil are responsible for the adsorption of heavy metals. They possess either high surface areas or high buffer capacity which indirectly exhibit higher retention for heavy metals.

### 2.3.2 Method

The above mentioned objectives will be examined through the batch equilibrium test followed by the sequential extraction technique and column leaching test as described by Yong *et al.* (1992).

#### 2.3.2.1 Batch Test

The batch equilibrium test was carried out in order to have a preliminary estimation of the adsorption characteristics of each heavy metal, and to compare this $K_d$ with the one computed through the column test. Batch tests may also be used to "obtain an estimate of how many pore volumes of flow will be necessary to achieve breakthrough of a constituent into the effluent liquid" (Bowders *et al.*, 1986). "Only a rough estimate can actually be obtained (if any at all !), because the adsorption characteristics of compacted material are not the same as that of soil in a suspension" (Cabral and Yong, 1993). The batch technique does not appear to reflect heavy metals migration and adsorption characteristics through a barrier as well as the "column leaching" technique due to following reasons (i) a very high solution to soil ratio is generally used in a batch test and this does not reflect leachate-soil interactions which exist in landfills, (ii) in most batch tests equilibrium is generally attained within 24 hours of shaking.

Batch equilibrium tests were performed following the procedure described by EPA (1987) (equivalent to the ASTM standards ES-10-85 and D4319, described in a simplified form in Bowders et *al.*, 1986). For the batch test, a set of solutions, each solution having the same concentration of Pb and Zn in the range of $1.0 \times 10^{-3}$ to $10.0 \times 10^{-3}$ mol/L but with increasing acid concentration (to determine the effect of soil solution pH on heavy metals retention), was applied separately and compositely to the soils at 1:10 soil-solution ratio (2 g of dry soil and 20 ml of solution). The amount of each heavy metal applied is equivalent to 1.0 cmol/kg and 10.0 cmol/kg soil. A set of batch tests was also carried out to study the effect of complexation with an inorganic complexing agent such as chloride on the mobility of heavy metals. In this type of batch test the same concentration of heavy metals with increasing chloride concentration in the range of 0.05 to 1.00 mol/L was used. Another set of batch tests was also carried out to study the effect of complexation with an organic complexing agent such as EDTA on the mobility of heavy metals. In this type of batch test the same concentration of heavy metals with increasing EDTA concentration in the range of 0.001 to 0.01 mol/L was used.

For the batch test procedure, the mixture suspension was placed in an acid-cleaned polycarbonate centrifuge tube, and the tubes were shaken overnight (preliminary experiments showed that equilibrium was attained within 1 hour ). After equilibration, the suspensions were centrifuged at 10,000 rpm for 10 min, filtered, lowered the pH of the solution to 3.0 (to prevent precipitation of heavy metals) and diluted to 1/10 or 1/100 for the case of high heavy metal concentrations. The dissolved metal concentrations in the clear supernatant were determined by atomic adsorption spectrophotometry (AAS). Five standard solutions were used for the calibration of the AAS. A standard deviation of 2-5 % was accepted for measuring dissolved concentration by AAS. A schematic of various solutions which were applied to the each type of prepared clay (kaolinite, kaolinite + silica gel, kaolinite + calcium carbonate, and kaolinite + silica gel and calcium carbonate) at 1:10 soil-solution ratio in the equilibrium test program is shown in Figure 2.2.

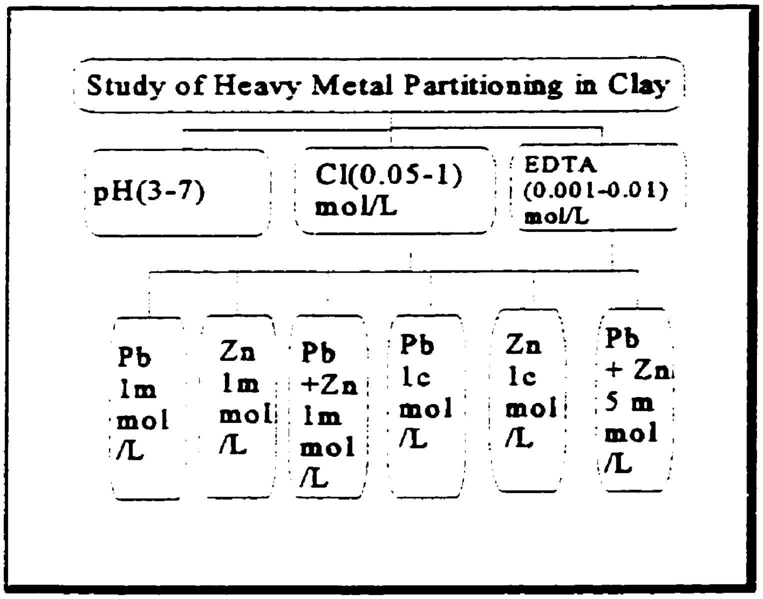

**Figure 2.2** Batch Test Program.

### 2.3.2.2 Selective Sequential Extraction

The contaminated soil, which was separated from supernatant, was subjcetd to a selective sequential extraction procedure to study the effect of the inorganic part of the soil (i.e. carbonate and oxides) on heavy metals partitioning. Sequential extraction techniques have been widely used for the speciation analysis of major and trace elements in soils (Rapin *et al.*, 1986; Yanful, 1986; Yong *et al.*, 1992). Selective sequential extraction uses appropriate chemical reagents in such a manner that different heavy metals fractions can be released from the solids.

The sequence of application of the extractant reagents is not uniform, and sequences appear to differ between different researchers. Most include up to five extractants: (i) cation exchange extractants, metals in this group are identified as in the exchangeable phase and are considered to be nonspecifically adsorbed and ion exchangeable, i.e. they can be replaced by competing cations, (ii) carbonate dissolving extractants, metals precipitated or coprecipitated as natural carbonates which can be released by application of an acid; (iii) extractants that release heavy metals associated with metal oxides, i.e. amorphous material, the metals considered here are those metals that are attached to amorphous or poorly crystallized oxides, this extractant uses a combination of an acid-reducing agent with acetic acid; (iv) extractants that release organic and sulphide-bound metals, and (v) strong acidic extractants for dissolving silicates that have not been attacked by the milder reagents. A more complete procedure of the various interacting-retentive mechanisms can be found in Yong *et al.* (1992). The procedure used in this research, for the sequential extraction, is basically the same as that recommended by Yanfull *et al.* (1988 b). Since the soil used in this study was free of organic matter, there was no heavy metals bound to the organic matter. The experiments included those with constant total metal concentration and pH variation, and others with constant pH and variable metal concentrations.

#### 2.3.2.3 Column Leaching Test

The column leaching test was designed to obtain the migration and retention profiles of heavy metals in the clay barrier and to compute the adsorption and transport parameters. Two types of column leaching were carried out; (1) using artificial heavy metals leachate in kaolinite and kaolinite mixtures (K, KS, KC, KSC) and (2) using actual leachate into natural soil. Prior to column testing, dry soil was mixed with distilled water at about 3% above optimum water content (Phifer *et al.*, 1995). The soil was then placed in a plastic container and allowed to equilibrate in a humid room for at least 24 hours, and then compacted statically in a lucite cell to its maximum dry density in 3 layers of 16 mm, each layer required a pressure of 1500 psi (10342.5 kPa).

The weight of soil needed for the individual compacted layers was calculated from the maximum dry density and initial moulding water content. The weight calculated for each layer varied between 50.00 to 60.00 g depending on the type of kaolinite mixtures (K, KS, KC, KSC).

Each cell consisted of a hollow plexiglass cylinder 5 mm thick, with an outside diameter of 50 mm , a height of 50 mm, a top cap with a 30 mm height for solution supply, and a base for outlet at the bottom of the cylinder. The Lucite cell with neoprene O-ring seals was sandwiched between the top cap and a Lucite bottom plate.

The soil height was kept at 50 mm. A 3 mm thick porous stone was placed on top of the soil core to ensure uniform distribution of the hydraulic pressure on the soil surface. Another similar porous stone was used at the column base to collect and channel the effluent to the drainage outlet. A schematic picture of the cell is shown in Figure 2.3.

A hydraulic head of 2.00 m was applied to simulate the pressure head by applying an air pressure of 2.75 psi (18.30 kPa) equivalent to a hydraulic head of 2 m, resulting in a hydraulic gradient of 40.

First, steady state fluid flow was established by distilled water through the soil sample; then the fluid flow in the influent reservoir was exchanged for the solution of heavy metals spiked with chloride salts or EDTA as inorganic or organic complexing agents that will be referred to as the multi-component contaminants of heavy metals. The pH of the leachate was also lowered to 3.0 by adding some concentrated $HNO_3$.

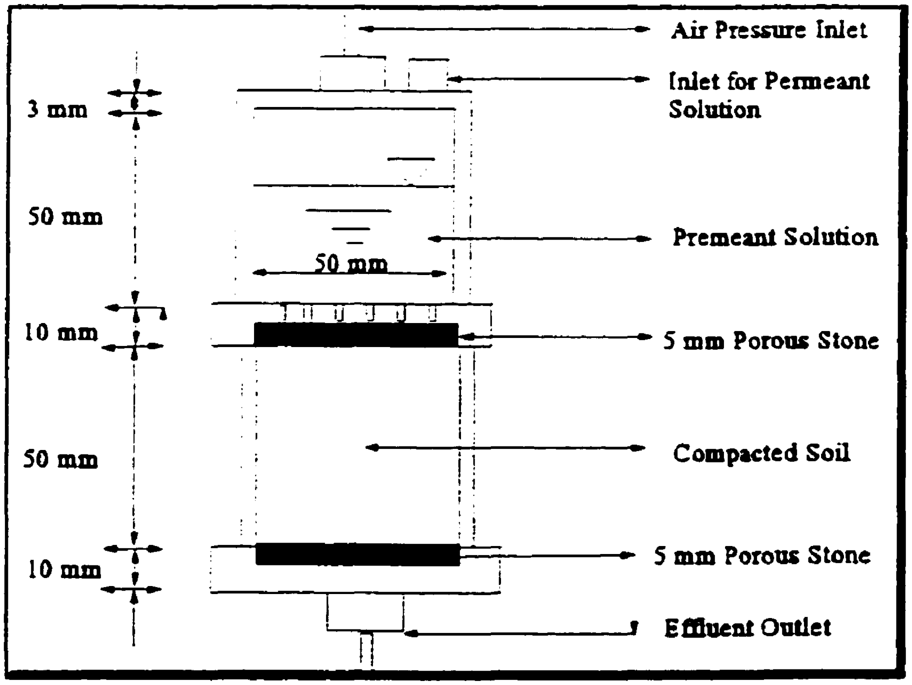

**Figure 2.3** Leaching Cell

The effluent of each cell was monitored and measured over time. Leaching was stopped at one, two, three, five and seven pore volumes of effluent (a PV of flow for a saturated soil is the cumulative volume of flow divided by the volume of the void space). The concentration C, of the chemical species appearing in the effluent, named "leached out concentration", was measured and then soil specimens were extruded, cut into 10-mm-thick slices, and the sliced specimens were analysed for pore fluid contents (soluble ions) and extractable ions (ASTM 1984). This is in order to compute the effective diffusion parameter and, effective adsorption characteristic of the sliced specimens by measuring migrated and retained heavy metals at each section along the depth.

Two types of heavy metals solution were chosen; lead and zinc. The choice of these two heavy metals is related to their mobility in soil (Phadungchewit, 1990), to the different selective affinity of clay minerals for these two heavy metals and to the fact that these two heavy metals are generally present in hazardous waste leachates. The concentration of each heavy metal was kept constant at 1 mmol/L (207 ppm for lead and 64 ppm for zinc) during the leaching which is a typical concentration of municipal landfill leachate ( a range of 5 ppm to 5000 ppm for Pb and 1 to 1000 ppm was reported,Yong *et al*, 1992). Two types of conjugate anions were used for the above mentioned heavy metals, namely nitrate, and chloride ($NO3^-$, $Cl^-$).

In order to keep an acidic environment for the solution of heavy metals, it was decided to lower the pH of the lead solution to 3.0 by the addition of nitric acid because ; (i) below pH of 3.0, no significant precipitation occurs, i.e., most of Pb remains in solution, (ii) migration of heavy metals is facilitated in acidic conditions, and it was also our purpose here to create the worst scenario of contamination (Yong, 1996). To simulate the mobilization or desorption of heavy metals from contaminated soil EDTA at a concentration of 0.01 mol/L and pH of 4.5 was used as a permeant. This is because the mobilization of contaminated illite soil with heavy metals through soil washing by EDTA has been successfully performed by Castellan (1996) in the batch test with the above mentioned concentration and pH for EDTA. The concentration of cations and heavy metals was determined using Perkin-Elmer Model 3110 atomic adsorption spectrophotometer (AAS). The procedures used in the preparation of the test, material, as well as the sequence of execution of the column leaching test are shown schematically in Figure 2.4.

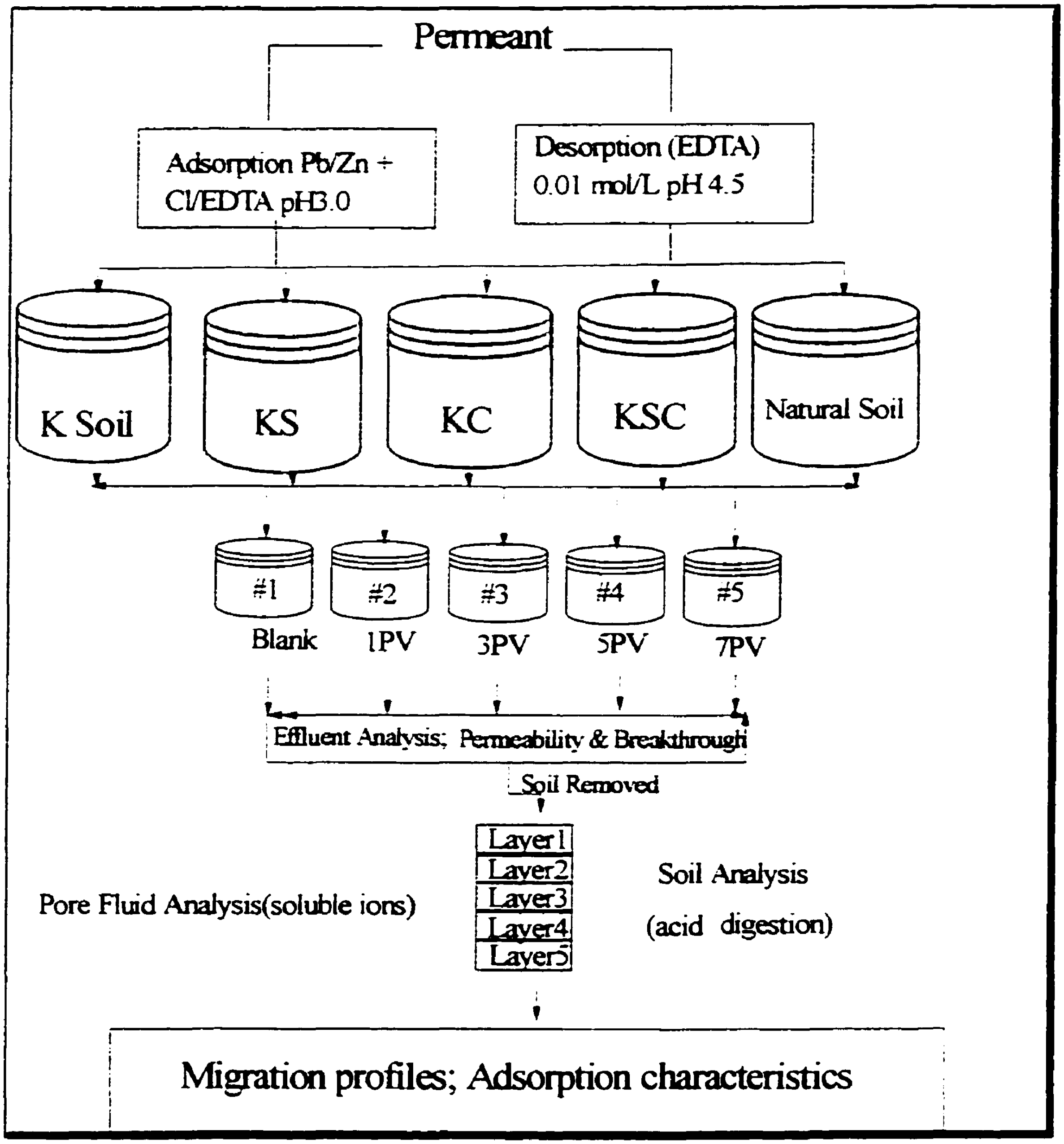

**Figure 2.4** Leaching Column Test Scheme.

## 2.4 Summary

In this chapter, the important factors which influence the partitioning of heavy metals within the soil systems were reviewed. A laboratory model was designed to simulate the one dimensional contaminant transport of multi-component heavy metals through a clay liner. A set of batch equilibrium tests was proposed in order to obtain an estimation of the role of pH of the soil solution, chloride and EDTA concentrations on the partitioning of heavy metals into different clay soils. A median chloride (0.05 mol/L) and EDTA (0.01 mol/L) concentration was selected for simulation of multi-component heavy metals into different clay soils to investigate how soil components partitioned the heavy metals.

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# Chapter 3

# Model Development

## 3.1 General Remarks

The recognized mechanisms that affect the transport of solutes through saturated geologic materials include, transport as result of the bulk motion of the fluid phase (advection); dispersive transport caused by velocity variation about the mean velocity, and by molecular diffusion; and geochemical retardation processes. The transport is described by a set of partial differential equations and the chemical reactions are described by a set of nonlinear algebraic equations.

In this chapter, the state-of-the-art in respect to geochemical and transport models and the coupled ones is reviewed. This review emphasizes the multi-component transport of heavy metals in clayey soil. Thereafter an effort will be made to develop a mathematical model for coupling the geochemical with transport models which generally represent physico-chemical interaction of multi components of heavy metals in a clay liner.

## 3.2 Geochemical Speciation Model

Due to the chemical interactions among the different ions in the aqueous phase and soil particles, geochemical models have been used as a tool to estimate the equilibrium distribution of chemical species. From the geochemical models concentrations and activities of dissolved, sorbed and precipitated species are predicted in a batch test when reactants are added to soil, temperature is changed, or pressure of gases alters. There are a variety of chemical reactions found in these speciation models which may include complexation, sorption, dissolution/precipitation, oxidation/redox reaction, mineral alteration, and gas-solution equilibria chemical reactions.

Prior to and up until 1980 there were numerous speciation models being developed. In contrast, the activity in the last decade has involved computer model documentation and model refinement which has produced fewer computer model versions. The equilibrium composition or distribution of dissolved species can be computed by two distinct techniques, namely, the equilibrium constant and the Gibbs free energy approach. These techniques are thermodynamically and mathematically related and are both subjected to mass balance and chemical equilibrium constraints.

Various geochemical models have been developed, each having a different purpose or application. The widely used models are PHREEQE (Parkhurst *et al.*, 1991), EQ3NR (Wolery, 1992) MINTEQ (Allison *et al.*, 1993) and GEOCHEM (Sposito and Mattigold, 1988). Several comparative studies ( Parkhust *et al.*, 1991; and Waite, 1989) have revealed either directly, or indirectly, that the major source of discrepancy is the thermodynamic data base belonging to each chemical model. The research done by Chan (1993) involving the comparison of the above mentioned models on the basis of model sensitivities to pH, temperature variations and consistency of program output speciation results, shows that the MINTEQA3 program is easier to operate, possesses a better method for input file preparation, and provides a more informative and useful output. Thus, the latest version of the MINTEQA3 (Allison *et al.*, 1993) was used for the chemical speciation part of this study. However, the geochemical speciation models do not have the capability to simulate transport of heavy metals.

### 3.3 Modelling of Heavy Metals Transport in Soil

In recent years, a great number of studies have been performed concerning the assessment of heavy metals transport in soil in order to prevent groundwater contamination (Yanful *et al.*, 1988; Mohamed *et al.*, 1994; Holm and Zho, 1994). The effect of multi-component contaminants on the diffusion and adsorption properties of some domestic waste in a natural clayey soil has been emphasized by researchers such as Gilham *et al.* (1984), Warith (1987), Baron *et al.* (1989), Fernandez (1989) and Yong *et al.* (1990).

The current prediction of contaminant transport in a clay barrier is based on migratio modelling of each individual component based on the law of conservation of mass. This law can be expressed in non-mathematical form as (Freeze and Cherry, 1979):

| | | | | | | |
|---|---|---|---|---|---|---|
| the rate of change of mass concentration of chemical species i within a given control volume | = | the net advective flux of the species i into the control volume | + | the net diffusive flux of the species i into the control volume | + | the net rate of production of species i within CV |

A mathematical equation of the above statement can be written for the chemical species i as:

$$\frac{\partial C_i}{\partial t} = D_z \frac{\partial^2 C_i}{\partial z^2} - V \frac{\partial C_i}{\partial z} - \frac{\partial S_i}{\partial t} \qquad \textbf{(3.1)}$$

where

$C_i$ = pore fluid concentration of component i (M/L$^3$ fluid)
$D_z$ = dispersion coefficient (L$^2$/T)
V = average pore velocity (L/T)
$S_i$ = total solid-phase concentration (retained) of component i (M/L$^3$ fluid)
z = depth of clay liner (L)
t = time (T)

The term on the left-hand side of equation 3.1 is called the transient term. It may be interpreted as the total rate of change of mass concentrations of species i at a point in depth at a given instance of time. If the rate of concentrations does not change with time, this term is zero and Equation 3.1 reduces to what is commonly called a steady- state mass balance. Since the primary function of a transport model is to predict and quantify these changes in solute concentrations, the steady-state assumption cannot be made.

The first term on the right-hand side of Equation 3.1 is the advective term. This term represents a change in concentration of the system resulting from the gross movement of fluid in the which species is transported. The mass average velocity vector of the fluid mixture, V, is a function of time, space, temperature, and the chemical composition of the mixture. If V is constant with respect to time, the flow is said to be steady. For longer simulations, the velocity cannot reasonably be assumed to be constant.

The second term on the right-hand side of equation is the diffusive or relative flux term. This term represents the change in concentration at a point in the system resulting from molecular diffusion and mechanical dispersion.The coefficient of hydrodynamic dispersion ($D_z$) is normally computed in terms of the above two components (Bear, 1987):

$$D_z = \alpha_z V + D^*$$

where $\alpha_z$ is a characteristic property of the porous medium known as the dynamic dispersivity (L), and $D^*$ is the coefficient of molecular diffusion for the solute in the porous medium. At a low velocity, which is the case for the clay liner, diffusion is the important contributor to the dispersion, and therefore, the coefficient of hydrodynamic dispersion equals the diffusion coefficient ($D_z=D^*$). At a high velocity, mechanical mixing is the dominant dispersive processes ($D_z=\alpha_z V$).

The last term is usually called the source/sink, reactive or nonconservative term. For the reactive contaminants, assuming a linear adsorption isotherm, Equation 3.1 yields

$$R\frac{\partial C_i}{\partial t}=D_z\frac{\partial^2 C_i}{\partial z^2}-v\frac{\partial C_i}{\partial z} \tag{3.2}$$

where

$$R = 1 + \frac{\rho}{n}\frac{\partial S}{\partial C} = 1 + \frac{\rho}{n}K_d$$

R = retardation factor

n = medium porosity ($L^3$ fluid/$L^3$ medium)

ρ = bulk density of medium (M solids/$L^3$ medium)

$K_d$ = the ratio of the total amount of a component in the solid to the aqueous phase

In the above equation it is assumed that neither the dispersion nor the interstitial velocity changes in the z-direction. Most often the interstitial velocity will be so high that all components have the same dispersion coefficient. In a clay liner with very low permeability, velocity differences between the individual components do occur as a result of their individual diffusion coefficients in the aqueous phase.

It sometimes happens that it is necessary to account for a component that does not move with fluid flow, e.g. precipitates and adsorbs. This means that the diffusion coefficient cannot be considered as a constant which most of the contaminant transport models are based upon except the transport model developed by Yong and Samani (1988).

Using the above $K_d$ approach, for prediction purposes, it is assumed that: (1) the dispersion coefficient is constant; (2) local chemical equilibrium is satisfied; (3) trace amounts of components prevail, (4) adsorption isotherm is linear, and (5) $K_d$ is spatially and temporally constant and is measured by the batch equilibrium test at a standard pH.

The limitations of using $K_d$ as a constant parameter are discussed by Reardon (1981) and Cherry *et al.* (1984). On the other hand, several studies (e.g. Rowe *et al.*, 1988; Shackelford *et al.*, 1989; and Airey and Carter, 1995) indicated that the batch test overestimates the adsorption in the ground.

A typical multi-contaminant and its interaction with soil particles before and after chemical equilibrium is shown in Fig. 3.1, where $Zn^{2+}$, $Pb^{2+}$, $Cl^-$ and $H^+$ represent zinc, lead, chloride and hydrogen ions, respectively. $ZnCl^-$ and $PbCl^-$ are metal ions complexed with chloride ions. As shown in the same figure, Zn and Pb ions are partly retained (adsorbed and precipitated) on soil and partly dissolved in the aqueous phase. The aqueous phase could be partly free ions or a complexed form with $Cl^-$ ions, depending on the surface characteristics of the soil, chloride concentration and pH.

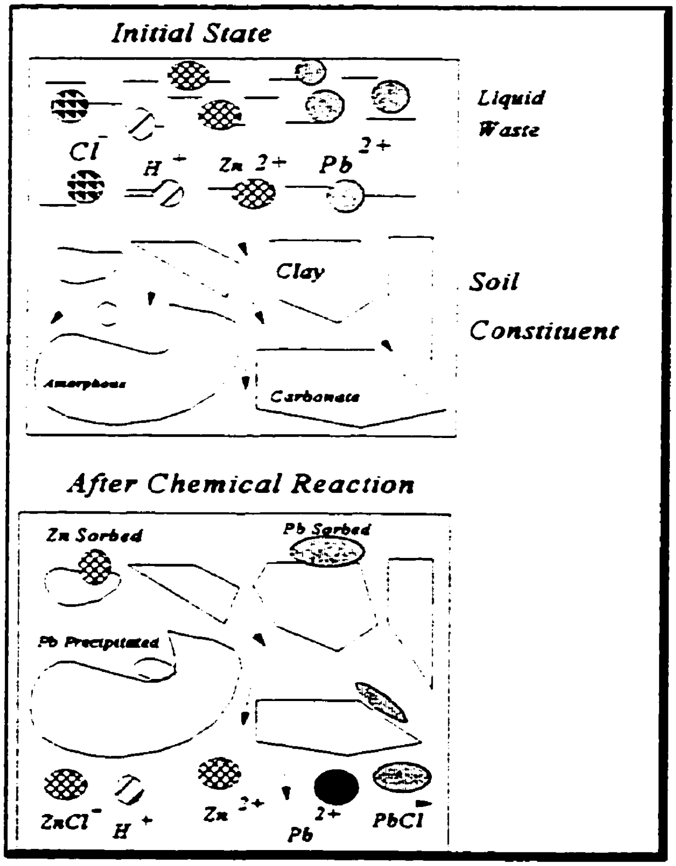

**Fig. 3.1** A Multi-contaminant Soil System before and after Achieving Chemical Equilibrium.

Using the multi-component contaminant illustrated in Fig 3.1, the distribution coefficients $K_d$

(the ratio of the total amount of a component in the solid phase to the total amount of component in the aqueous phase for $Zn^{2+}$ and $Pb^{2+}$) yields

$$K_d(Zn) = \frac{[Zn]_{adsorbed}}{[Zn^{2+}]+[ZnCl^{+}]+[ZnCl_2]}$$
$$K_d(Pb) = \frac{[Pb\ ]_{adsorbed}}{[Pb^{2+}]+[PbCl^{+}]+[PbCl_2]} \qquad \textbf{(3.3)}$$

In this simple example, it is clear that for $K_d$ to remain spatially and temporally constant in a multi- species solution, the partitioning of the component $Zn^{2+}$ or $Pb^{2+}$ between the solid and solution must remain constant, even though a change in chemical speciation may occur due to varying concentration levels of Cl.

Even modelling of the fate of the particular contaminant species via evaluation of adsorption by using the nonlinear partitioning function does not represent the actual physico-chemical reactions. Both D (diffusion coefficient) and S (adsorption) or R (retardation) pay attention to a particular solute (contaminant species) at any one time. Thus in a multi-component transport, each constituent species should be computed and analysed separately. However, if one recognizes that the behaviour and fate of each constituent species depends on the concentration and type of other constituents, (Gilham *et al.*, 1984; and Yong *et al.*, 1990), then it becomes clear that extrapolation of any of the coefficients or relationships for general field application must pay particular attention to how well the field contaminant leachate is mimicked in composition variation (constituent concentration and distribution) with time and space (Yong *et al.*, 1992). Baron *et al.* (1989) in an experiment involving the diffusion controlled column leaching test showed that migration of cations in a multiple contaminant is different from that of the single system. Thus, the $K_d$ or a similar approach to transport modelling does not account for changes in contaminant concentration due to geochemical processes such as complexation or pH changes. In addition, in the $K_d$ approach some of the basic soil parameters which affect the adsorption of pollutants, i.e., specific surface area and Cation Exchange Capacity (CEC), are not considered. Also, the outcome of any contaminant introduced into the clay liner in a landfill system is largely dependent on the capacity of the solid matrix material to adsorb substances. This is because the surface areas exposed to ion reactions differ in physico-chemical behaviour, as represented by cation and anion exchange properties. Changes in soluble solute concentrations, organic matter and pH levels in soil solution, all have significant effects on the extent of the adsorption process.

However, for contaminants that are hazardous at a very low concentration level, prediction of the arrival time of the contaminant front zone is more important than the prediction of the arrival time of the mean location of the contaminant zone. For the toxic components, one species containing that component may be more toxic than another. Existing chemical transport models (Volacchi *et al.*, 1981; Jenning *et al.*, 1982; Cederberg, 1985; Jauzein *et al.*, 1989; Engesgarrd, 1991; Walter *et al.*, 1994) cannot be applied to the clay liner since they do not consider soil composition, pH, effective diffusion coefficient, and osmotic pressure effects on heavy metals transport in a multi-component system.

The proposed geochemical transport model will provide the partitioning profiles of specific ions (i.e., adsorbed or precipitated on soils and remaining in the solution). This type of model provides a useful tool for geo-environmental engineers for :

(i) assessing the importance of geochemical speciations on the transport of heavy metals in groundwater, considering contaminants interaction, and soil composition under different environmental conditions, i.e. pH, temperature and $CO_2$ pressure

(ii) predicting the forms by which the metals are partitioned in the clay barrier; and

(iii) indicating the potential availability of the heavy metals, particularly, if one recognizes that the local equilibrium pH environment is neither stagnant nor uniform throughout the subsurface beneath the waste landfill.

## 3.4 Development of COSTCHESP Formulation

The development of geochemical transport models is a fairly new pursuit although some date back to the late 1960's. The majority of the effort, however, took place in the 1980's following the trend of adding more complex chemistry to single- and multi-dimensional groundwater and solute transport models. Very few models, though, include all types of possible geochemical reactions. Transport is described by a set of partial differential equations and the geo-chemical reactions are described by set of nonlinear algebraic equations. A coupled model may be used to simulate the effect of specific chemistries on reactive solutes during transport through porous media.

Reconciling chemical equilibria with the prediction of inherently non-steady contaminant transport has been approached in various ways. An excellent review of the different approaches to coupling has been published by Mangold and Tsang (1991). The coupled solute transport and chemical equilibrium model is divided into three broad categories: i) the mixed differential and algebraic equation approach (DAE), ii) the direct substitution approach (DSA), and iii) the sequential iteration approach (SIA).

Briefly, the DAE approach combines the transport equations and equilibrium reactions into a single set of partial differential and algebraic equations which are solved simultaneously. In the DSA approach, the chemical equations are also substituted directly into solute transport terms and the resulting partial differential equations solved simultaneously. In the SIA, which is used in this study, the transport and chemistry are decoupled and the governing equations are solved iteratively in a sequential manner. The DAE and DSA approaches would result in an excessive number of dependent variables and hence would require too much central process unit (CPU) storage and CPU time for realistic applications. They might provide a good research tool for one dimensional (1-D) simulation with a limited number of chemical species. In addition, solving the multi-dimensional non-linear partial differential equations (PDEs) and non-linear algebraic equations (AEs) simultaneously is more complex.

In the present work, the sequential iteration approach has been adopted, and the rest of the discussion and model development will focus on this approach. The system is based on two coupled sequential sets of nonlinear PDEs and nonlinear AEs. The sequential interaction approach has been used to separate chemistry from transport, this simplifies the coupling between the physical and chemical processes and leads to a simple and efficient two-step sequential solution algorithm. The advantages of this type of coupled model include access to the comprehensive geochemical database and the ability to simulate hydrogeological systems with realistic soil properties and boundary conditions under complex geochemical conditions and also makes all transport equations independently solvable. The later approach is used in this research.

In order to assess the reliability of the model, some laboratory experiments were carried out and the simulated model will be compared with experimental results. Since different parameters have different effects on the solution, the sensitivity of the parameters in the simulated model will be evaluated. Theoretical, laboratory and mathematical modeling thus can make important contributions to the development of an improved predictive capability. In the following sections the formulation of Chemical Equilibrium Speciation (CHESP), COupled Solute Transport (COST) and the proposed iteration approach are presented.

### 3.4.1 CHESP Formulation

In order to describe the chemical reactions mathematically, a subset of the species must be chosen as components. All other ions, complexes, sorbed species, and minerals can be formed from the these components. In this work, the free ions have been chosen as components. It is assumed that all chemical interactions between soluble components in the aqueous phase and soil constituents in the solid phase are controlled by local equilibrium and that local equilibrium exists at every point of the system considered. In local equilibrium-controlled transport systems, the reaction rates are much faster than the rates of physical transport. This assumption may be the most restrictive relative to conditions that may pertain to the real system. Hence, the assumption will be investigated more throughly in section 3.5.1. A reversible process is one in which the direction of the reaction can always be changed with a variation in the system variables. The equilibrium interaction chemistry must contain all of the phase-exchange and/or mass-equations necessary to describe the chemical processes affecting the transport, i.e. sorption, complexation, dissociation, and ion exchange. In the chemical model, we have the species ($c_1$, $c_2$, $c_3$,...$c_{naq}$, $s_1$, $s_2$, $s_3$,..$s_{ns}$, $p_1$, $p_2$, $p_3$,...$p_{np}$), where $c_i$'s are concentrations in aqueous phase; $s_n$'s adsorbed on the solid phase, and $p_i$'s precipitated on the solid phase. The formation of species $c_i$ in the aqueous phase or species $s_i$ and $p_i$ in the solid phase can be described by the mass action law as follows (Sposito and Mattigold, 1988):

$$
\begin{aligned}
c_i &= K_{c_i}\prod_{j=1}^{N_c} X_j^{a_{ij}^{a}} && i=1,2,\ldots,n_a \\
s_i &= \frac{\rho \dot{c}_i}{n} = K_{s_i}\prod_{j=1}^{N_c} X_j^{a_{ij}^{s}} && i=1,2,..,n_s \qquad (3.4) \\
K_{sp_i} &\geq \prod_{j=1}^{N_c} X_j^{a_{ij}^{p}} && i=1,2,..n_p
\end{aligned}
$$

where

$K_{ci}$ = equilibrium formation constant for species $c_i$

$K_{si}$ = equilibrium formation constant for species $s_i$

$\prod$ = product operator over all components

$K_{spi}$= solubility product for species $p_i$

$X_j$ = activity of component j

$X_j$ = $\gamma_j\, C_j$

$\gamma_j$ = activity coefficients of j-th component

$C_j$ = concentration of component j

$a_{ij}^{a}$ = stoichiometric coefficient of component j in species $c_i$

$a_{ij}^{s}$ = stoichiometric coefficient of component j in species $s_i$

$a_{ij}^{p}$ = stoichiometric coefficient of component j in species $p_i$

$n_a$ = number of species in the aqueous phase

$n_s$ = number of species adsorbed in the solid phase

$n_p$ = number of species precipitated in the solid phase

Nc = total number of components

An expansion of the equation 3.4 for the case of lead and chloride in the experimental program, mentioned in section 2.0, yields the following:

$$\begin{gathered}
c_1=\gamma_{c_1}[Cl^-]=K_{c_1}\\
c_2=\gamma_{c_2}[Pb^{2+}]=K_{c_2}(\gamma_{x_2}[Pb^{2+}])^1\\
c_3=\gamma_{c_3}[PbCl^+]=K_{c_3}(\gamma_{x_2}[Pb^{2+}])^1(\gamma_{x_1}[Cl^-])^1\\
c_4=\gamma_{c_4}[PbCl_2]=K_{c_4}(\gamma_{x_2}[Pb^{2+}])^1(\gamma_{x_1}[Cl^-])^2\\
c_5=\gamma_{c_5}[H^+]=(\gamma_{x_3}[H^+])^1\\
s_1=[PbSO^+]=K_{s_1}(\gamma_{x_2}[Pb^{2+}])^1(\gamma_{x_3}[H^+])^{-1}[SOH]
\end{gathered}$$

In this formulation sorptive sites are treated as one of many components, ($X_j$). The mass balance equation requires that the sum of mass for each species in both aqueous and solid phase must be equal to the total amount of mass in the system. Hence, the total concentration of each component $T_j=C_j+S_j+P_j$

$$\begin{aligned}
C_j&=\sum_{i=1}^{n_a} a_{ik}^{a} c_i \qquad k=1,2,..n_a\\
S_j&=\sum_{i=1}^{n_s} a_{im}^{s} s_i \qquad m=1,2,..n_s\\
P_j&=\sum_{i=1}^{n_p} a_{il}^{p} p_i \qquad l=1,2,..n_p
\end{aligned} \tag{3.5}$$

$$T_j=\sum_{i=1}^{n_a} a_{ik}^{a} C_i+\sum_{i=1}^{n_s} a_{im}^{s} S_i+\sum_{i=1}^{n_p} a_{il}^{p} P_i \qquad j=1,2,..N_c \tag{3.6}$$

where

$T_j$ = total concentration of component j($M/L^3$ fluid)

$C_j$ = concentration of component j in the aqueous phase ($M/L^3$ fluid)

$\dot{C}_j$ = total concentration of component j on the solid phase (M/M solids)

$S_j$ = total concentration of component j adsorbed on the solid phase ($M/L^3$ fluid)

$S_j = \rho\dot{C}_j/n)$

$P_j$ = total concentration of component j precipitated on the solid phase ($M/L^3$)

An expansion of the Equation 3.6 for the case of lead and chloride can be written as

$$T_1 \equiv ([Cl^-]_T = \sum_{i=1}^{5} a_{ij}c_i = (Cl^- 1) + (PbCl^+) + 2(PbCl_2)$$

$$T_2 = [Pb^{2+}]_T = \sum_{i=1}^{5} a_{ij}c_i + \sum_{i=1}^{2} a_{ij}s_i = (Pb^{2+}) + (PbCl^+) + (PbCl_2) + (PbOH^+) + (SOPb^+)$$

### 3.4.2 COST Formulation

The derivation of the basic reactive transport equations has been presented before. The presentation here will therefore, only be focused toward a discussion of the limitation behind the application of the existing contaminant transport model in clay soil. The general transport equation for computing the concentration of a single dissolved chemical species in the porous media can be expressed as (Bear, 1987)

$$\frac{\partial c_i}{\partial t} + \frac{\partial s_i}{\partial t} = \nabla.D.\nabla c_i - \nabla.Vc_i \qquad i = 1,2,...n_a \tag{3.7}$$

where

$s_i = (\rho\dot{c}_i/n)$

$\dot{c}_i$ = concentration of species i in the solid phase (M/M solids)

D = hydrodynamic dispersion tensor ($L^2/T$)

V = velocity vector (L/T)

Considering the coupled processes (Mohammed, 1995, Mohamed *et al.*, 1995, Yong *et al.*, 1992) Eq. 3.7 could be expressed in a one dimensional form for the migration of each individual component as follows:

$$\frac{\partial c_i}{\partial t}+\frac{\partial s_i}{\partial t}=\frac{\partial}{\partial z}(D_z\frac{\partial c_i}{\partial z})-R_I V\frac{\partial c_i}{\partial z}-R_o\frac{\partial^2 c_i^{\,2}}{\partial z^2} \tag{3.8}$$

where

$R_I$ = $(k_{ch}/k_h)+1$ = ion restriction effect
$R_o$ = $(k_{ch}\, k_{hc})/2k_h$ = osmotic effect
$k_{ch}$ = ion restriction coefficient
$k_{hc}$ = osmotic coefficient
$k_h$ = permeability coefficient
$D_z$ = $a\, e^{bC}$

where $k_{ch}$, $k_{hc}$, a and b are material parameters to be determined based on the experimental results and an optimization technique.

In a multi-species solution where the sorbed-phase concentration of species i, $s_i$, is a function of the aqueous species concentration, a nonlinear system of solute transport equations can be obtained. By making use of the definitions in Equations (3.5) and (3.6) for $C_j$, $S_j$, $P_j$ and $T_j$, the set of $n_s$ equations described by Eq. (3.8) can be reduced to a set of $N_c$ mass transport equations as:

$$\frac{\partial T_j}{\partial t}=\frac{\partial}{\partial z}(D_z\frac{\partial C}{\partial z})-R_I V_v\frac{\partial c}{\partial z}-R_o\frac{\partial^2 C^2}{\partial z^2} \tag{3.9}$$

The COupled Solute Transport (COST) model represented by Eq. (3.9) and the CHemical Equilibrium Speciation (CHESP) by Eq. (3.4) constitute the basis for COSTCHESP development. The key point in the above formulation is that instead of formulating the transport equations around the mass balance for each species in the aqueous phase, $c_i$, they have been formulated around the mass balance for the total concentration of each component, $T_j$. The time derivative of the total component concentration is a function only of the transport by advection and dispersion of the total aqueous component concentration, $C_j$. When $S_j$=0, Eq. (3.6) reduces to a nonreactive transport equation, where $T_j = C_j$. This formulation allows the interaction chemistry to be posed independently of the mass-transport equations and the subsequent coupling of the two sets in a precise manner.

The formulation procedures for the case of chloride and lead transport into the column clay are briefly discussed. As described in Section 3.1.1 the total concentration of chloride, Tj, is equal to the sum of the concentrations of chloride in three species. Adding the mass-transport equations for these three species yields the following equation:

$$\begin{aligned}&\frac{\partial}{\partial t}(Cl^-)+\frac{\partial}{\partial t}(PbCl^-)+\frac{\partial}{\partial t}(PbCl_2)\\ &=L(Cl^-)+L(PbCl^-)+L(PbCl_2)\end{aligned} \qquad \textbf{(3.10)}$$

where

$$L=bD_z\left(\frac{\partial}{\partial z}\right)^2+D_z\frac{\partial^2}{\partial z^2}-R_IV\frac{\partial}{\partial z}-R_o\frac{\partial^2}{\partial z^2} \qquad \textbf{(3.11)}$$

Adding the left hand side of the Equation 3.10 gives

$$\frac{\partial}{\partial t}(Cl_T)=L(Cl_T) \qquad \textbf{(3.12)}$$

where $Cl_T$ is the total $Cl^-$ concentration (mole/litre). Since $Cl^-$ is a conservative component, the total $Cl^-$ concentration equals the total aqueous concentration $^-$of Cl. The total concentration of lead, the non conservative component, is equal to the sum of the concentrations of $Pb^{2+}$ in aqueous, adsorbed and precipitated species as follows:

$$\begin{aligned}&\frac{\partial}{\partial t}([Pb^{2+}]+[PbCl^{+}]+[PbCl^{2}]+[PbOH^{+}])+\\&\qquad\frac{\partial}{\partial t}(\frac{\rho}{n}([Pb(OH)^{2}]+[SOPb^{+}]))\\&=L([Pb^{2+}]+[PbCl^{+}]+[PbCl_{2}]+[PbOH]^{+})\end{aligned} \tag{3.13}$$

As shown the transport of lead can be formulated in a similar manner even though it is a non conservative component. Equation 3.13 can be written as

$$\frac{\partial}{\partial t}(Pb_T)=L(Pb_{aq}) \tag{3.14}$$

where $Pb_T = Pb_{aq}+\rho/n\ (Pb_s+Pb_p)$ represents the total concentration of lead in the system.

### 3.5 Solution Technique

The final set of COST and CHESP equations constitute a coupled system of transport and chemical equilibrium reactions and is a system of differential equations. Analytical solution to the system in general is beyond the capability of present-day applied mathematics. Numerical methods are the only tool that can be used to achieve a solution.

### 3.5.1 Solution of CHESP

To get $c_1$, $c_2$ .... $c_{na}$ , $s_1$, $s_2$.... $s_{ns}$, and $p_1$, $p_2$,... $p_{np}$ from the set of chemical equilibrium equations (Eq. 3.4) and also, $C_1$, $C_2$, ...$C_{Naq}$, $S_1$ ,$S_2$,....$S_{Ns}$, $P_1$ , $P_2$ ,..... $P_{np}$ from Eq. (3.5) , a computer code, CHESP (which is a modified geochemical model of USEPA; Allison et al., 1993, MINTEQA3 ) is used. In this program Eq. (3.4) and (3.5) are implemented to calculate the mass distribution of each component (adsorbed and precipitated on solid and available in solution).

CHESP uses the simultaneous solution of the non linear mass action expressions and linear mass balance relationships to formulate and solve the multiple- component chemical equilibrium problems. It uses mass-law equations and formation constants for the set of species and material balance equations for each component to define the chemical equilibrium problem. In the CHESP model, from an initial guess of the activity of each component (noncomplexed), the provisional concentrations of each species are computed through the mass action expressions written in terms of component activities (Eq. 3.4). The total mass of each component is then calculated from the concentrations of every species containing that component (Eq. 3.5). The calculated total mass for each component is then compared with the known input total mass for each component. If the calculated total mass component differs from the input total mass for any component by more than a pre-set tolerance level with the total mass, a new estimate of the component activity is made and the entire procedure is repeated. After equilibrating the aqueous phase, CHESP computes the saturation index (SI) for each possible solid with respect to the solution. The solid with the most positive SI is allowed to precipitate. The reverse process occurs if an existing solid is found to be under-saturated with respect to the solution.

The information required from CHESP after execution is the total aqueous concentration of all components ($C_1$, $C_2$, .., $C_{N_c}$), where $N_c$ is the number of components. The solution procedures, through iteration, are shown schematically in Figure 3.2. Details of the main subroutines and source code of CHESP can be found in Appendix A and Appendix F, respectively.

The aqueous concentration has units of mol/L water (molarity). A component which is sorbed on the soil is given the concentration $S_j$. $N_s$ sorbed components can be present. $N_p$ minerals can exist with concentrations $P_k$. The solid concentrations have units of mol/kg soil. If the dry soil bulk density is $\rho$ ( kg soil/m$^3$ soil) and the porosity is n (m$^3$ water/m$^3$ soil), then the units of $(\rho/n) \times P_k$ and $(\rho/n) \times S_j$ are equal to the aqueous phase units. The geochemical code that has been used to solve the geochemical equation uses internal concentration units of mol/kg water (molality).

The total aqueous component concentration is the concentration that can be obtained by standard laboratory analysis techniques and, as such, is not only relevant for developing a geochemical transport model, but also relevant, when comparing the results of the model simulations with observations. The total component concentration is defined as

$T_{pb2-} = C_{Pb2+}\ \rho/n\ (S_{Pb2+}+PbCO_3)$

which is the sum of the concentrations of the $Pb^{2+}$ component in the aqueous and solid phase.

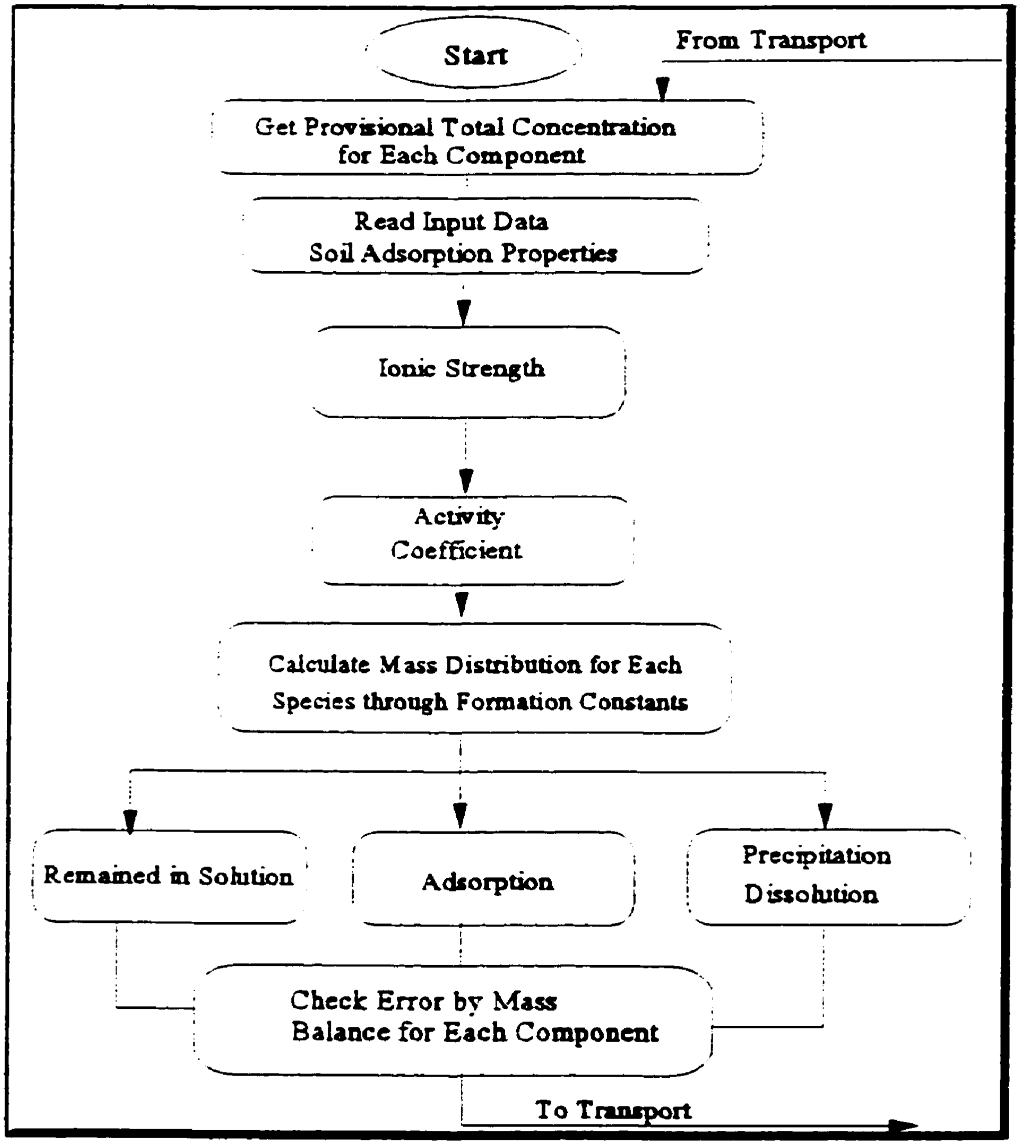

**Figure 3.2** CHESP Flow Chart.

### 3.5.2 Solution of COST

Since a proper analytical solution for COST represented by non-linear partial differential equations does not exist, a numerical technique, in particular, a finite- difference method (FDM), has been used in this study. The finite element method (FEM) has advantages such as the ability to discretize complex boundaries, ease to deal with flux-type boundary conditions, and flexibility to include cross-derivative terms (Rubin, 1983). Disadvantages of the finite element method (FEM) include the requirements of central processes unit (CPU) time to obtain element matrices and the inflexibility of using iteration methods to solve the resulting matrix equation. On the other hand, the FDM offers great computing time because of the simple interpolation for the derivatives and provides the flexibility of solving the resulting matrix equation with various iteration methods. FDM can deal even more than the FEM with discretizing the complex boundaries if the physical representation of the method is clearly understood (Haffman and Chiang, 1993). In light of these discussions, FDM was the preferred numerical method in this study. Hence, assuming an exponential function of concentration for the diffusion coefficient (Yong *et al.*, 1992), Eq. (3.9) yields:

$$\frac{\partial T}{\partial t}=bD_z\left(\frac{\partial C}{\partial z}\right)^2+D_z\frac{\partial^2 C}{\partial z^2}-R_l V\frac{\partial C}{\partial z}-R_o\frac{\partial^2 C}{\partial z^2} \tag{3.15}$$

The explicit finite difference forward in time and central in space (FTCS) of Eq. (3.15) is given by:

$$\begin{aligned} T_j^{n+1}={}&T_j^n+\Delta t[-R_i(V_z)\frac{C_{j+1}^n-C_{j-1}^n}{2\Delta z}\\ &-R_o\frac{(C_{j+1}^n)^2-2(C_j^n)^2+(C_{j-1}^n)^2}{(\Delta z)^2}\\ &+bD_z\left(\frac{C_{j+1}^n-C_{j-1}^n}{2\Delta z}\right)^2+D_z\frac{C_{j+1}^n-2C_j^n+C_{j-1}^n}{(\Delta z)^2}] \end{aligned} \tag{3.16}$$

Using Eq. (3.16) concentrations at advanced time step (n+1) can be determined in terms of known concentrations at previous time steps, starting from initial conditions. A conceptual approach of the transport part of the proposed model is shown in Figure 3.3. Details of the assumption and formulation of the COST can be found in Appendix B.

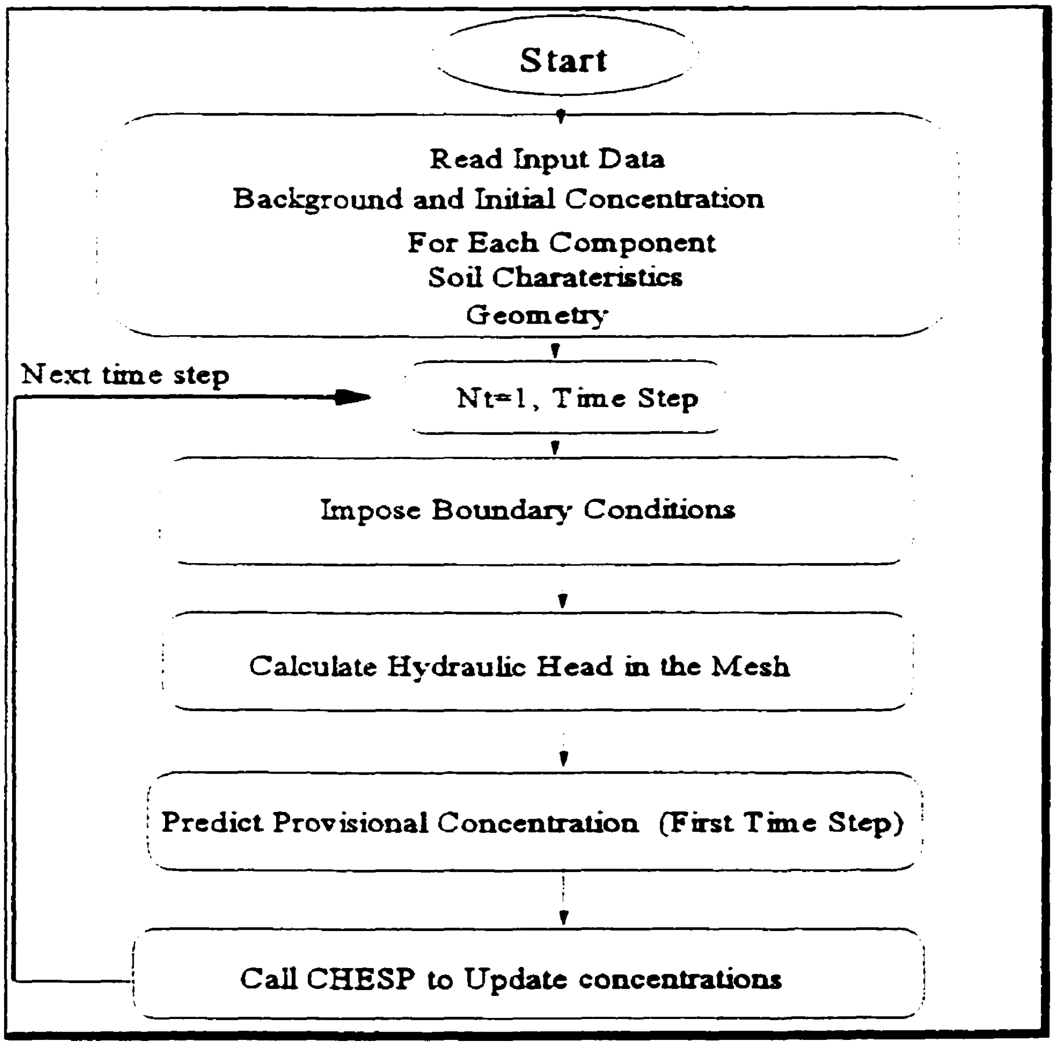

**Figure 3.3** Cost Flow Chart

### 3.5.3 Linking COST and CHESP

The sequential iteration approach, proposed to link the COST and CHESP is shown schematically in Figure 3. 4. It can be described as follows:

1. Construct grids.
2. Use CHESP to initiate the system into equilibrium.
3. Use COST model to calculate the total concentration of all components at new time step.
4. Use CHESP to compute dissolved, adsorbed and precipitated concentrations of reactive components using the total concentration of nonreactive components at step 3 and old value of total concentration.
5. Use COST to compute a provisional solution for the total concentration for the reactive components using the results from step 4.
6. Given this provisional solution from the transport equation for reactive components, use CHESP to compute a new estimate of the aqueous concentration for reactive components.
7. Use COST to compute a new provisional solution using, results from step 6.
8. Repeat steps 6 and 7 until the prescribed convergence tolerance is met, for total concentration for each component.
9. Compute new value of total concentration for each component at advanced time.

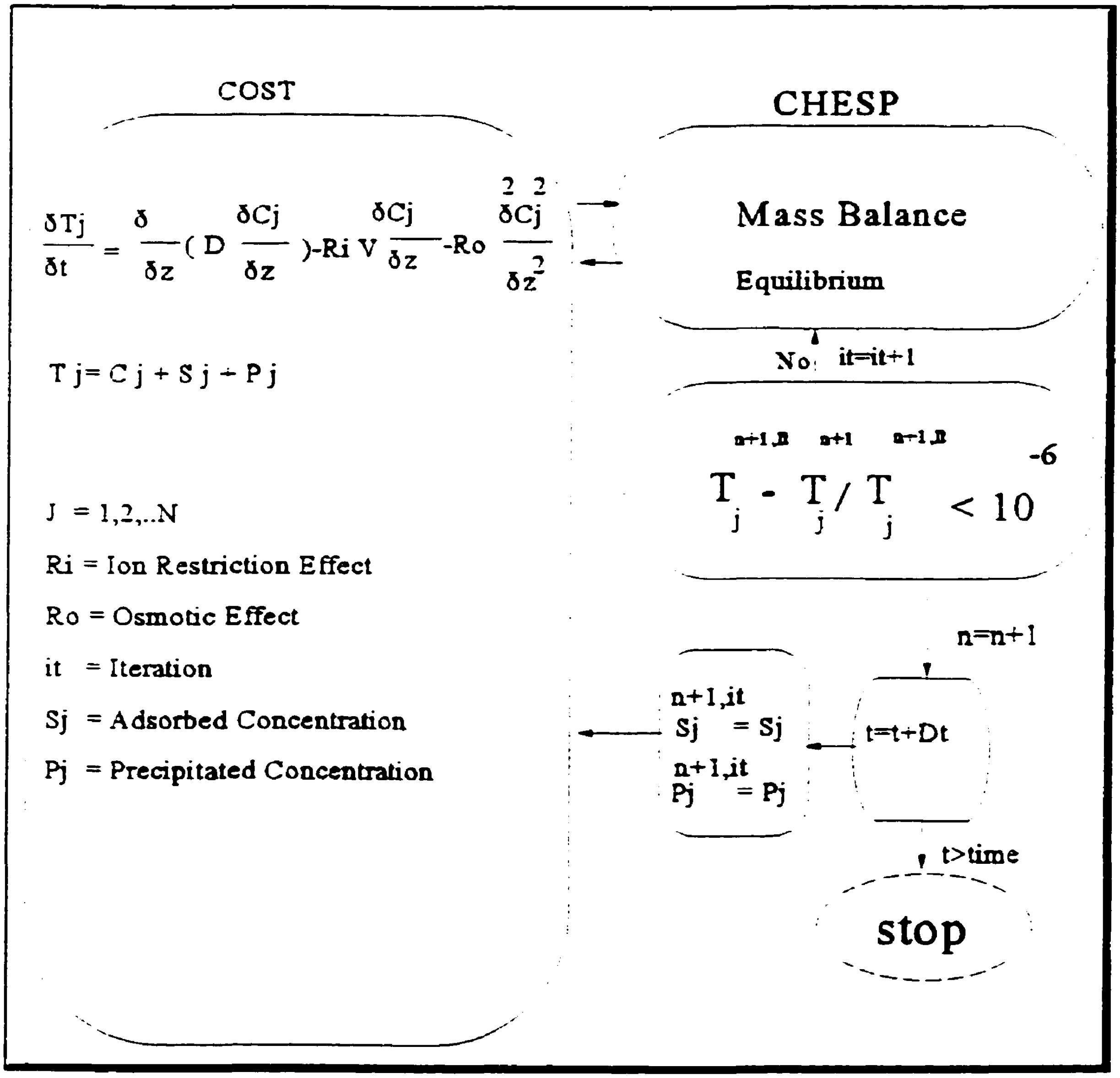

**Figure 3.4** Linking between COST and CHESP

### 3.5.4 Boundary Conditions

The contaminant transport model in a clay liner beneath a landfill was assumed as a one-dimensional problem because the depth of the liner is essentially very small compared to the area of the landfill. The concentration of each contaminant in the landfill, $C_{ij}$, was considered as the total aqueous concentration in CHESP and upper boundary condition in COST. The concentration of each contaminant in a soil layer was specified as the background concentration, $C_{bj}$. At the lower boundary condition there is no change in the concentration of the contaminant species at the drainage layer or $\partial C/\partial Z=0$.

### 3.5.5 Accuracy of the Model

The error of the numerical solution in the finite difference method, in which the forward in time and central in space (FTCS) scheme is used, is of the order $[(\Delta t), (\Delta z)^2]$. Clearly, increasing the step size increases the error. It should be noted that selecting a very small step size should be avoided, since in addition to the enormous amount of computer time required for a solution, the accuracy of the solution will be dominated by round-off errors. On the other hand the stability requirements impose limitations in FTCS method. FTCS is stable for $D\Delta t/(\Delta z)^2 \leq 0.5$ (Haffmann and Chiang, 1993)

The numerical dispersion error is greater when the advective velocities are high. The advective velocity in clay is very low, besides, during diffusion/dispersion-advection with retention, the apparent advective velocity and apparent diffusion/dispersion coefficients are both reduced by the retardation factor. This effect makes the numerical scheme less susceptible to numerical dispersion.

### 3.6 Adsorption Models

In the proposed coupled solute transport models seven adsorption models can be used for adsorption of the heavy metals into the clay barrier. These include both empirical equilibrium models such as distribution coefficient (linear isotherm) $K_d$, Langmuir isotherm and Freundlich isotherms, and complexation models such as the Diffuse Double Layer Model

(DDLM), introduced by Huang and Stumm (1973), Constant Capacitance Model (CCM) originally developed by Schindler and Kamber (1968) and reviewed by Sposito (1984) and Schindler and Stumm (1987), and Triple Layer Model (TLM) proposed by Westall (1986).

Recent studies have shown that the ability of the surface complexation models, which have been used in this study, to fit the adsorption are relatively insensitive to the value of the site density used (Kent et al., 1986; Hayes et al., 1990). Clearly, the absolute value of the binding constants, that describe the adsorption reactions, are dependent on the choice of the site density. However, Hayes et al. (1990) showed that the ability to fit experimental data over a wide range of conditions is independent on the choice of the site density over two orders of magnitude. This is true as long as the molar ratio of adsorbate to the surface site is small, i.e., there is an excess of surface sites over adsorbate in the system. When the adsorbing solute is present in excess, the ability to fit adsorption data becomes more sensitive to the value of surface site density used (Davis and Kent, 1990). Thus, the site density in this study was assumed to vary with time and space because the surface complexation theory treats surface functional groups in the same fashion as dissolved components in an equilibrium speciation framework. The adsorption capacity of the clay liner in the column test will decrease as more permeant passes through the column. Details of the assumption and formulation of each adsorption model can be found in Appendix C.

## 3.7 Model Parameters

Two types of parameters are required to use the proposed COSTCHESP: (1) parameters for COST and (2) parameters for CHESP. At the present time, the major difficulty in applying coupled solute transport and chemical reactions in the clay barrier is the lack of data on the transport parameters involved in the governing equation (3.10) considering adsorption of the contaminant into the clay barrier. The transport coefficients or diffusion parameters are often considered to be constant, independent of the pore fluid velocity, concentration of the contaminant, adsorption characteristics of the clay liner, transport time and depth of the clay liner. These parameters are either measured for uncoupled sets of the experiments or estimated empirically from physics and chemistry handbooks. In the case of transport of heavy metals into the clay liner the computation of diffusion parameters is very important because the heavy metals must be retained mostly in the clay liner.

The calculated diffusivity parameter will not be representative of the coupled solute transport and chemical reaction because the diffusion parameters are independent of adsorption, time, and space. To overcome the difficulty, procedures can be developed to provide some capability of accommodating the results of coupled solute transport and chemical reactions. Mohamed *et al.*, (1994) used the square root-time procedure for the calculation of the diffusion parameter which is based on the analytical solution of the simplified version of the differential equation for the contaminant transport. The diffusion parameter calculated from this technique is also used for the steady state condition. In this study a new method is proposed which is based on method of optimization between the experimental data and numerical prediction and discussed in the following sections.

### 3.7.1 Parameters for COST

The parameters required for COST can be classified into two groups: (1) parameters related to initial and boundary conditions, i.e., soil dry density, soil porosity, hydraulic conductivity, and (2) parameters related to physio-chemical processes, i.e., diffusion, osmotic and ion restriction effects. The first group can be determined directly from experiments. However, the second group requires experimental data and application of a numerical technique to optimize the difference between the numerical prediction and experimental results. As indicated in Equation 3.10, if the concentration profiles of the contaminant at time j are known, then, the concentration profiles at time j+1 can be found numerically. Thus, having an experimentally measured concentration profile at a certain time and assuming an exponential function for the diffusion parameter, one can predict the concentration profile at the next time. Based on a matching process of predicted and experimental values, the optimum material parameters (i.e., a, b, $k_{hc}$ and $k_{ch}$) are those which minimize the following:

$$F=\sum_{i=1}^{N} |C_{Exp.}-C_{Calc.}| \qquad (3.17)$$

Where N is the number of the points at which the concentration of each contaminant is measured; $C_{Exp.}$ is the experimentally obtained concentration; and $C_{Calc.}$ is the calculated concentration from the model.

The best way to obtain a minimum value of F is to use a searching technique. One of the most efficient searching techniques is Powell's conjugate directions method of non-linear optimization (Powell, 1964; Devlin, 1994). For the problem under consideration, the derivative of F, with respect to a specific unknown parameter, cannot be determined simply. This makes Powell's method more useful because it does not require derivatives of the objective function.

### 3.7.2 Parameters for CHESP

The parameters required for CHESP may be divided into two groups: (1) The aqueous parameters, i.e., initial aqueous concentration of each component and pH. The pH can be fixed or be specified as the initial concentration of hydrogen ions and determined equilibrium concentration pH. (2) The solid phase parameters including adsorption parameters, specific surface area, CEC, and total density of the solid in the aqueous phase. The former parameters (aqueous parameters) can be measured easily while the latter parameters (the solid phase) will be obtained experimentally. The equilibrium k for heavy metals adsorption in soil was initially obtained from the batch test and calibrated by experimental data from the column leaching test. The surface adsorption site density was initially assigned as CEC for the first trial and then calibrated from the column experiment.

## 3.8 Assumptions and Limitation

The proposed model is based on the following assumptions:

- the porous medium is assumed to be continuous;
- the soil is homogenous and isotropic and the effect of preferential paths is neglected;
- the transport is considered under the isothermal conditions;
- water flow is one-dimensional;

- the effect of the solute on water properties /viscosity, specific mass is neglected;
- porosity, hydraulic conductivity and other characteristics are constant in time;
- adsorption/desorption is assumed to be a fully reversible process;
- saturated clay soil being permeated by contaminants;
- the diffusion/ dispersion coefficient is a function of the concentrations of ionic species;
- validity of Darcy's law;
- biological uptake of mineral is negligible;.
- the chemical reactions are reversible and are governed by the thermodynamic equilibrium.

The model will, most likely, because of the equilibrium assumption, also be restricted to the cases of soil inorganic constituents effects on heavy metals retention. This is because transformation or degradation of organic constituents typically is driven by microbiological processes, which cannot be described by equilibrium theory.

### 3.8.1 Equilibrium Assumption in Geochemical Reactions

The assumption that the geochemical processes follow the thermodynamic equilibrium theory will, at first hand, seem to restrict the application of the model to a few special cases of contaminant transport into a clay barrier. In the real world the geochemical reactions will approach equilibrium over a given time scale where the length of that time scale will decide the applicability of the equilibrium geochemical transport model. An equilibrium-based model has many advantages over a kinetics-based model. In fact, the state of equilibrium is the limiting case for all systems. If all geochemical reactions are controlled by kinetics, then a transport equation must be written for all species. The mathematical system of equations then consists of many partial differential equations for transport coupled to many ordinary differential equations for chemistry, which would be very difficult to solve. In addition, this approach requires knowledge of the reaction rate laws and reactions constants which are seldom known. The advantages of the equilibrium approach: (i) includes more readily available equilibrium constants than the rate parameters. (ii) it is possible to modularize the solution of the system equations into a solution of separate sets of equations for the transport and geochemical systems, as well as reducing the number of transport equations, (iii) with the modularized system it is possible to use existing models for the transport and geochemical components; and (iv) with the high reaction rate the equilibrium approach is much more computationally efficient than a kinetic approach.

The equilibrium approach may not be applied where the reaction rates are very slow compared to the rate of groundwater flow.

### 3.8.2 Validity of Equilibrium Approach

According to Engesgaard (1991), the equilibrium assumption in geochemical reactions of contaminants moving through the geologic media is a function of $T_R/ V \times L$ and dispersion where $T_R$ is the reaction rate and V is flow velocity. He indicated that the validity of the equilibrium assumption thus involves two time scales: a time scale for transport processes and a time scale for geochemical processes.

The time scale for transport could be considered as being the result of two individual time scales, one for advective transport ($T_c = L/v$) and one for dispersive transport ($T_D = L^2/D$), where v and D are the characteristic velocity and dispersion coefficients in the system, respectively, and L is the length from the source to an observation point. In order for the equilibrium assumption to be valid the reaction time scale $T_R$ must be smaller than $T_c$ and $T_D$. A low ratio of reaction rate to velocity over a short length step is typical of a kinetic governed transport system.

Flow velocity in a clay barrier is low because of low permeability, thus the residence time for the chemical flow to react with the clay is potentially quite large, compared to sandy porous media or fractured clay. In other words, an aqueous solution, when applied to compacted clay soil, has a sufficiently long residence time at a given point in the system for the geochemical reaction to proceed to equilibrium, before the solution is transported away. On the other hand, adsorption of heavy metals into a clay barrier is mostly governed by ion exchange and complexation which is often a fast reaction. The experimental studies performed by Bailey and Lynch (1996) show that the sorption rates of all metal ions on humic acid were very rapid, most adsorption occurred within 2 minutes, but sorption did not reach equilibrium in 1 day under competitive conditions. A preliminary test, shown in Figure 3.5., performed by Coles (1997) for the effect of time on the adsorption of two types of heavy metals (lead and cadmium) into kaolinite clay. This figure shows that almost all adsorption took place within hours.

The other parameter which may affect the equilibrium is the mechanical dispersion. The mechanical dispersion of solutes depends on the hydraulic conductivity of the clay and flow velocity. The more dispersion in the transport of solutes, the faster the system can approach equilibrium because the total mass of solute is spread over a larger area causing local changes in concentration.

Using the equilibrium approach is more promising in field applications where total dispersion is large, in contrast to laboratory columns with low dispersion. Also geochemical reactions will approach equilibrium over a given time scale where the length of that time scale will decide the applicability of the equilibrium geochemical transport model.

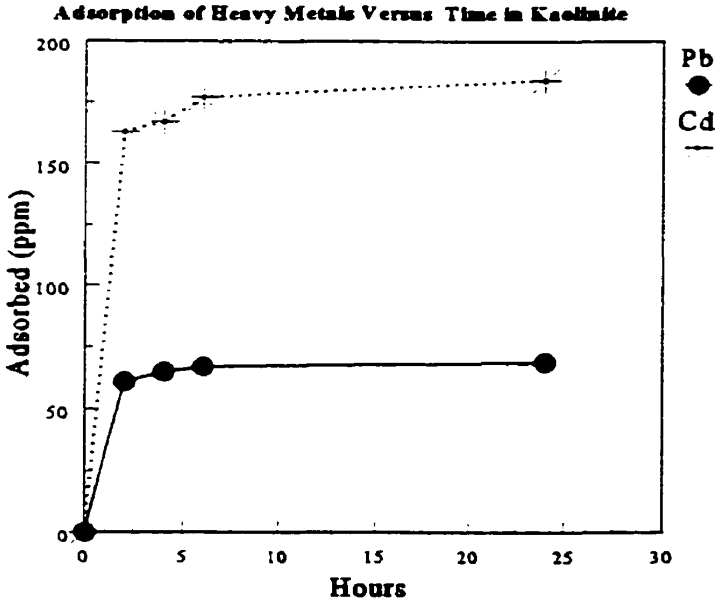

**Figure 3.5** The Effect of Time on Adsorption of Heavy Metals on Kaolinite Clay (After Coles, 1997).

### 3.9 Summary

In this chapter, the state-of-the-art in respect to geochemical and transport models and their limitation for the application of multi-component transport of heavy metals in clay soils has been reviewed and then a (COSTCHESP) model was proposed. The model consists of two main modules, a finite difference transport module (COST), and an equilibrium geochemistry module (CHESP). By making use of the local equilibrium assumption, the inherent chemical nonlinearity is confined to the chemical domain. This linearizes the coupling between the physical and chemical processes and leads to a simple and efficient two-step sequential solution algorithm. The model is capable of simulating both the solute transport and the geo-chemical reaction of heavy metals with other contaminants and soil compositions in a clay barrier system. It provides the distribution of heavy metals concentrations (adsorbed, precipitated, and dissolved ) along the depth of a clay liner to assist in evaluation of the role of the various clay soil solids (clay minerals, amorphous materials, and carbonate) in heavy metals retention. The limitations of the equilibrium assumption and the advantages of equilibrium over the kinetic approach were discussed. It was concluded that the equilibrium assumption for the geochemical reaction provides a good approximation because of the close agreement for equilibrium constant in chemical reactions.

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# Chapter 4

# Batch Equilibrium Test Results

## 4.1 General

The results of the effects of bulk solution composition on heavy metals distribution in different clay soils for batch tests, using different concentrations of chloride or EDTA as the complexing agent are presented in this chapter. Discussion of the results is included in order to explain of the effect of the multi-component to the partitioning of heavy metals in different clay soils. The contents of the chapter are divided into 4 sections corresponding to the experimental sections, given in Chapter 2. The first section contains the results of the tests of the properties of the soil, the second section gives the results of the partitioning coefficient, using a composite heavy metals solution (lead and zinc) at a concentration of 1mmol/L with increasing acid concentration followed by sequential extraction techniques applied to different kaolinite mixtures. In the third section the same experiment was repeated with the application of 1 cmol/L of each heavy metal. In the fourth section the effect of chloride concentration, as a inorganic complexing agent, and EDTA, as an organic one, on adsorption and desorption of the composite heavy metals is provided. For each case the partitioning coefficient, $K_d$ is computed and will then be compared with the one in the column leaching test.

## 4.2 Soil Properties

The pertinent physical and chemical properties of pure kaolinite and its mixture with different percentages of carbonate and amorphous are shown in Table 4.1.

Table 4.1: Prepared Soil Characteristics

| properties | kaolinite (K) | silica gel (S) | 10% silica gel+kaolinite (KS) | 10% carbonate+ kaolinite (KC) | 5% carbonate+ 5% silica gel + kaolinite (KCS) |
|---|---|---|---|---|---|
| pH | 4.5±0.5 | 6.3±0.2 | 5.15±0.4 | 7.07±0.3 | 7.01±0.4 |
| CEC (meq/100 g) | 8±0.4 | 82±5 | 67±5 | 17±2 | 55±3 |
| surface area (m$^2$/g) | 12±0.2 | 276±10 | 118±7 | 66±4 | 97±7 |

### 4.2.1 Discussion on Soil Properties

As shown in Table 4.1, the natural pH, specific surface area (SSA) and cation exchange capacity (CEC ) of the kaolinite used is low. The CEC of kaolinite, a variable charge type of clay, arises from isomorphous substitution within the crystal lattice, and from hydroxylated edges at broken bonds (Yong et al, 1992). Due to the latter, it is pH dependent. In the acidic range H$^+$ and Al$^{3+}$ become very important for the calculation of the total CEC (Grim, 1968). Also, at low pH, the Al is dissolved from the crystal structure and has the ability to replace index cations on the exchange sites (Boland et al, 1980; Duquette and Hendershot, 1987).

As expected, the measured CEC and SSA of the soil treated with a silica gel is much higher than the untreated soil. The increase in CEC is likely due to high CEC and SSA associated with amorphous silica. On the other hand, soil treated with calcium carbonate shows an increase in the pH of the soil solution, much more than silica gel, but its CEC and SSA is lower than amorphous treated soil. Since the CEC of pure carbonate is minor to insignificant (Yong and MacDonad, 1997) the effect of the addition of the calcium carbonate on the CEC of the kaolinite is marginal. The calcium carbonate has higher SSA (40 $m^2/g$) than the kaolinite mixture, due to the bonding effect provided by the carbonate and the greater opportunity for particle dispersion. A comprehensive study of the effect of amorphous silica on liquid limit and plastic limit can be found in research reported by Yong and Sethi (1980) and Habibagahi (1986), and the effect of amorphous silica and iron hydroxides on specific surface area and cation exchange capacity in clay soil material was extensively studied by Wang (1990).

### 4.3 Distribution Coefficient ($K_d$)

The distribution coefficient ($K_d$) is a valid representation of the partitioning between liquid and solids only if the reactions that cause the partitioning are fast and reversible and only if the isotherm is linear (Freeze and Cherry, 1979). The distribution coefficient for heavy metals onto soil can be expressed as

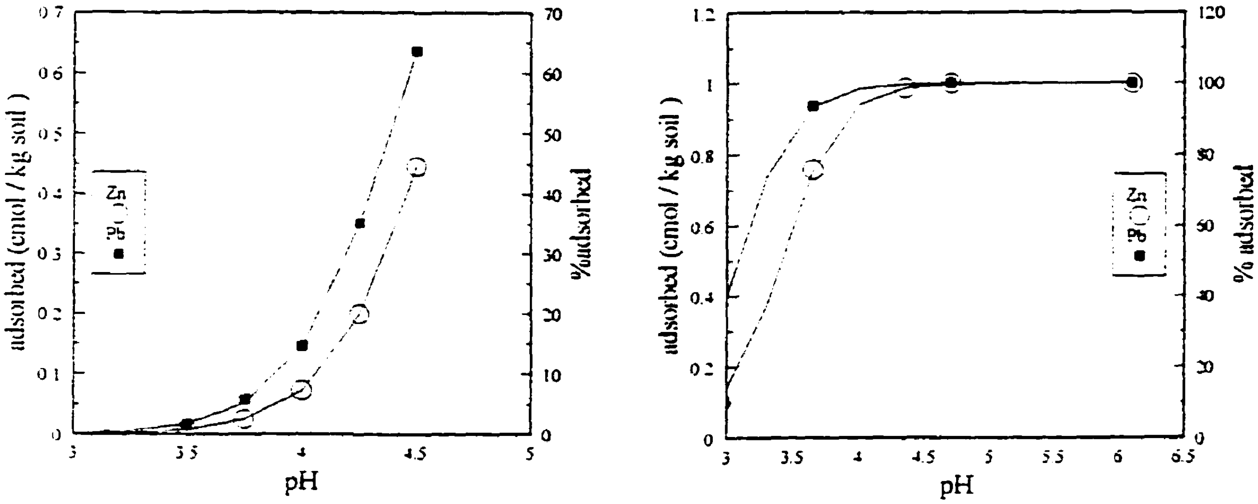
$$K_d = \frac{\text{mass of heavy metals retained on the soil per unit mass of soil}}{\text{supernatant concentration of heavy metals in solution measured by AAS}}$$

The term in the numerator represents the mass of the solute species which is retained on the soil per unit bulk dry mass of the soil (S) in a isotherm adsorption experiment. This could be obtained through batch equilibrium tests by subtracting the supernatant concentration of the heavy metals or other cations, measured by Atomic Adsorption Spectrophotometer (AAS) from the total concentration applied on the soil. This concentration (mg/L) should be converted to (g /g soil). The term on the denominator represents the supernatant concentration or equilibrium concentrations in the aqueous phase, C (g/L). Thus, the dimension for this expression reduces to $L^3/M$. Measured $K_d$ values are normally reported as millilitres per gram (mL/g). In the following sections the retention of each heavy metal for each soil, using different environmental conditions such as pH, dissolved organic and inorganic concentration are presented and the $K_d$'s are computed for each case.

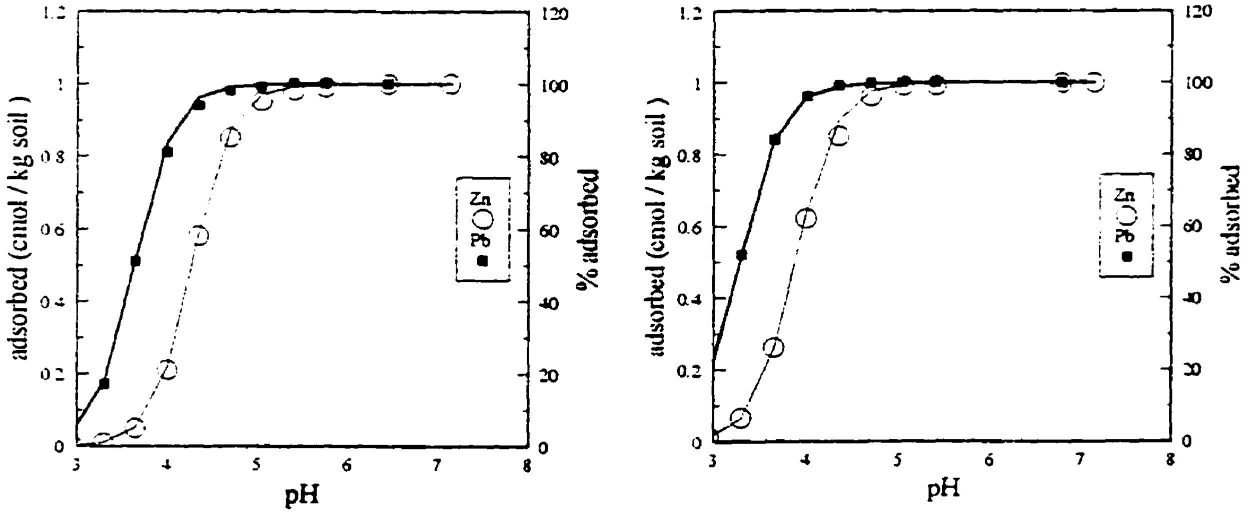
### 4.3.1 pH Effect on Distribution of Heavy Metals in Clay Soil

To evaluate the effect of pH on the distribution of heavy metals in different clay soils, a set of solutions, each solution having the same concentration of Pb and Zn at 1.0 x $10^{-3}$ mol/L and 5.0 x $10^{-3}$ mol/L but with increasing acid concentration, was applied to the soils (K,KS, KC and KSC as defined in Table 4.1) at a 1:10 soil-solution ratio, using 2 g of soil and 20 ml of solution. The amount of each heavy metal applied is equivalent to 10.0 mmol/kg and 50.0 mmol/kg soil. The initial pH of the lead solution was 4.15 at a concentration of 1mmol/L and 5.12 at a concentration of 10 mmol/L and the zinc's were 4.70 and 5.23 respectively.

The soil suspension samples were equilibrated by shaking in an end-over-end shaker at 25° C for 24 h after the solutions were applied to soils. The samples were then centrifuged at 3,000 rpm for 10 minutes. The pH of the soil solutions was measured. The amount of heavy metals remaining in the supernatant (dissolved concentrations) was measured by a double beam atomic absorption spectrophotometer. The amount of heavy metals retained (adsorbed+precipitated) in the soils was calculated as the difference in the heavy metal applied and dissolved. The results of retained heavy metals, lead and zinc, versus equilibrium pH for the different clay soils (K,KS, KC, KSC) are shown in Figures 4.1a, 4.1b, 4.1c and 4.1d for 1cmol/kg soil. The computed distribution coefficient, $K_d$, versus pH is shown in Figures 4.2a, 4.2b, 4.2c and 4.2d. The results of retained heavy metals and the computed distribution coefficient for the case of 5cmol/ kg of soil are also illustrated in Figures 4.3a to 4.3d and 4.4a to 4.4d.



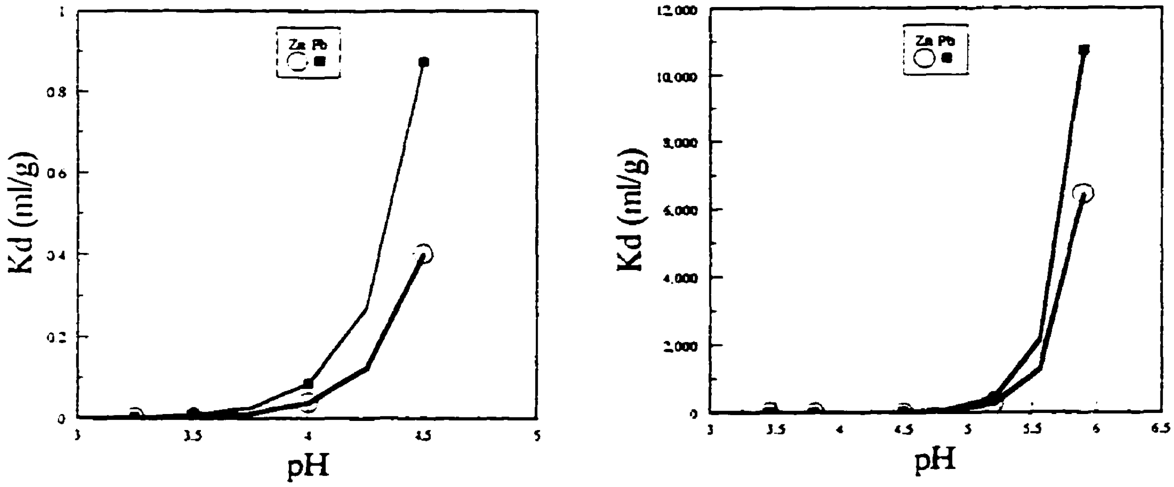
(a) Kaolinite (b) KS Soil



(c) KC Soil (d) KSC Soil

Fig 4.1 Retention of Heavy Metals as a Function of pH Using 1 mmol of Lead and Zinc.

(a) Kd Values for Kaolinite (b) Kd Values for KS



(c) Kd Values for KC (d) Kd Values for KSC

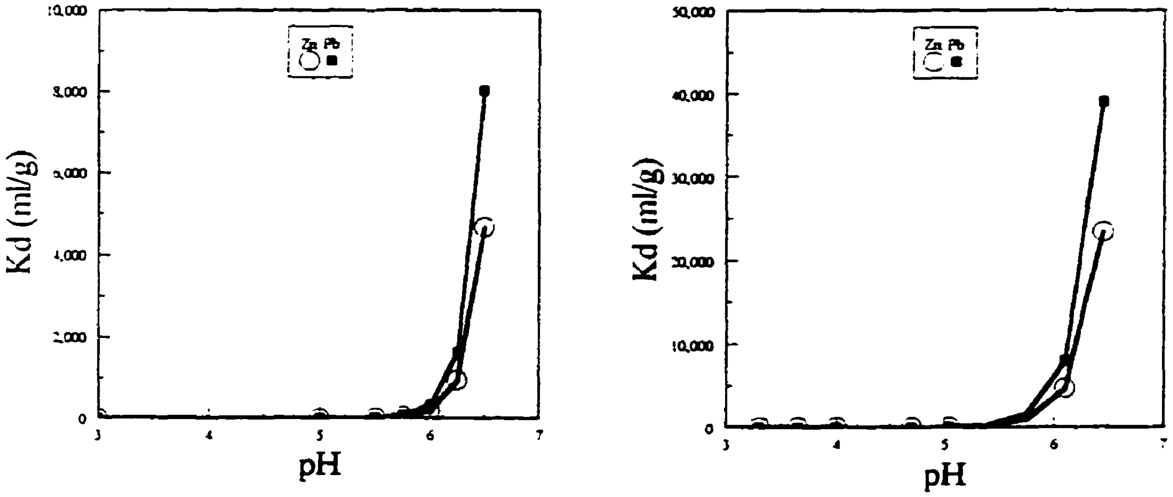
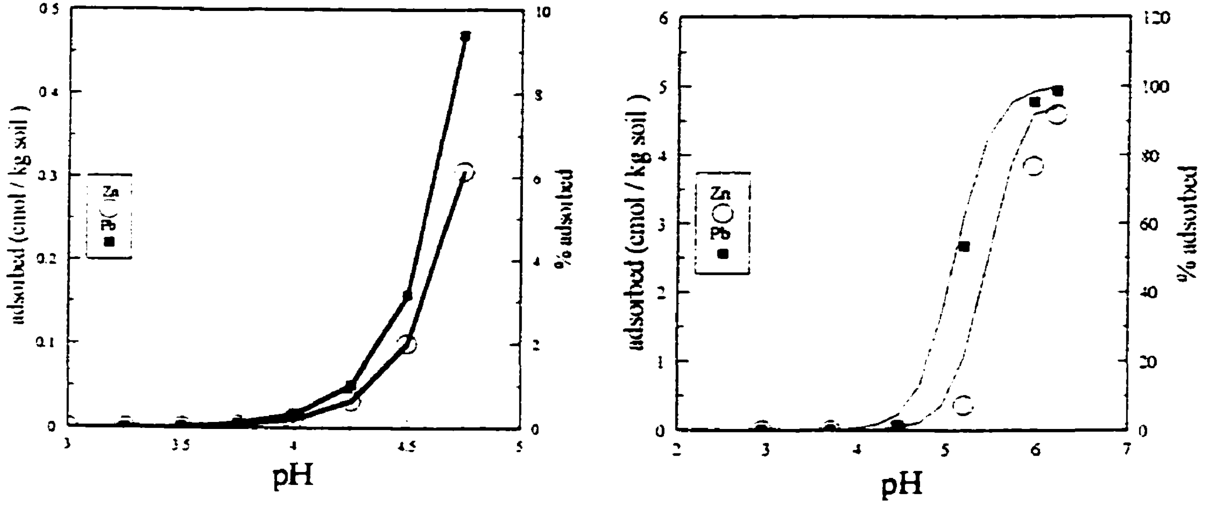
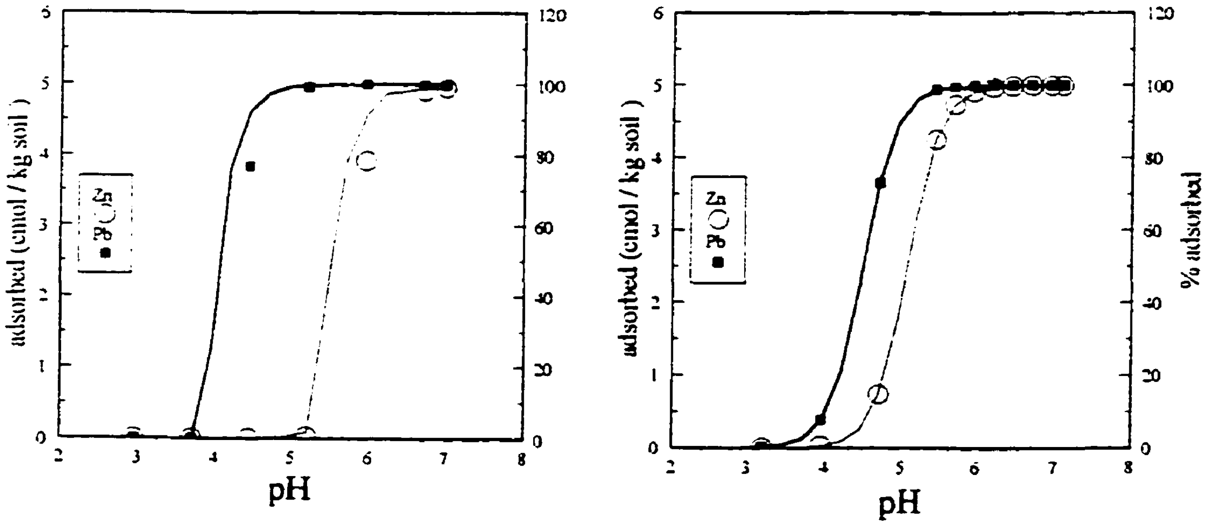


Fig. 4.2 Kd Variation for Different Clay Soils Using 1 mmol of Lead and Zinc Solution.

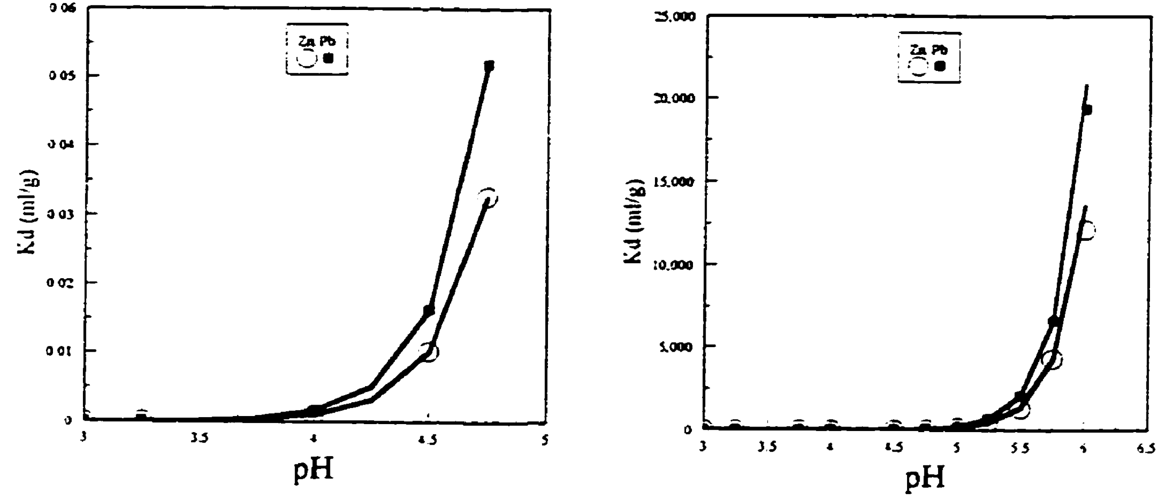

(a) Retention Variation with pH for K

(b) Retention Variation with pH for KS

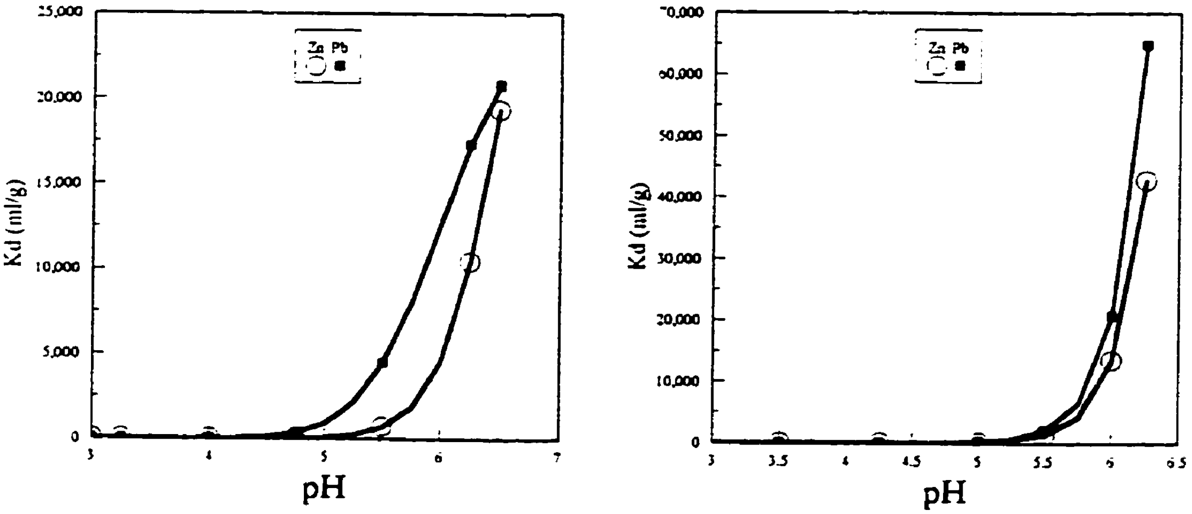

(c) Retention Variation with pH for KC Clay

(d) Retention Variation with pH for KSC Clay

Fig 4.3 Retention of Heavy Metals as a Function of pH Using 5 mmol of Lead and Zinc.


(a) Kd Variation with pH for K Clay

(b) Kd Variation with pH for KS Clay


(c) Kd Variation with pH for KC Clay

(d) Kd Variation with pH for KSC Clay

Fig. 4.4 Kd Variation for Different Clay Soils Using 5 mmol of Lead and Zinc.

### 4.3.2 Discussion on pH Effect on Distribution of Heavy Metals

It can be seen from the graphs in Fig. 4.1 that the amounts of Pb and Zn retained are different. As shown, in the case of kaolinite, at natural pH around 58% Pb and 40% of Zn were adsorbed on the soil while, in case of the kaolinite mixture (KS, KC, and KCS) almost all lead was adsorbed. The results show that the amounts of both heavy metals retained increased with higher pH values. When soil solution pH is >5, most of Pb and 80% of Zn are retained in the soil, whereas when soil solution pH is <5 the amounts of both metals retained decreases rapidly. The amounts of Pb and Zn retained in KS soil when soil pH is <5 are higher than in the other three soils.

The kaolinite, which has a very low CEC and SSA, and does not have any significant amount of soil constituent, apparent from its clay mineral, results in the lowest retention of both heavy metals compared to the three other soils. The addition of solutions with pH values above the zero point of charge (ZPC) could result in the situation where the soil tends to deprotonate or surrender $H^-$ from its edges, thereby resulting in a reduction of the soil solution pH. Kaolinite has variable charge at the different pH levels with ZPC of 4.2 (Yong and Ohtsubo, 1987).

In the case of a kaolinite mixture with silica gel (KS), the clay soil has a very high CEC value, a pH of 6.2 and has a higher retention for lead at lower pH values than the three other cases. This is because silica gel has a ZPC of 2.1 (Fein, 1994). The KC, which has the highest carbonate content, low CEC and medium SSA, results in the highest retention of both heavy metals provided the soil solution pH does not drop below 5.3. High amounts of Pb and Zn were retained in the KSC at high pH due to the carbonate content which causes the retention to be dominated by precipitation into carbonate forms or various hydroxides species. In the case of KSC which has a soil pH, CEC and SSA, similar to natural soil, almost of all heavy metals were adsorbed at high pH values.

From the results of $K_d$ values shown in Figure 4.2 for each soil material, it may be concluded that the distribution coefficients for each heavy metal is greatly affected by the type of soil, pH of the soil solution and the concentration of heavy metals and other contaminants in the solution. Distribution coefficients range from values near zero to $10^4$

mL/g or greater. These results agree with the general values of $K_d$ reported in the literature (Freeze and Cherry, 1979; Melisson *et al.*, 1995).

As shown, Zn and Pb retention is affected by pH. The amount of Pb retained in kaolinite soil is very much less than the other three soils, not only at natural pH but also throughout all the pH values. The heavy metals retention curve in the case of kaolinite appeared only up to pH 4.5 and KS soil to 6.1 when amounts of heavy metals retained are plotted with the soil solution pH. In order to extend the curves for these two cases, a base has to be added instead of acid. This is beyond the scope of this research which focused only on the retention of the heavy metals in the acidic environment.

It is obvious from Figs. 4.1 and Fig. 4.2 that, with the exception of Pb on the silica gel mixture, significant removal of metals from the solution does not occur until a pH of 5 is attained. This is the pH at which adsorption may occur due to cation exchange capacity and cannot be distinguished from precipitation (Yong and MacDonald, 1997). The addition of carbonate and silica gel increase the pH of the soil solution which results in higher retention of heavy metals. The carbonate addition provides a higher pH for the soil mixture than the silica gel. Consequently, pH adjustments to lower values would have involved the dissolution of carbonates and lower adsorption of heavy metals. The adsorption of both metals in the silica gel mixture at lower pH values is more than the other cases. The high CEC value of KS soil helps it retain higher amounts of Pb and Zn than KC and KCS soils as the soil solution pH decreases. These results indicate that silica gel has the potential of being used as a soil treatment material in a low pH environment. Metal removal from the solution increases abruptly in pH ranges 3-5. This finding agrees well with the work of Yanful *et al.* (1988) and Yong *et al.* (1995).

As shown in Figs 4.1b, 4.1c, 4.1d, 4.3b, 4.3c 4.3d for the case of kaolinite soil mixtures, the sharp upswing in the removal of Pb in the retention curves occurred at a pH of around 5.0 (Phadungchewit, 1990). This is being attributed to the initiation of precipitation which is not distinguishable experimentally from adsorption (Yong and MacDonald, 1997). The precipitation occurs at high pH levels where aqueous metal cations hydrolysed, resulting in precipitation of heavy metal hydroxides onto soil. The general equation for the divalent metals can be expressed as follows (Yong *et al.*, 1992):

$$M^{2+}(aq) + n\,H_2O \rightleftharpoons M(OH)^{2-n}_{n} + nH^{+}$$

The precipitation mechanisms may also occur as the carbonate species, which cause the high retention of Pb and Zn on KC soil due to the high carbonate content. The precipitation depends on the type of heavy metal, heavy metal concentration, pH of the solution, other contaminants in solutions (Yong *et al.*, 1995). The precipitation of lead may occur at lower pH values than the Zinc due to lower solubility of Pb than Zn. However, at acidic pH values, heavy metals adsorption becomes less effective due to competition at the exchange sites from the $H^+$ ions.

Clearly, the addition of carbonates to the kaolinite increases the amounts of Pb removed from the solution. The efficiency of Zn removal, however, appears to be lower than that of Pb, at all pH values. This is because, Zn is more mobile, and has a lower selectivity for charged surfaces (Farrah and Pickering, 1979; Phadungchewit, 1990). A higher mobility and lower selectivity implies that the contaminant will not be retained as effectively by the clay particles. This may be explained by the reduced availability of free uncomplexed $Zn^{2+}$ ions for precipitation or by ion exchange as observed in the work of Yong et al . (1992). In all cases zinc is less adsorbed than the lead. Competitive adsorption or retention between the heavy metals was involved in this case.

As shown in Figures 4.3 and 4.4, the amount of heavy metals retained in each case of the kaolinite mixture is different when higher concentrations of heavy metal are applied. This is because at low $Pb^{2+}$ or $Zn^{2+}$ concentration, clay particles tend to disperse due to the full development of the diffuse double layer (Yong et al. 1992). Hence, an increase in the net repulsive forces between clay particles within the first order fabric unit, as well as between first order fabric units themselves, is obtained (Mohamed et al. 1994). In this case, the clay particle surfaces, in contact with the $Pb^{2+}$ or $Zn^{2+}$ solution, tend to be at maximum. With an increase in $Pb^{2+}$ or $Zn^{2+}$ concentrations, the thickness of the diffuse double layer tends to decrease. Hence, clay particles tend to become coarser and form aggregates. The resultant surface areas exposed to $Pb^{2+}$ or $Zn^{2+}$ solution are less than those of low concentrations. Therefore, the $Pb^{2+}$ or $Zn^{2+}$ adsorption capacity of a newly formed structure for high concentrations is less than that of low concentrations. Also, the decrease in $Pb^{2+}$ or $Zn^{2+}$ adsorption at high concentrations could be attributed to the decrease in ion activity (Yong et al. 1992).

On the other hand, the higher the concentration of Pb or Zn applied, the higher the $H^+$ remaining in the solution, which results in a reduction of the equilibrium soil solution pH. The amounts of Pb retained in all cases are higher. The amounts of Pb retained increased with higher pH levels. When soil solution pH is >5, almost all applied Pb is retained in the soils whereas, when soil solution pH is <5 the amounts of Pb retained decreased rapidly. The amounts of Pb retained in KS at lower pH are considerably higher than in the other three cases.

In the case of kaolinite, the amounts of Pb retained are very much less than in the other three cases. This is because the CEC value of kaolinite is low compared to the others, as shown in Table 4.1. On the other hand, adding materials to kaolinite increases the pH of the soil, which indirectly enriches the buffer capacity of the soil.

The amounts of Zn retained in all mixtures are less than the amounts of Pb. This is because when more than one species of heavy metals is applied to the soil, competition between the metallic ions for adsorption sites occurs in addition to competition by other ligands within the system. What is interesting to note is not only that the retention characteristics for each metal are different, but they also differ as the soil composition is changed. The differences in selective adsorption are due to the differences in soil and heavy metal properties. The ease of exchange with which cations of equal charges are held to the soil particle surfaces is, in general, inversely proportional to the hydrated radii. Zn (0.074nm) is less adsorbed in exchangeable form than Pb (0.12nm) (Yong *et al.*, 1992). The affinity of the heavy metals to be retained in soils could also be related to the pK value of the first hydrolysis product of the metals (Elliott et al., 1986) where K is the equilibrium constant for the above reaction. Ranking the pK value of Pb and Zn, the order follows Pb (6.2)>Zn (0.9). On the other hand, precipitation as a mechanism which can result in higher amounts of Pb being retained in each soil because each heavy metal has its own range for precipitation which depends on solubility of a metal hydroxide species and pH values. In between the precipitation pH and high pH values, precipitation of the hydroxide species occurs. Zn hydroxide has higher solubility and it precipitates at higher pH values, which causes less Zn to be retained in each soil.

### 4.4 Soil Inorganic Contribution to Heavy Metal Partitioning

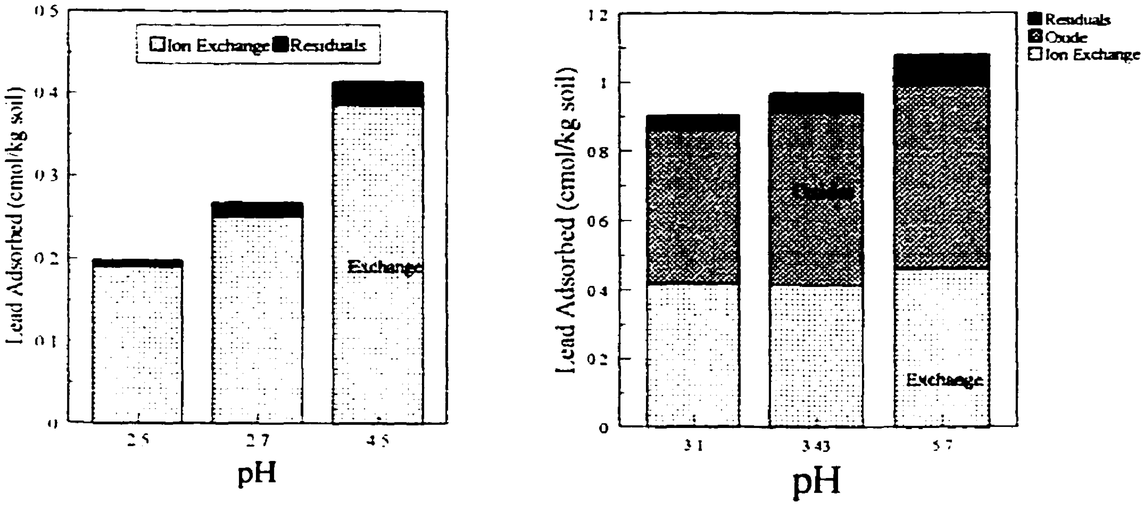
As was indicated in the previous section, in adsorption isotherm analysis, the amounts of metal removed by spiked samples are compared against those amounts remaining in the equilibrating solutions. This approach yields information on the attenuation capability and absorption capacity of the samples for heavy metals, but it does not indicate what chemical forms are present. It is also unable to distinguish between chemisorption and precipitation mechanisms of fixation.

Sequential extraction analysis involves equilibrating a sample successively with reagents in a manner that releases the different heavy metal fractions from the contaminated soil solids by destroying the binding agent between the heavy metals and soil solids, thus, permitting the individual metal species to be detected through appropriate analytical procedures. This method reveals empirically the chemical partitioning of the metals, but the information is less specific with regard to the sorption characteristics of the sample. The chemical partitioning of heavy metals in a contaminated clay liner, is therefore, of great significance in risk assessment and remedial investigations. It is important to know the dominant retention mechanisms of heavy metals in order to predict the possible remobilization of heavy metals from clay liner into groundwater.

The selective sequential extraction method is based on the fact that the different forms of heavy metals that are retained in soil (e.g., as exchangeable, carbonates, oxides, heavy metal bound to organic matter, and as residuals fraction) can be extracted selectively by using appropriate extractant reagents. The SSE method was used to investigate the contribution of each fraction of soil to heavy metal retention and to obtain a better appreciation of the capability of the candidate soil barrier to fulfill the necessary functional (i.e., contamination attenuation) requirements (Yong, Raymond N., Phadungchewit, 1993). The amounts of each heavy metal retained as exchangeable, carbonate, oxides and residual for each kaolinite and kaolinite mixture (KS, KC, and KCS) are plotted in Figs. 4.5a to 4.5d and Figs 4.6a to 4.6d show the amounts of Pb and Zn fractions retained as a function of pH, for the K, KS, KC and KSC soil, respectively. The selective sequential extraction was not carried out for the KC and KSC soils at lower pH values because in the column leaching test the pH of the soil solution may not reach to less than 5.0 in the range of this study.

(a) Kaolinite

(b) KS Soil



(c) KC Soil

(d) KSC Soil

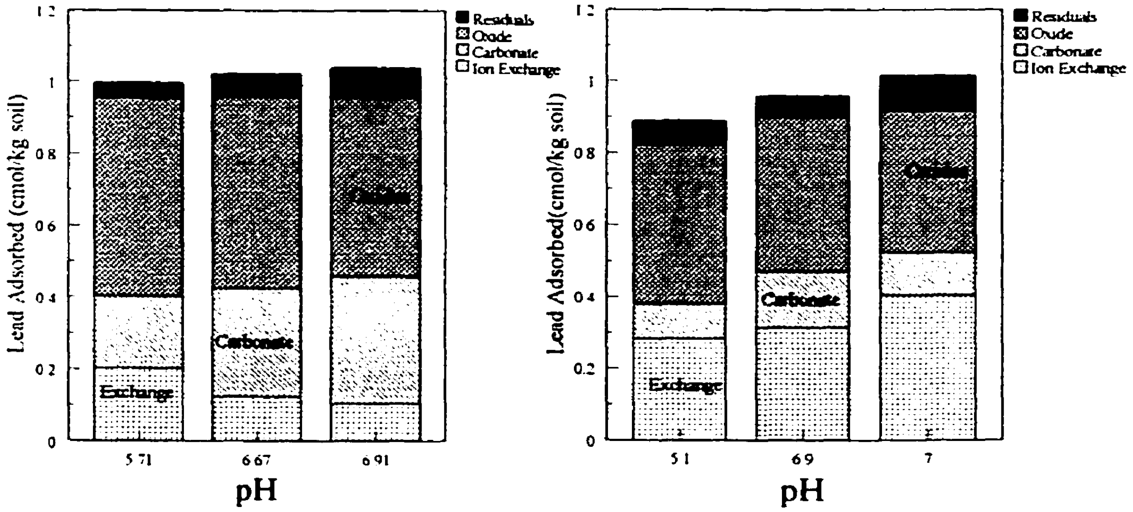


**Fig. 4.5** pH Effects on Distribution of Lead Retention in Different Soils.

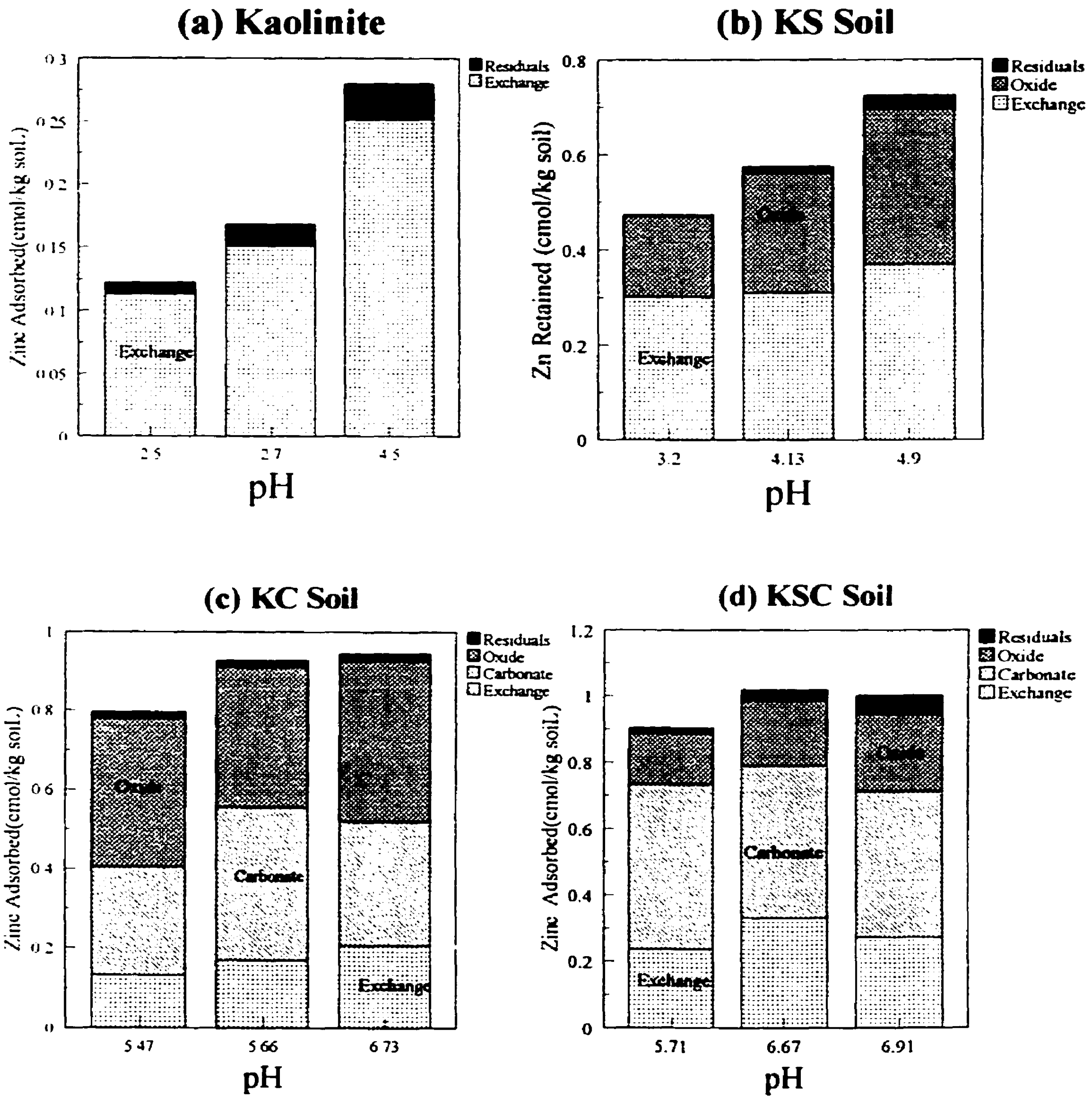


**Fig 4.6** pH Effect on Distribution of Zinc Retention in Different Soils.

### 4.4.1 Discussion on Soil Inorganic Contribution to Heavy Metal Partitioning

From all the figures shown, it is evident that the amounts of heavy metals fractions retained by each soil fraction change according to the change in soil solution pH. Retention of Pb appears to be greater than Zn by the four different soils. Except for pure kaolinite, all other kaolinite mixtures could retain almost all of the heavy metals at the high pH levels. The CEC of kaolinite is low compared to the others, as shown in Table 4.1 The amounts of Pb or Zn retained, moreover, is far greater than its CEC and becomes gradually lower as the pH decreases. This is consistent with the situation where, under low pH, Al is dissolved from the crystal structure and adsorbed on exchange sites, thus blocking the adsorption of Pb or Zn by kaolinite as pH decreases.

The amount retained as pH increases, however, is different for each fraction, depending on the type of soil. This is because of the different compositional features of the soil. The results show that when the pH of the soil solution is greater than 5, retention is dominated by precipitation mechanisms, which account for the very high amounts of Pb being retained. In the partial precipitation region at intermediate pH (4-6), various hydroxides species are formed, and retention of Pb by cation exchange and precipitation is indistinguishable. High amounts of Pb retained at high pH could also be due to bonding to the existing carbonates and oxides, thereby resulting in high amounts of total heavy metals retained. But as the pH become less than 4, only the exchangeable metal fraction predominates, resulting in lower amounts of total heavy metals retained. KS or KSC is less sensitive to the pH variation. Both heavy metals, especially lead are retained in the exchangeable and oxide phase at low pH. This is because the mechanism of adsorption of heavy metals to silica gel is mostly predominated by specific adsorption or complexation. Also, KS soil has the highest CEC compared to other soils. The high CEC value of KS helps it retain higher amounts of Pb than KSC or KC soil as the soil solution pH decreases. The decrease in pH of the soil solution means that cation exchange is the more likely an adsorption mechanism. The presence of carbonates in KCS or KC soil contributes measurably to the retention of the heavy metals, through precipitation with the carbonates, as seen in Figs, 4.5c, 4.5.d, 4.6c, and 4.6d. The higher the carbonate content of the soil, the greater the amount of heavy metals that can be retained in the carbonate phase. The amounts of heavy metals retained in the carbonate phase in KC soil are higher than in KCS soil because of the higher amounts of carbonate in KC. The amounts of heavy metals retained in the carbonate phase becomes negligible when the pH decreases to less than 4 for KC and less than 3 for the KCS. The dissolution of carbonates, at low pH levels, appears to be responsible for the decreased amounts of heavy metals retained by the carbonate phase at low pH values. The amounts of heavy metals retained in the exchangeable phase of KS are higher than those in the other soils because of the much higher CEC of silica gel. The larger number of exchangeable sites increases the potential for heavy metals retention in the soil by the exchangeable phase.

## 4.5 The Effect of Complextion on Heavy Metals Distribution

Coordination or complex formation of heavy metals or other cations is any combinations of cations with molecules or anions containing a free pair of electrons (Stumm and Morgan, 1996). This process occurs through electrostatic or covalent bonding or a mixture of both. The metal cation, in a complex formation, is the central atom and the participating anions or molecules the *ligands*. The ligand, or donor, must have at least one pair of free (unbonded) electrons to be shared between it and the central atom. By and large, the complexes formed between the metal ions and inorganic ligands are much weaker than those complexes formed with organic ligands (Yong *et al*., 1992). The inorganic ligands which will complex with the metalic ions include most of the common anions, e.g. $OH^-$, $Cl^-$, $SO^{2-}_4$, etc..

For organic ligands, such as the amines, phenols, etc. complexation occurs when a central metalic cation becomes attached to two or more inorganic or organic groups by coordinate covalent bonds. Complexation by coordination with multidenate ligands is called chelation, and the complex formation is commonly referred to as chelates. The effectiveness of complexing ligands depends not only on the choice of the chelating agent used, but also on the stability, absorbability of the complexes formed and on the pH of the system. The control parameters in carrying out an application would be the type and concentration of the complexing agent, the presence of other cations, and the pH of the system. EDTA has been justified by many researchers (Elliott and Brown, 1989; Mohamed and Trasente, 1996) as a complexing agent and was used in this study to investigate how EDTA affects the partitioning of the heavy metals in different clay soils. metal-ethylene- diamine-tetra acetic acid or EDTA which has been used in this study is known for strong complexing organic agents. It acts as multidenate ligands which wrap themselves around metal ions in chelate formation. In the following sections the results of the effect of chloride as an inorganic and EDTA as an organic complexing agent on heavy metals retention in batch equlibrium tests are addressed.

### 4.5.1 Chloride Concentration on Distribution of Heavy Metals

Chloride, under certain circumstances, may also be of great significance in determining heavy metals distribution in the environment, due to its effects on heavy metals mobilization. Chloride concentrations in municipal and industrial waste are reported as ranging from 25 to 100000 ppm (Hahne and Kroontje, 1973. In addition, since the Early 1969's, NaCl and $CaCl_2$ have been used extensively to keep roadways free of snow and ice (Elliott and Linn, 1987). Road salt, besides being a contaminant itself, stimulates the release of Hg and other toxic heavy metals to groundwater. In this section the effect of chloride concentrations on heavy metals distribution into different clay soil (K, KS, KC, KSC) is presented.

Two heavy metals, lead and zinc, solutions with two levels of concentration ,1mmol and 5mmol/L, were separately and compositely applied to each clay soil with increasing amounts of chloride. The chloride concentrations used in this study range from 0.01 to 1 mole. This made the amount of each heavy metal applied to each soil equal to 1.0 cmol and 5.0 cmol/kg and the amounts of chloride concentration ranged from 0.1 to 10 mol/kg soil. The prepared solution was applied to the soil at a ratio of 1/10 in the same manner as in the batch equilibrium test, The amount of heavy metal retained in the soils was calculated as the difference in the heavy metal applied and what remained in solution. The heavy metal retained and the computed $K_d$ distribution coefficient versus amounts of chloride added in mol $Cl^-$/kg to soil for kaolinite and kaolinite mixtures (KS,KC,KSC) are shown in Figures 4.7a-d to 4.14a-d, respectively.

As shown , the addition of chloride as a complexing component reduced the amounts of heavy metals retained for all type of soils. The amount of Pb retained begins to drop when the chloride concentration is greater than 0.05 mol/l of solution and lead and zinc mobilities increased with increasing concentrations of Cl. The effect was found to be directly related to the degree of chloro-complex formation. The greater the amount of chloride present, the higher the observed mobility of lead and zinc.

In the case of kaolinite, there is a relative drop in Pb and Zn retention with increasing chloride concentrations. As shown in Figures 4.8 a-d, in kaolinite, the partitioning coefficients, Kd, of Pb and Zn are very much less than in the other three cases. $K_d$ s vary from 0.98-0.28 to 0.35-0.07 ml/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 0.14- 0.09 to 0.20-0.06 ml/g using high heavy metal concentration, depending on of the chloride concentrations due to complex formation of chloride with heavy metals. $K_d$ s vary in the range of 0.31- 0.15 to 0.11-0.09 ml/g for zinc using low heavy metals concentrations separately and compositely, respectively and from 0.13-0.09 to 0.13-0.08 ml/g using high heavy metals concentrations. However, using heavy metals compositely reduced the partitioning coefficients for both zinc and lead due to the competition between the metallic ions for adsorption sites in addition to competition by other ligands within the system.

In case of kaolinite mixtures (KSC and KC), heavy metal retention and partitioning coefficients were less affected using a concentration of 5 cmol/ kg soil separately or compositely due to the precipitation of lead and zinc. As shown in Figures 4.12 a-d, in KSC soil $K_d$ s vary in the range of 324.0-136.0 to 319.8-130.3 ml/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 1231.5- 463.8 to1050.4-366.5 ml/g using high heavy metal concentration. $K_d$ s vary in the range of 262.63-110.7 to 258.5-96.7 ml/g for zinc using low heavy metals concentrations separately and compositely, respectively, and from 213.2- 82.2 to 141.4-62.7 ml/g using high heavy metal concentration.

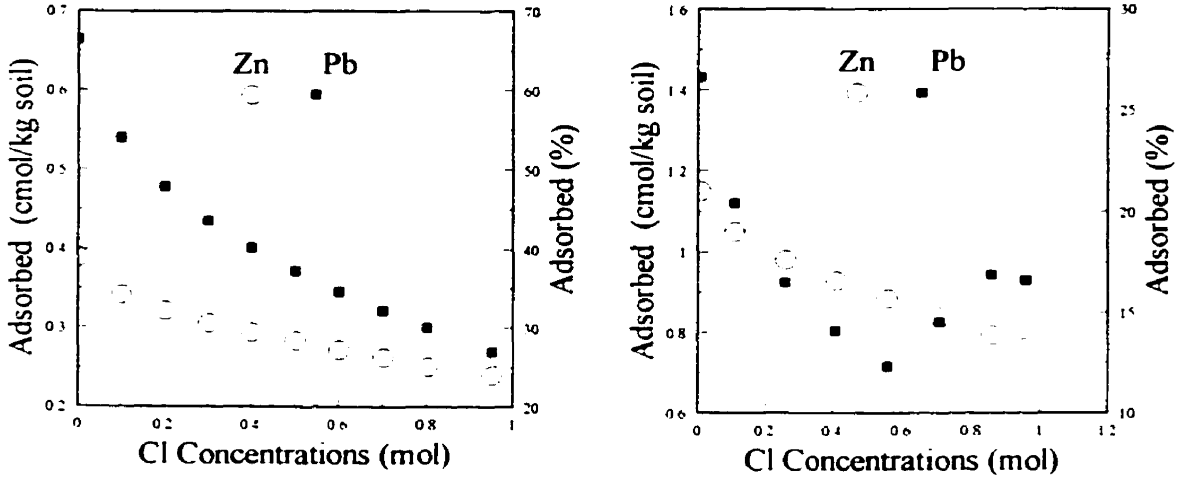
In case of KC soil, in Figures 4.13a-d and 4.14a-d, $K_d$ s vary in the range of 803.1-423.3 to 1366.1-205.3 ml/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 1573.3- 662.2 to 680.8-220.7 ml/g using high heavy metal concentration. The resulting higher $K_d$ s in the case of high concentration of heavy metals is due to the precipitation of lead and preferable adsorption of lead to zinc in KC soil. $K_d$ s vary in the range of 293.5-98.9 to 258.5-96.8 ml/g for zinc using low heavy metals concentrations separately and compositely, respectively, and from 82.5- 31.3 to 114.2–42.4 ml/g using high heavy metal concentrationsIn case of KS soil, in Figures 4.9a-d and 4.10a-d, $K_d$ s vary in the range of 324.0-136.0 to 304.2-130.3 ml/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 1231.5- 463.8 to 1116.0-366.5 ml/g using high heavy metals concentrations. The resulting higher $K_d$s in the case of high concentration of heavy metals is due to the precipitation of lead and preferable adsorption of lead to zinc in KS soil. $K_d$ s vary in the range of 262.6-101.7 to 224.7-96.8 ml/g for zinc using low heavy metals concentrations separately and compositely, respectively, and from 213.2- 82.3 to 157.5-62.8 ml/g using high heavy metal concentrations.

The amounts of Zn retained in all mixtures are less than the amounts of Pb. This is because when more than one species of heavy metals is applied to the soil, competition between the metallic ions for adsorption sites occurs in addition to competition by other ligands within the system. What is interesting to note is, not only that the retention characteristics for each metal are different, but they also differ as the soil composition is changed. The differences in selective adsorption are due to the differences in soil and heavy metal properties. Macroscopically, the tendency of an ion to be sorbed depends on its concentration in the aqueous phase relative to the concentration of other sorbable ions, the selectivity of the sorptive substrate for an ion relative to the other ions, and the number of sites on the sorptive substrate (Yong *et al.*, 1995 ). Given similar concentrations of sorbable ions in the aqueous phase, the selectivity of $Pb^{2-}$ is higher than the selectivity of $Zn^{2-}$.

From the results of $K_d$ and retention values shown in Figures 4.7 to 4.14 for each soil material, it may be concluded that the distribution coefficients for each heavy metal are greatly affected by the type of soil, the concentration of heavy metals and other contaminants in the solution. Distribution coefficients range from values near zero to $10^4$ ml/g or greater. These results agree with the general values of $K_d$ reported in the literature ( Freeze and Cherry, 1979; Melisson *et al.*, 1995).

(a) Zn or Pb (1cmol/kg soil) separately

(b) Zn or Pb (5cmol/kg) soil separately



(c) Zn and Pb (1cmol/kg soil) compositely

(d) Pb and Zn (5cmol/kg soil) compositly

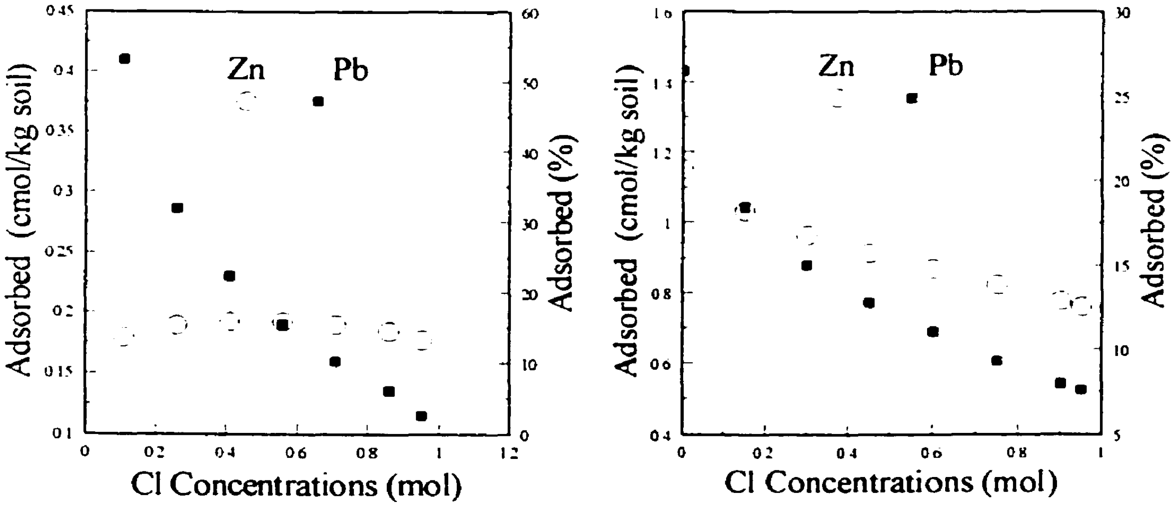
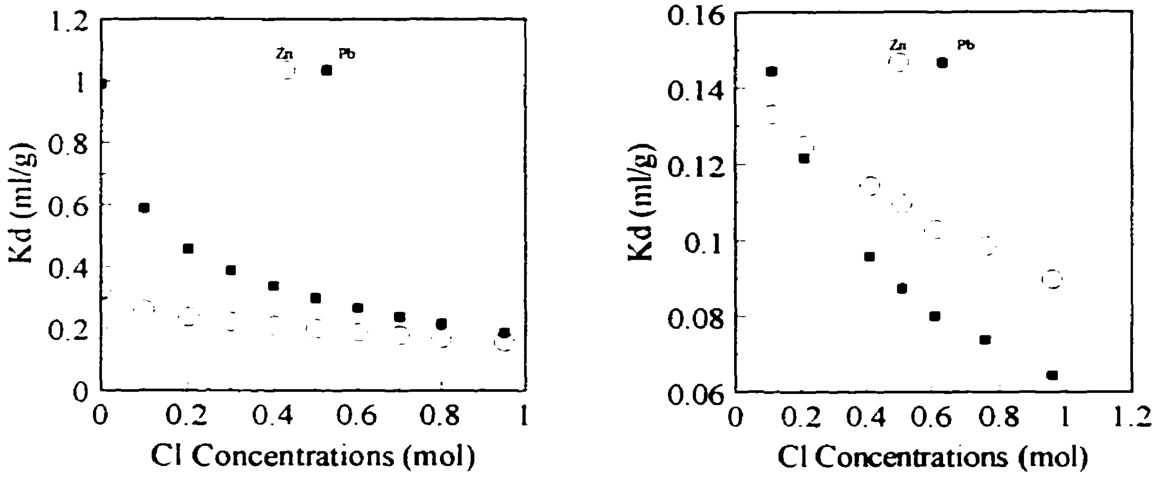
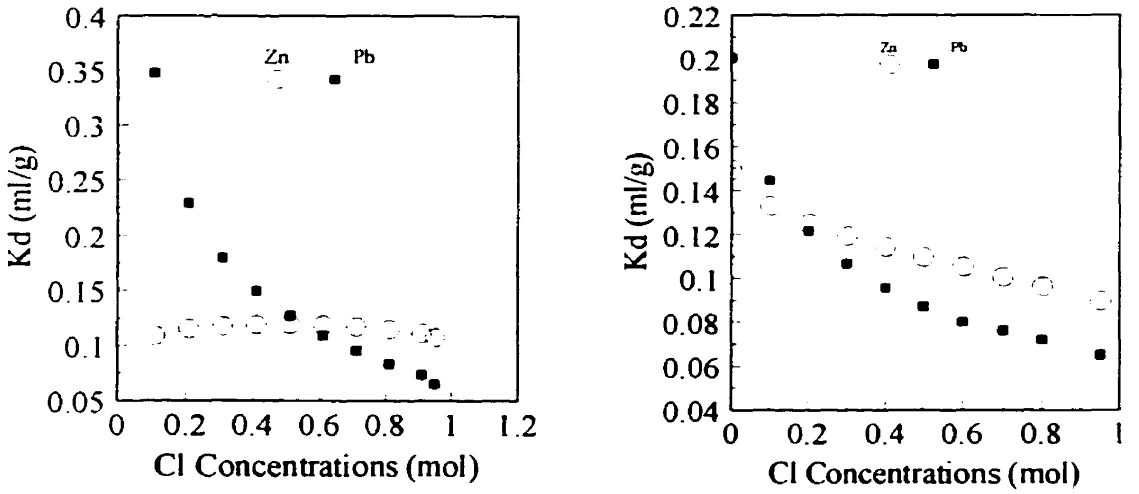


**Fig. 4.7** Cl Concentration Effects on Retention for Kaolinite.


(a) Zn or Pb (1cmol/kg soil) separately

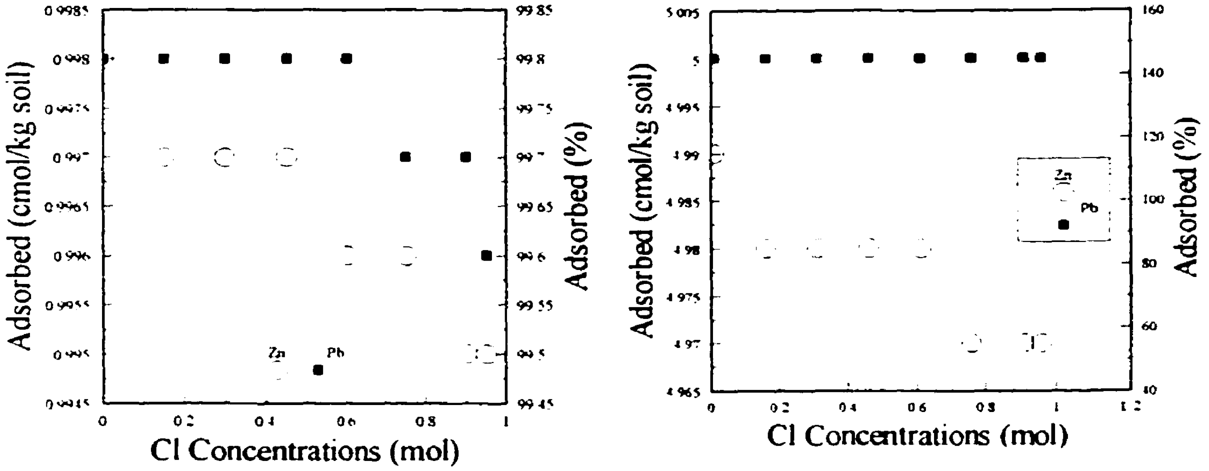
(b) Zn or Pb (5cmol/kg soil) separately


(c ) Zn and Pb (1cmol/kg soil) compositely

(d) Pb and Zn (5cmol/kg soil) compositely

**Fig. 4.8** Cl Concentration Effects on Kd for Kaolinite.

(a) Zn or Pb (1cmol/kg soil) separately (b) Zn or Pb (5cmol/kg soil) separately



(c) Zn and Pb (1cmol/kg soil ) compositely (d) Pb and Zn (5cmol/kg soil) compositely

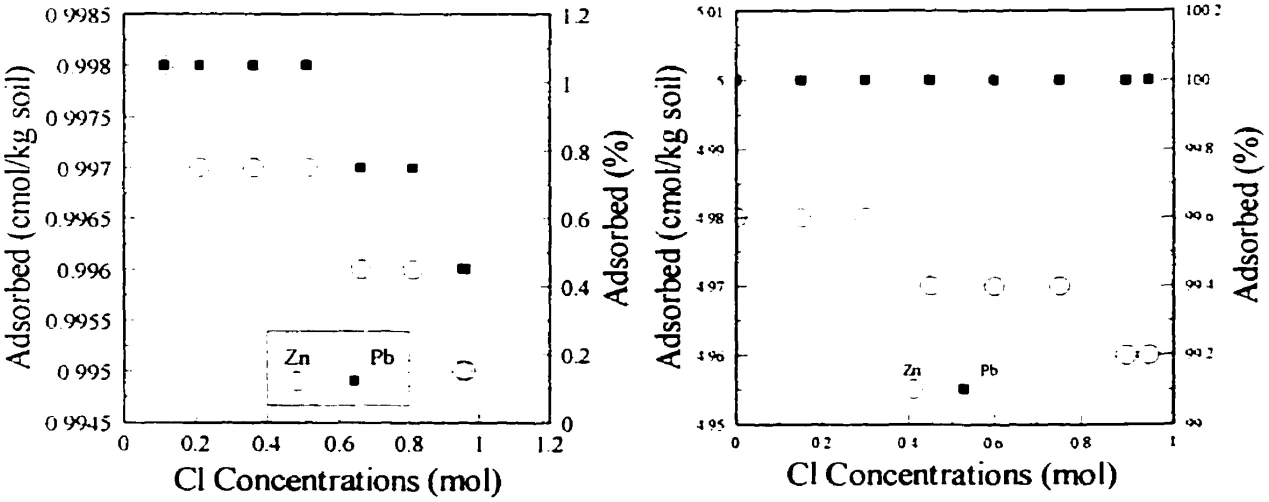
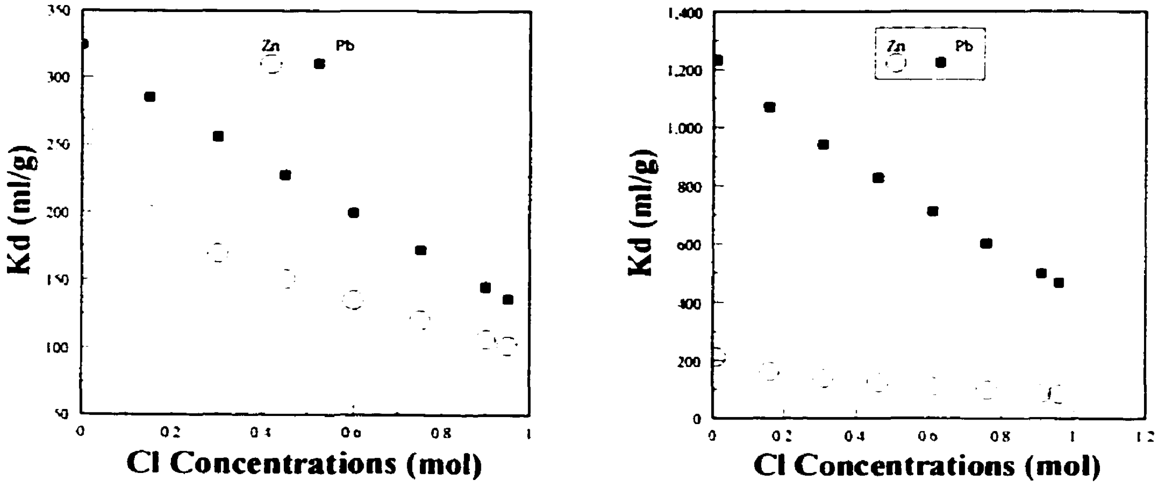


**Fig. 4.9** Cl Concentration Effects on Retention for KS Soil.

**(a) Zn or Pb (1cmol/kg soil) separately** **(b) Zn or Pb (5cmol/kg soil) separately**



**(c) Zn and Pb (1cmol/kg) soil compositely** **(d) Pb and Zn (5cmol/kg soil) compositely**

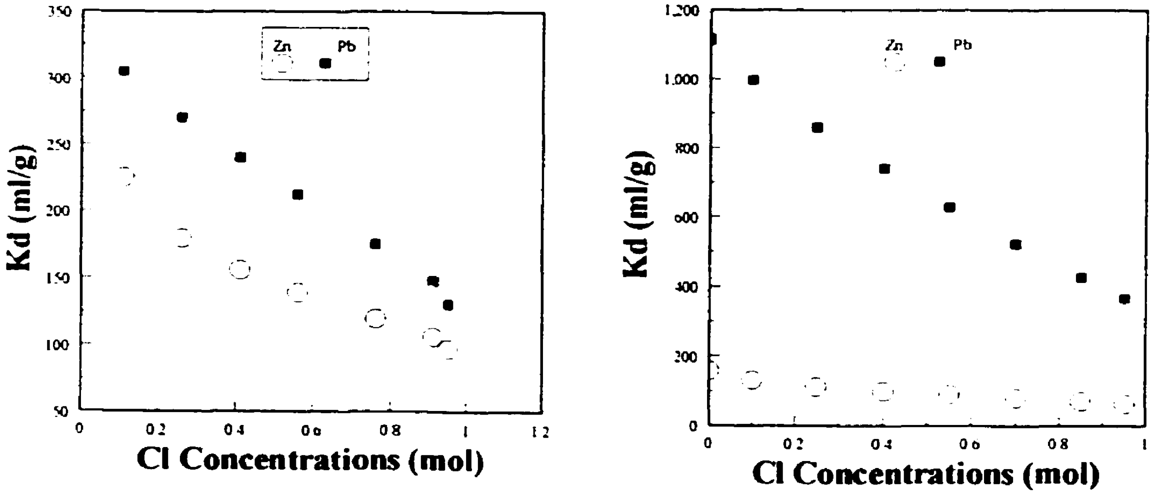
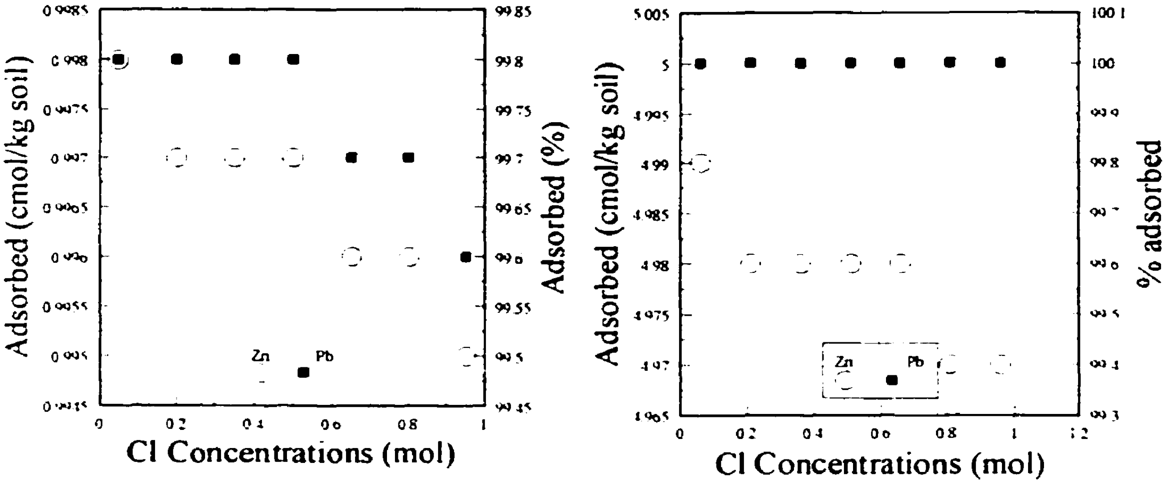
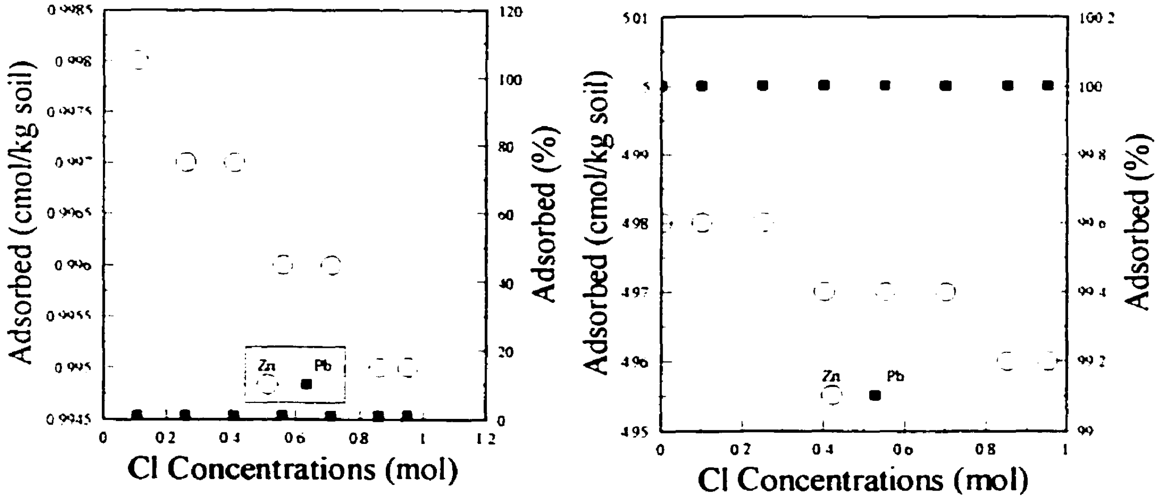


Fig. 4.10 Cl Concentration Effects on Kd for KS Soil.



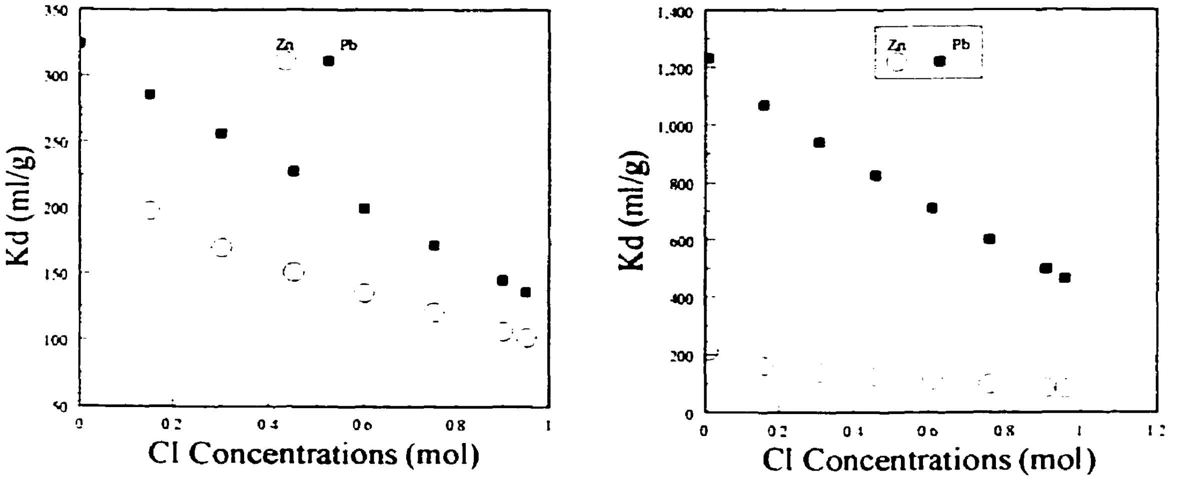
**(a) Zn or Pb (1cmol/kg soil) separately** **(b) Zn or Pb (5cmol/kg soil) separately**



**(c) Zn and Pb (1cmol/kg soil) compositely** **(d) Pb and Zn (5cmol/kg soil) compositely**

**Fig. 4.11** Cl Concentration Effects on Retention for KSC Soil.

**(a) Zn or Pb (1cmol/kg soil) separately** **(b) Zn or Pb (5cmol/kg soil) separately**



**(c) Zn and Pb (1cmol/kg soil) compositely** **(d) Pb and Zn (5cmol/kg soil) compositely**

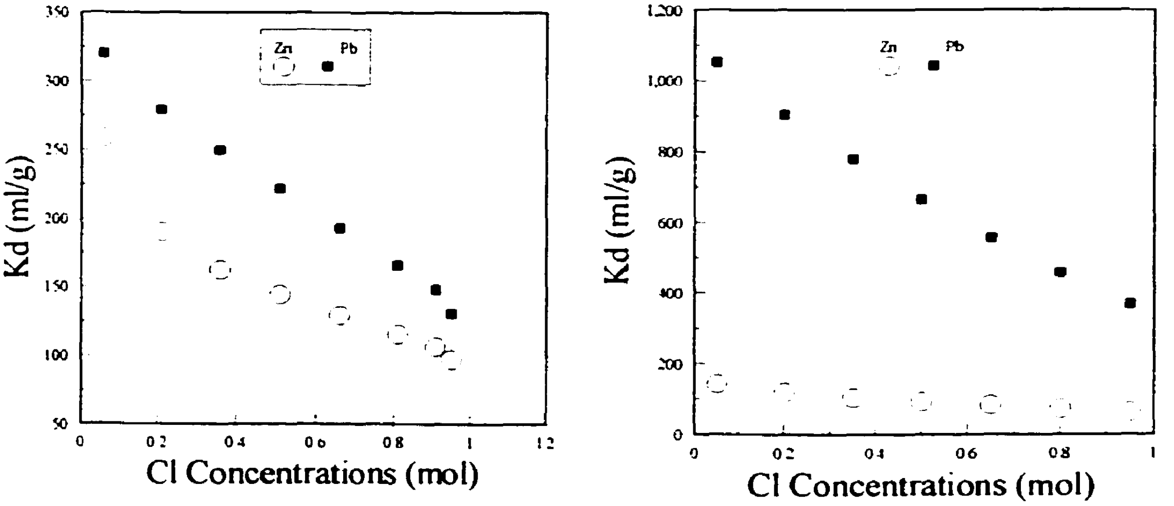
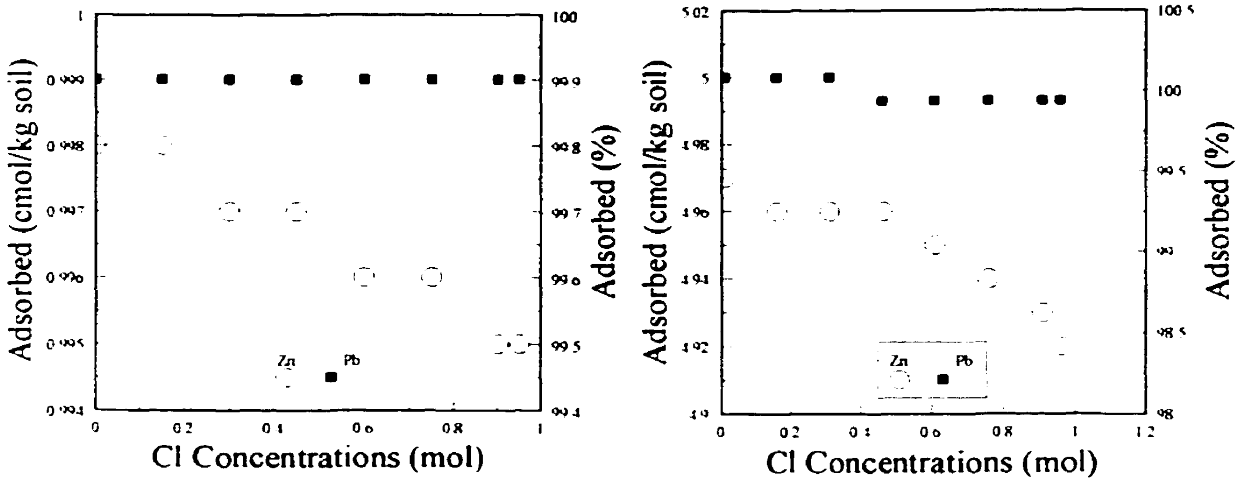
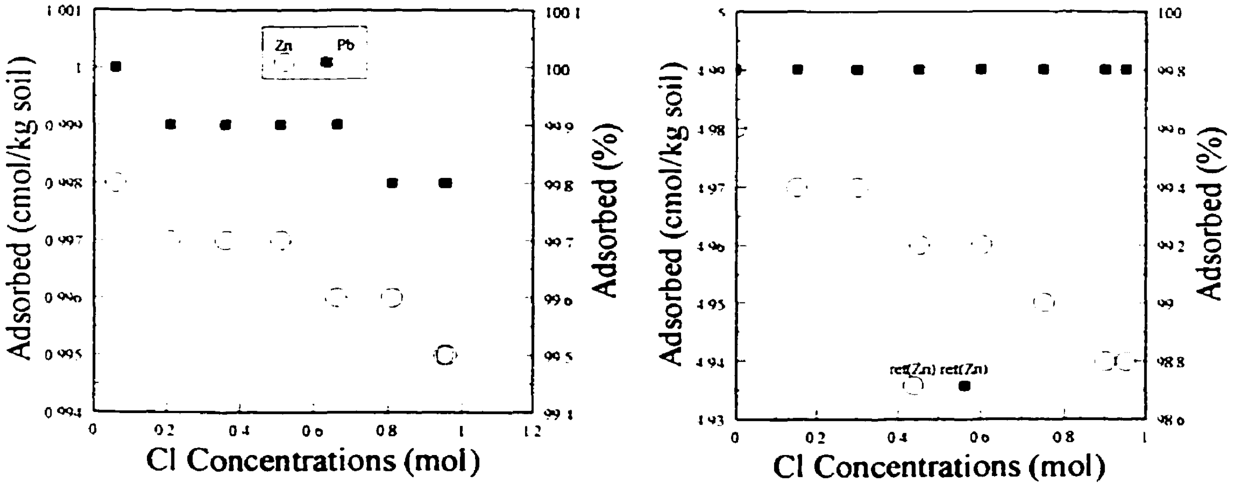


**Fig. 4.12** Cl Concentration Effects on Kd for KSC Soil.



(a) Zn or Pb (1cmol/kg soil) separately

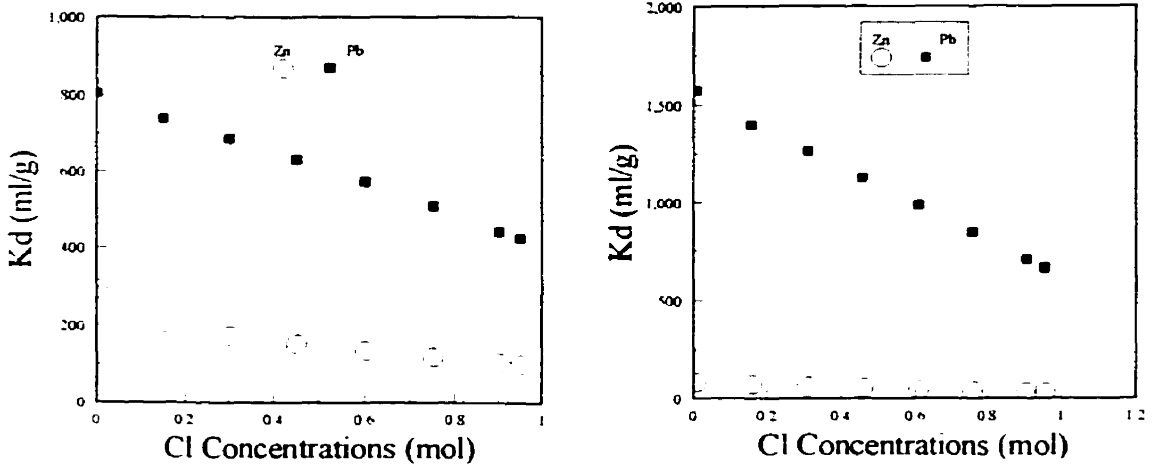
(b) Zn or Pb (5cmol/kg soil) separately



(c) Zn and Pb (1cmol/kg soil) compositely

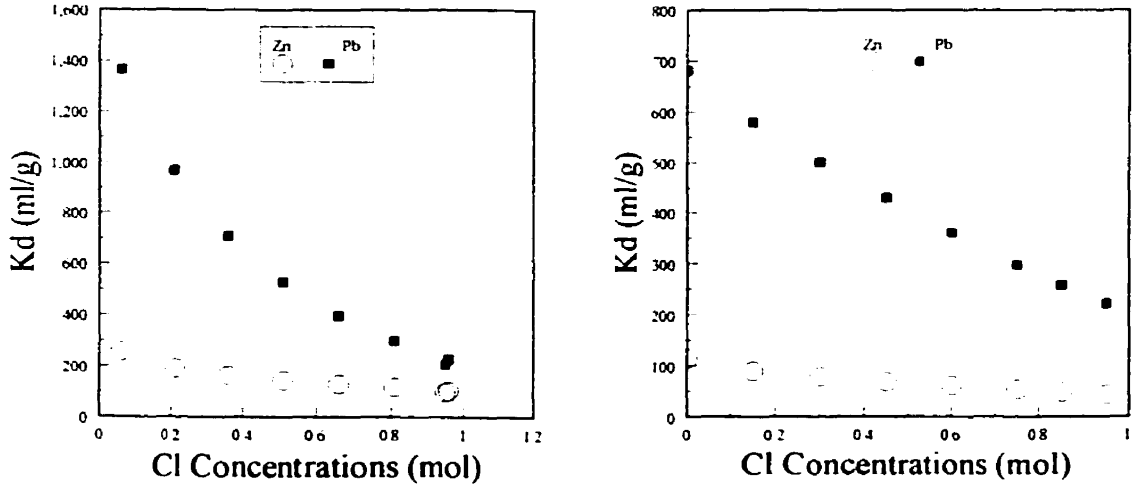
(d) Pb and Zn (5cmol/kg soil) compositely

**Fig. 4.13** Cl Concentration Effects on Retention for KC Soil.



(a) Zn or Pb (1cmol/kg soil) separately

(b) Zn or Pb (5cmol/kg soil) separately



(c) Zn and Pb (1cmol/kg soil) compositely

(d) Pb and Zn (5cmol/kg soil) compositely

**Fig. 4.14** Cl Concentration Effects on Kd for KC Soil.

### 4.5.2 EDTA Concentrations on Distribution of Heavy Metals

EDTA has relatively low solubility in water, therefore, it is usually used in aqueous solutions in the form of its disodium salt, Na-EDTA. The molecular weight of Na-EDTA is 452.21 g, and it has a solubility of 10.8g in 100 $cm^3$ at 22°C. EDTA, known as a strong organo-metal complexing agent, could strongly affect the heavy metals retention in a multi-component heavy metal solution. EDTA concentrations and pH were extensively studied by (Castellan, 1996) for the desorption of heavy metals from contaminated soil in a batch equlibrium test. In this section the effect of EDTA on the distribution of heavy metals in different soil materials is presented. Again, two heavy metals, lead and zinc, solutions with two levels of concentration, 1mmol and 5mmol/L, were separately and compositely applied to each clay soil increasing amounts of EDTA.

Mohamed and Trasente's (1996) research indicated that EDTA at a pH level of 4.50 and a minimum concentration of 0.01 mol/L had maximum effectiveness in removing the heavy metals from the clay soil in batch equilibrium tests. The initial pH of the EDTA at a concentration of 0.1 mol/L is 10.75. The pH of the samples was reduced to 4.50 by adding nitric acid. The EDTA concentrations used for this study range from 0.001 to 0.01 mole. This made the amount of each heavy metal applied to each soil equal to 0.01mol and 0.05 mol/kg soil and the amounts of EDTA concentration ranged from 0.01 to 0.1 mol/kg soil. The prepared solution was applied to the soil at a ratio of 1/10 in the same manner as in the batch equilibrium test. The amount of heavy metal retained in the soils was calculated as the difference in the heavy metal applied and that remaining in the solution. The heavy metal retained and the computed $K_d$ distribution coefficient versus amounts of EDTA added in mol EDTA/kg soil for kaolinite and kaolinite mixtures (KS, KC, KSC) are shown in Figures 4.15a-d to 4.22a-d. As shown, the presence of EDTA significantly reduced the retention and distribution coefficient of both heavy metals in all soils. The amount of Pb retained begins to drop as the EDTA concentration becomes greater than 0.005 mol/l of the solution and lead mobility increased with increasing concentrations of EDTA. As the concentration of EDTA became close to 0.01, the amounts of both heavy metals retained on all clay soil is around zero. The presence of the EDTA affected the complex formation of the carbonate, chloride or hydroxy of the lead and zinc and thus, there is no evidence of the precipitation of either heavy metals even with a high concentration of lead and pH of the soil solution. The greater the amount of EDTA present, the higher was the observed mobility of lead and zinc.

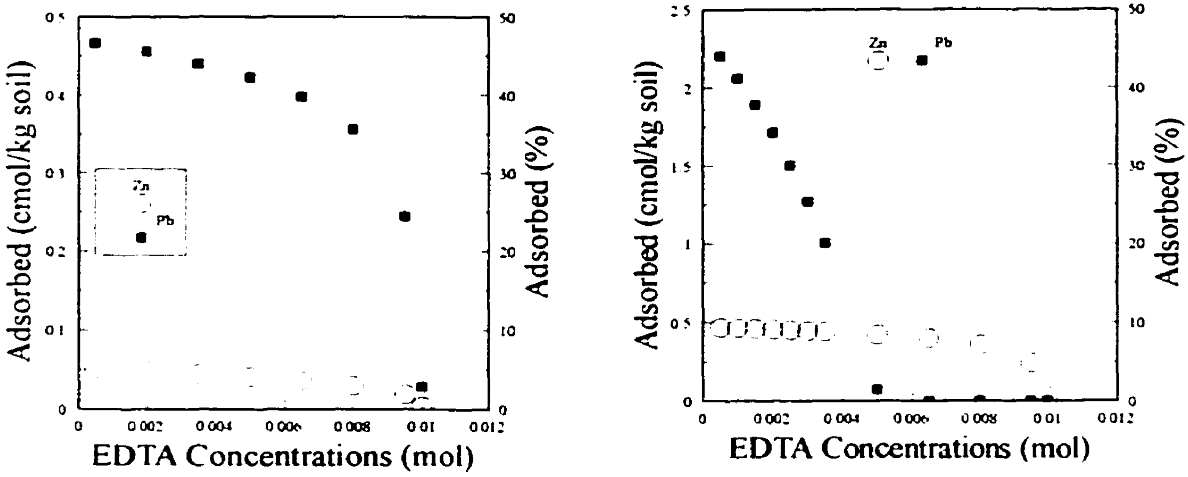
In the case of kaolinite, there is a relative drop in Pb and Zn retention with increasing EDTA concentrations. As shown in Figures 4.15a-d and 4.16a-d, the partitioning coefficients, $K_d$, of Pb and Zn are very much less than in the previous cases using chloride as a complexing agent. $K_d$ s vary in the range of 0.0014- 0.022 to $1.5 \times 10^{-5}$ - 0.122 mL/g for lead using low heavy metals concentrations separately and compositely, respectively, and from $3.4 \times 10^{-14}$ - 0.392 to 0.003 - 0.1459 mL/g using high heavy metal concentration, depending on the EDTA concentrations due to complex formation of EDTA with heavy metals. $K_d$ s vary in the range of $1.8 \times 10^{-4}$ - 0.002 to $4.1 \times 10^{-6}$ - 0.0105 mL/g for zinc using low heavy metals concentrations separately and compositely, respectively and from 0.037-$5.5 \times 10^{-15}$ to 0.082-1.2 x 10-7 mL/g using high heavy metals concentrations. However, using heavy metals compositely reduced the partitioning coefficients for both zinc and lead due to the competition between the metallic ions for adsorption sites occur in addition to competition by other ligands within the system.

In the case of KC soil, in Figures 4.17a-d and 4.18a-d, the retention and partitioning coefficients of both lead and zinc were reduced as EDTA concentrations increased. $K_d$ s vary in the range of 0.0043- 0.65 to $6.9 \times 10^{-4}$ - 7.07 mL/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 0.07-10.86 to 0.06 110.69 mL/g using high heavy metal concentration. The resulting higher $K_d$ s in the case of high concentration of heavy metals are due to lower complex formation of EDTA with both lead and zinc, and preferable adsorption of lead to zinc in KC soil. $K_d$ s vary in the range of 0.0006- 0.065 mL/g for zinc using low heavy metals concentrations separately and compositely, respectively, and from 0.004- 1.58 to 0.0034- 0.55 mL/g using high heavy metal concentrations.

In the case of KSC soil, shown in Figures 4.19a-d and 4.20a-d, $K_d$ s vary in the range of $9.1 \times 10^{-4}$- 0.63 to $6.9 \times 10^{-4}$- 4.82 mL/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 0.074 - 10.86 to 0.057- 111.090 mL/g using high heavy metal concentration. $K_d$ s vary in the range of $6.1 \times 10^{-4}$ - 0.25 to $3.9 \times 10^{-5}$ - 0.222 mL/g for zinc using low heavy metals concentrations separately and compositely, respectively and from $6.1 \times 10^{-5}$ -1.58 to $8.1 \times 10^{-3}$ - 0.55 mL/g using high heavy metal concentration.

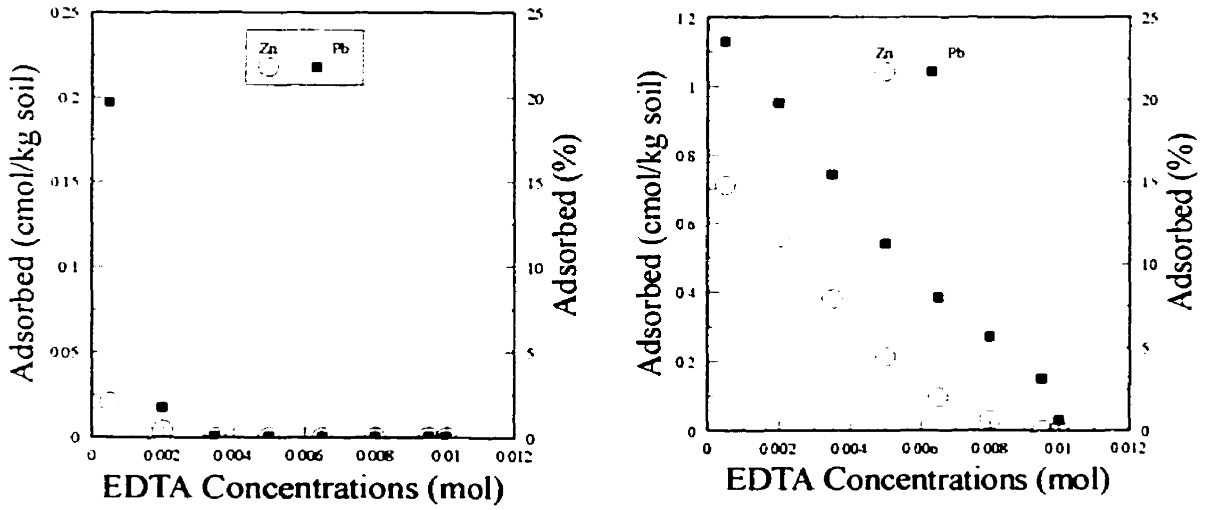
In the case of KS soil, in Figures 4.21a-d and 4.22a-d, $K_d$ s vary in the range of $8.9 \times 10^{-3}$ - 0.65 to $9.7 \times 10^{-4}$ - 1.13 mL/g for lead using low heavy metals concentrations separately and compositely, respectively, and from 0.041- 6.481 to 0.0016 - 2.75 mL/g using high heavy metals concentrations. $K_d$ s vary in the range of $3.5 \times 10^{-4}$ -0.125 to $4.8 \times 10^{-5}$ - 0.067 mL/g for zinc using low heavy metals concentrations separately and compositely, respectively, and from $4.8 \times 10^{-5}$ - 0.067 to 0.0012 - 0.112 mL/g using high heavy metal concentrations.

The amounts of Zn retained in all cases are less than the amounts of Pb. As shown, in all cases higher $K_d$ values were found in the case of applying EDTA to composite heavy metals. This is because when more than one species of heavy metals is applied to the soil, the lower the possibility of the complex formation of EDTA with both heavy metals. What is interesting to note is not only that the retention characteristics for each metal are different with increasing EDTA concentrations, but they also differ as the soil composition is changed.



(a) Zn or Pb (1cmol/kg soil) separately

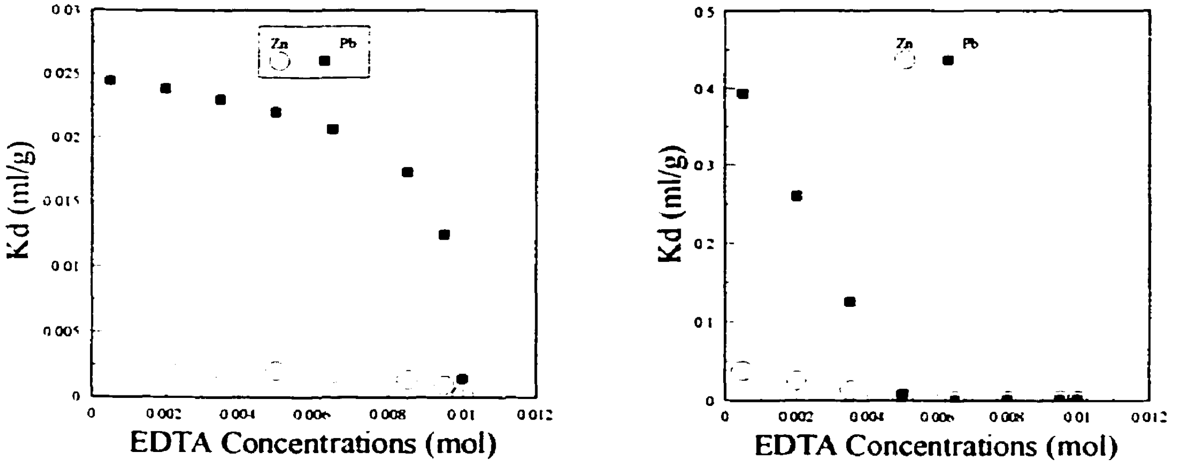
(b) Zn or Pb (5cmol/kg soil) separately



(c) Zn and Pb (1cmol/kg soil) compositely

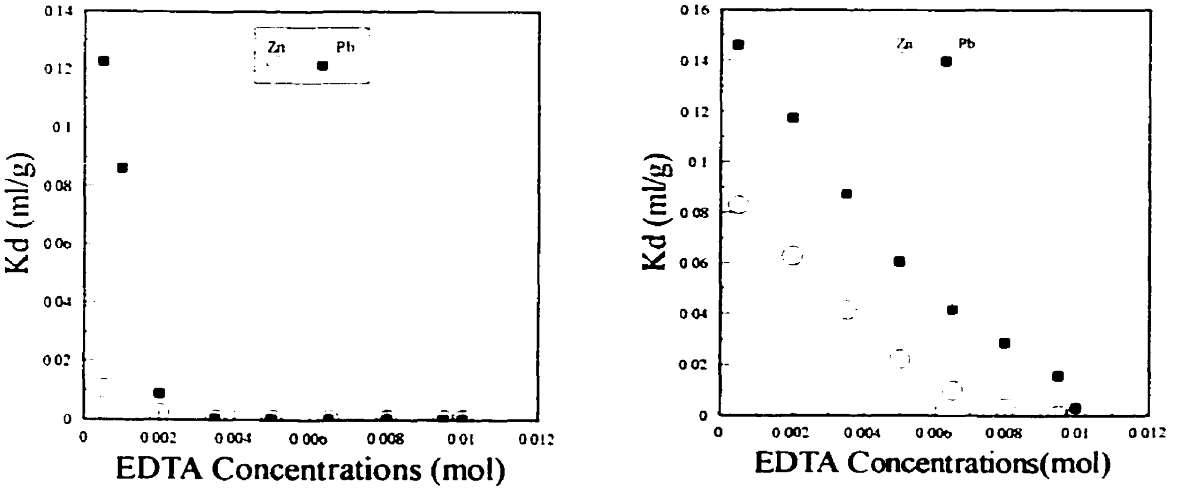
(d) Pb and Zn (5cmol/kg soil) compositely

Fig. 4.15 EDTA Concentration Effects on Retention for Kaolinite.



**(a) Zn or Pb (1cmol/kg soil) separately**

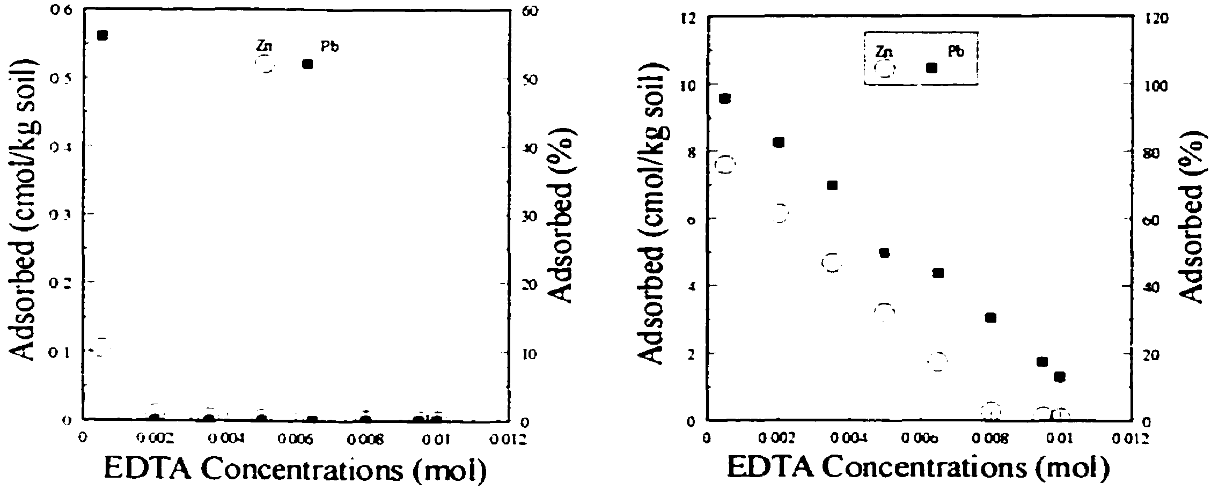
**(b) Zn or Pb (5cmol/kg soil) separately**



**(c) Zn and Pb (cmol/kg soil) compositely**

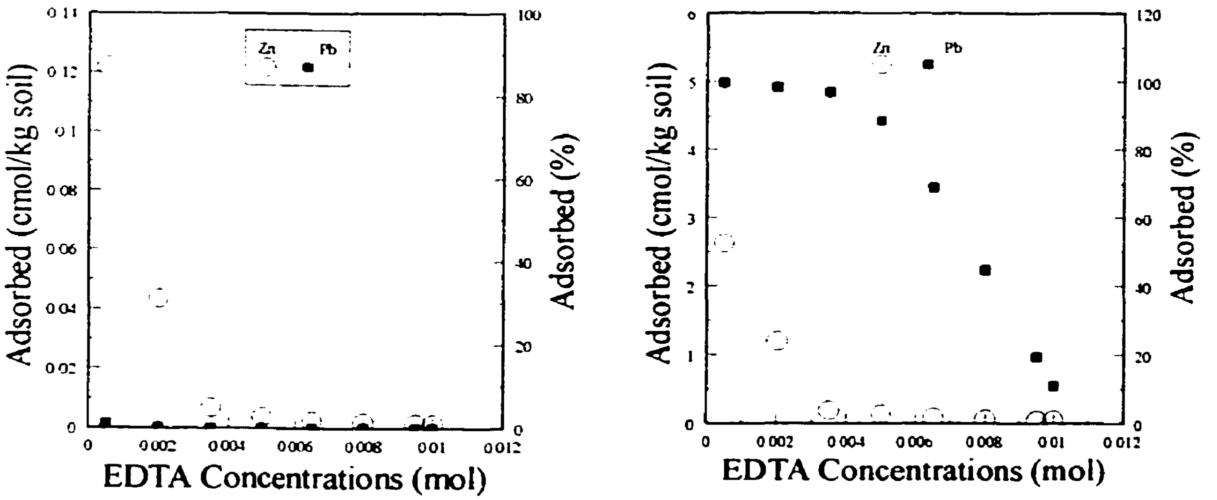
**(d) Pb and Zn (5cmol/kg soil) compositely**

**Fig. 4.16** EDTA Concentration Effects on Kd for Kaolinite.



**(a) Zn or Pb (1cmol/kg soil) separately**

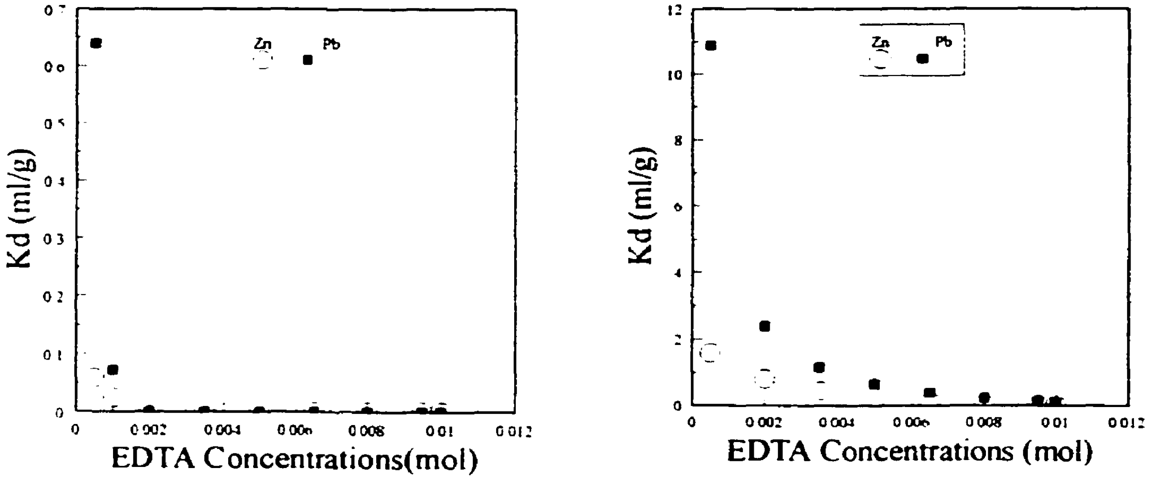
**(b) Zn or Pb (10cmol/kg soil) separately**



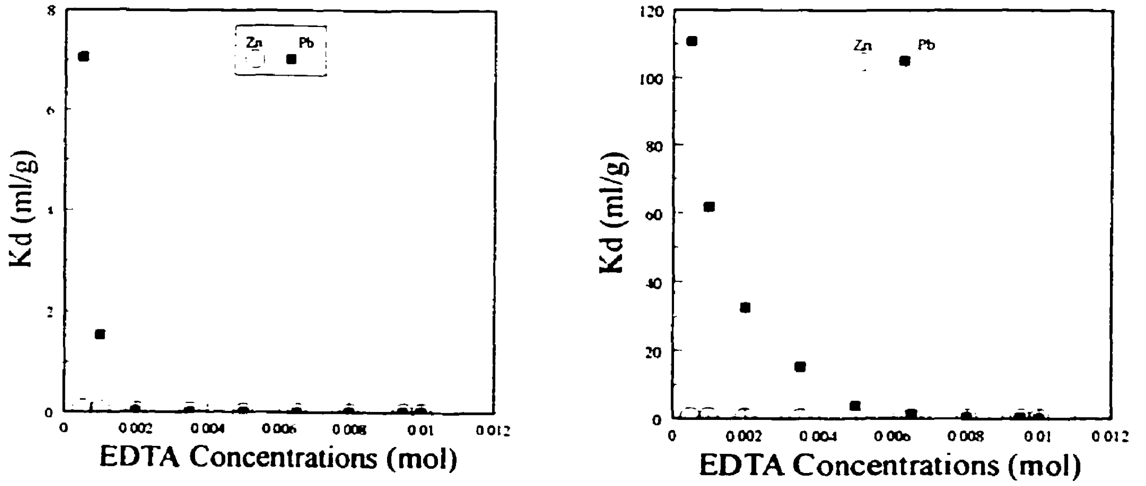
**(c) Zn and Pb (1cmol/kg soil) compositely**

**(d) Zn and Pb (5cmol/kg) soil compositely**

**Fig. 4.17** EDTA Concentration Effects on Retention for KC Soil.

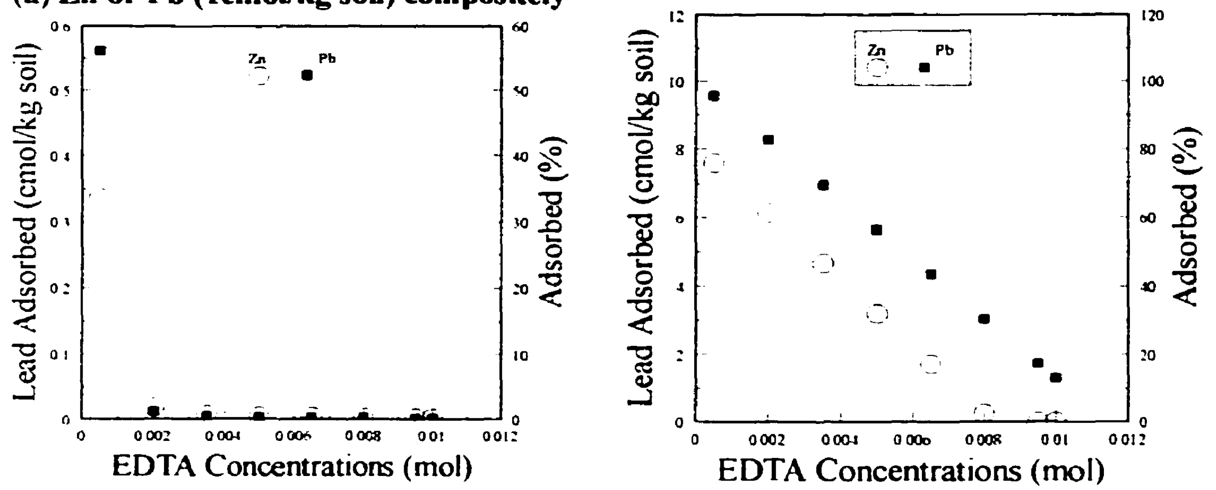

**(a) Zn or Pb (1cmol/kg soil) separately**

**(b) Zn or Pb (10cmol/kg soil) separately**


**(c) Zn and Pb (1cmol/kg) soil compositely**

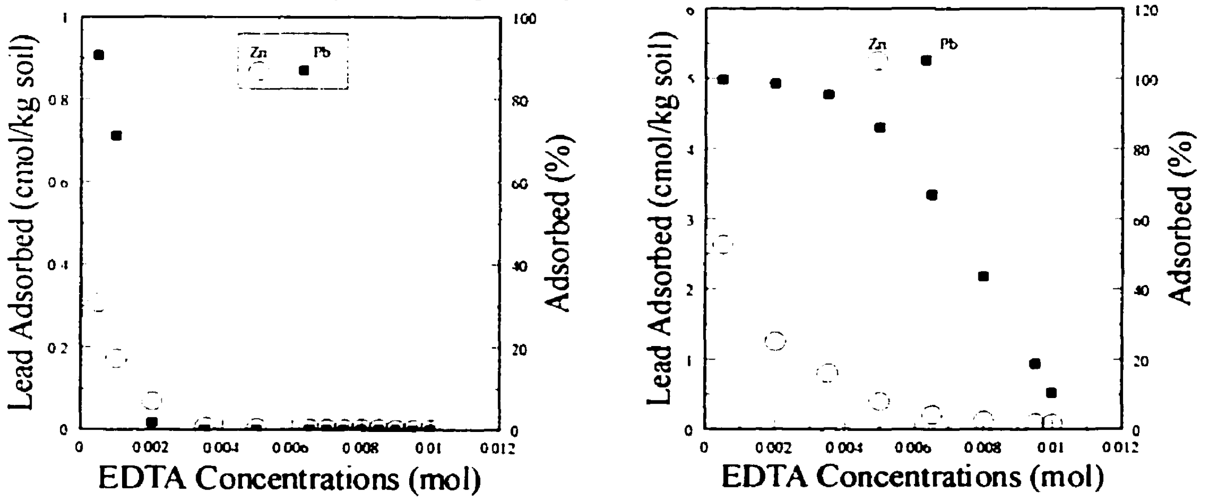
**(d) Zn and Pb (5cmol/kg soil) compositely**

**Fig. 4.18** EDTA Concentration Effects on Kd for KC Soil.



**(a) Zn or Pb (1cmol/kg soil) compositely**

**(b) Zn or Pb (10 cmol/kg soil) separately**

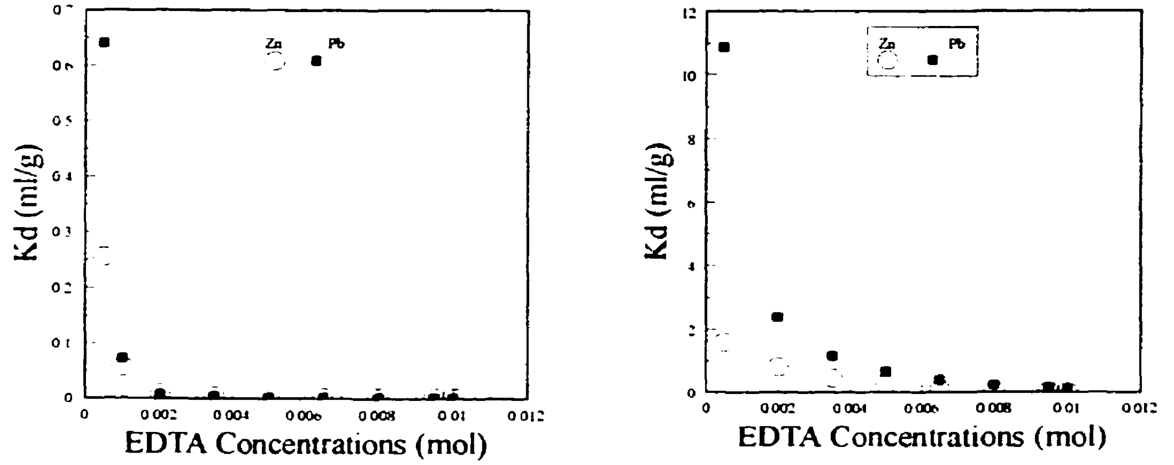


**(c) Zn and Pb (1cmol/kg) soil compositely**

**(d) Zn, Pb 5cmol/kg soil compositely**

**Fig. 4.19** EDTA Concentration Effects on Retention for KCS Soil.

**(a) Zn or Pb (1cmol/kg soil) separately** **(b) Zn or Pb (10cmol/kg soil) separately**



(c) Zn and Pb (1cmol/kg soil) compositely (d) Zn and Pb (5cmol/kg soil) compositely

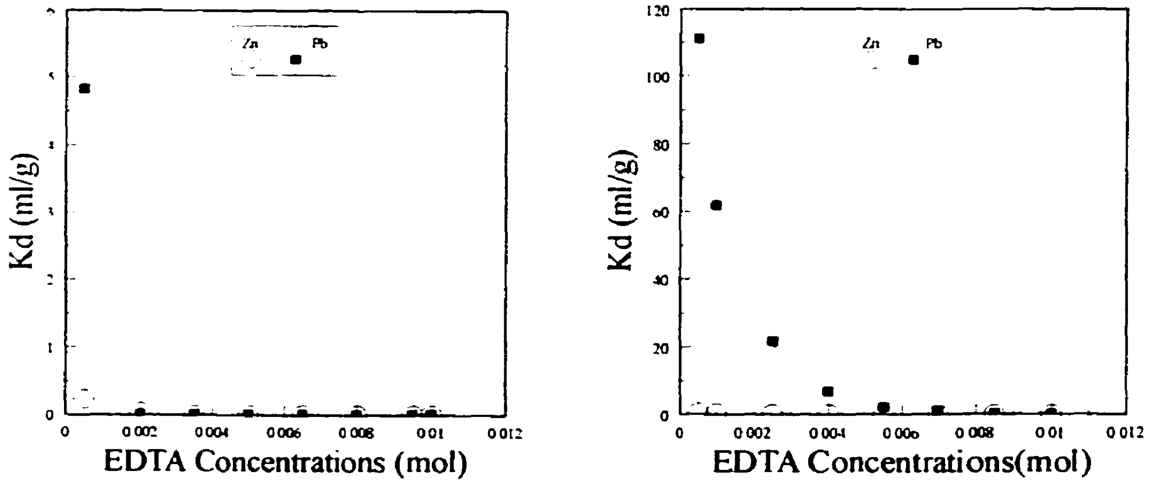
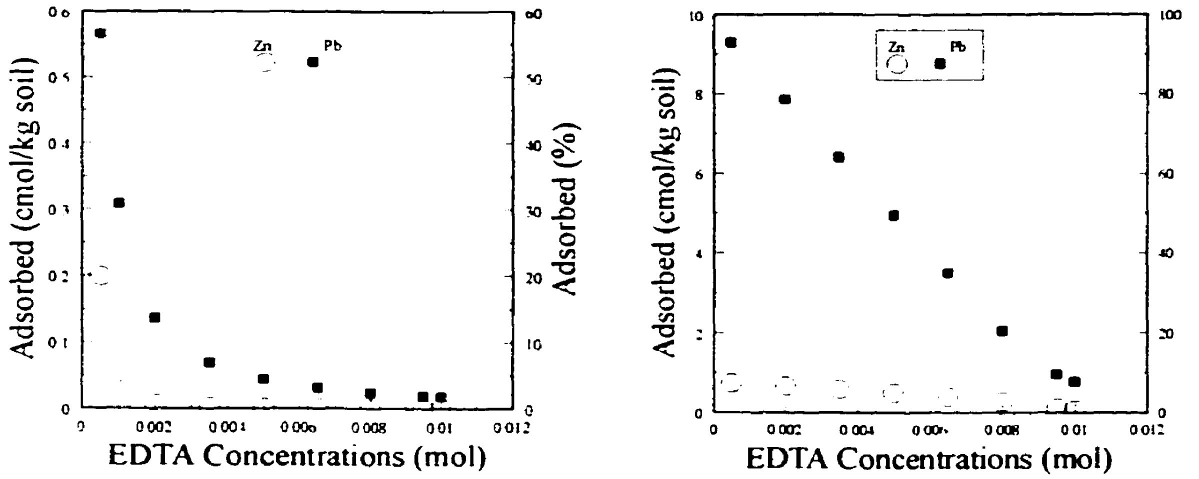
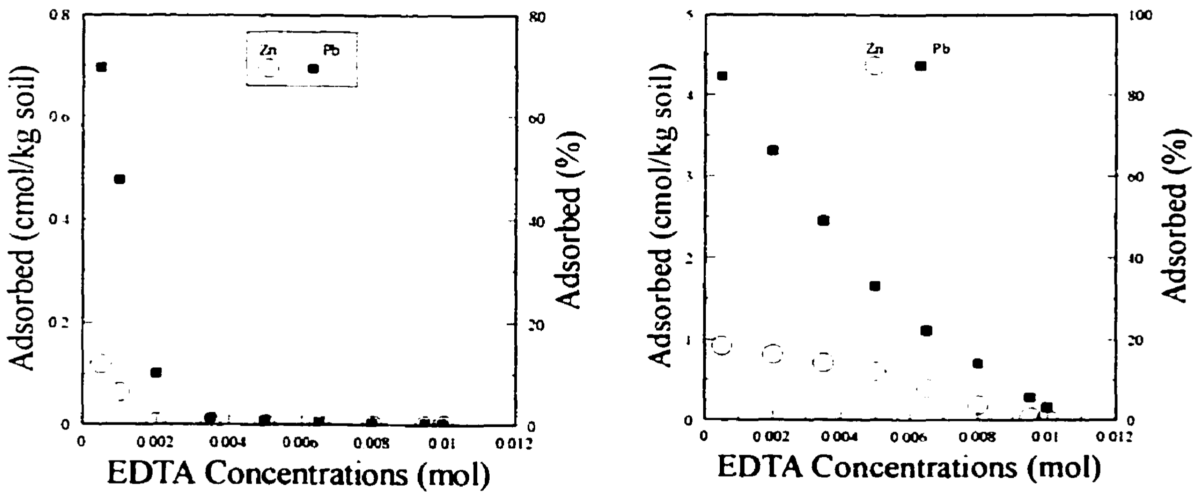


Fig. 4.20 EDTA Concentration Effects on Kd for KSC Soil.

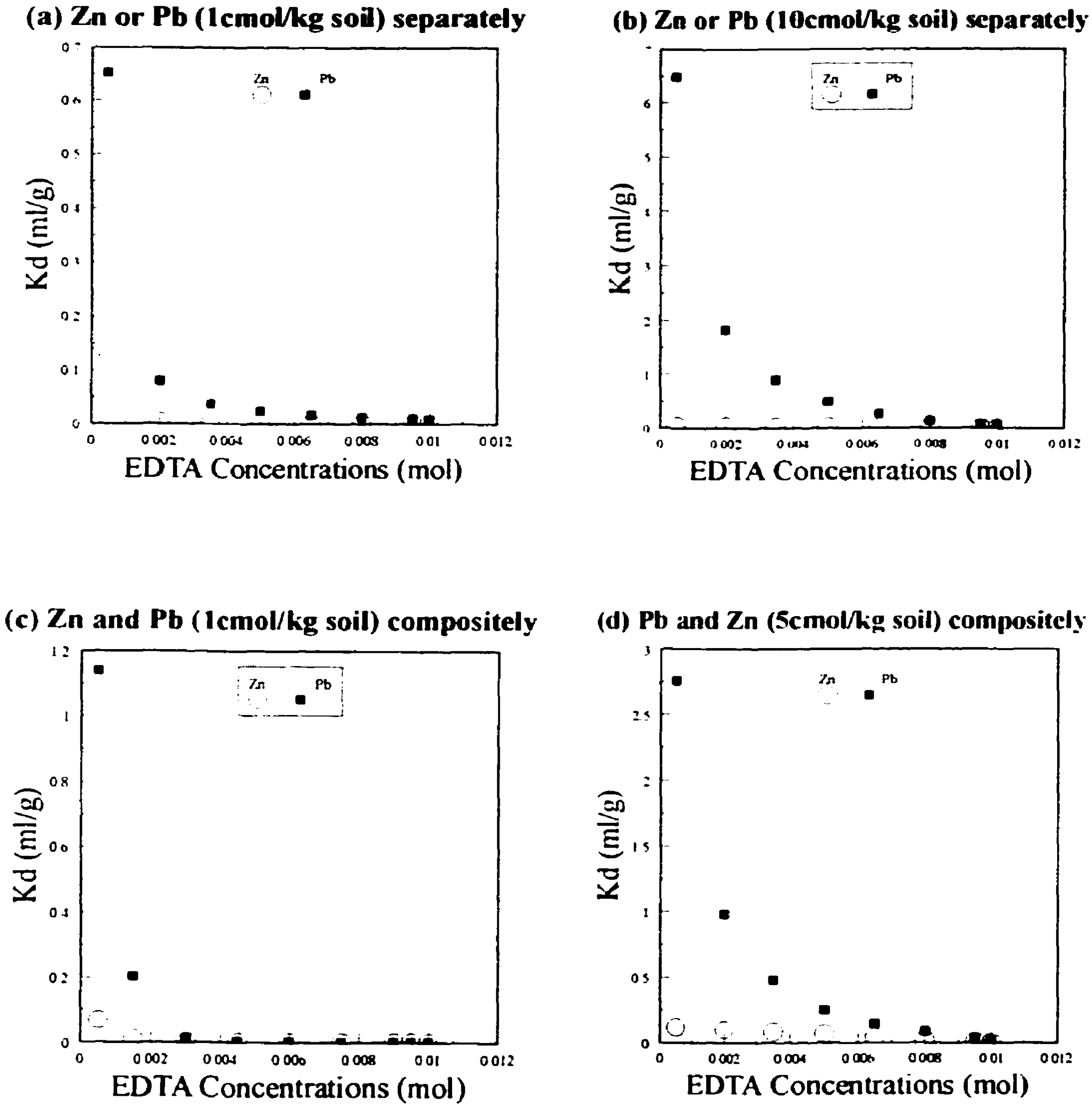

(a) Zn or Pb (1cmol/kg soil) separately

(b) Zn or Pb (10cmol/kg soil) separately


(c) Zn and Pb (1cmol/kg soil) compositely

(d) Zn and Pb (5cmol/kg soil) compositely

Fig. 4.21 EDTA Concentration Effects on Retention for KS Soil.


(a) Zn or Pb (1cmol/kg soil) separately

(b) Zn or Pb (10cmol/kg soil) separately

(c) Zn and Pb (1cmol/kg soil) compositely

(d) Pb and Zn (5cmol/kg soil) compositely

**Fig. 4.22** EDTA Concentration Effects on Kd for KS Soil.

## 4.6 Summary

The effect of multi-component heavy metals (lead and zinc) on the distribution coefficient, $K_d$, for different clay soils at variable pH has been discussed in this chapter. It has been shown that the presence of other contaminants, their concentrations, especially inorganic and organic complexing agents, affect the distribution coefficient, and varies with soil constituents, CEC, SSA and pH of the soil solution. As the pH decreased and soil CEC and SSA decreased, the distribution coefficient decreased. In the presence of a conservative complexing component such as EDTA the distribution coefficient significantly decreased as the concentration of EDTA increased. Thus, the $K_d$ parameter can have an important effect on the uncertainty associated with the modelling results. This parameter is often used to describe the partitioning of a contaminant between the ground-water solution and the solid soil matrix. In addition, the batch equilibrium test, which has been used as a tool for measuring the distribution coefficient, does not represent the compacted clay liner in field. The purpose of the next chapter is to investigate the partitioning of heavy metals in the column leaching test, compare the results with batch equilibrium tests and whether it is possible to use the distribution coefficient computed through batch tests for the prediction of the coupled solute transport in the clay liner material.

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# Chapter 5

# Column Test Results for Artificial Soil

## 5.1 General

The results of the effects of bulk solution composition on heavy metals distribution in different clay soils for batch tests, using different concentrations of chloride or EDTA as the complexing agent were discussed in the previous chapter. In this chapter, the effects of bulk solution composition on heavy metals mobilization and immobilization in different clay soils is investigated.

The immobilization process minimizes the migration of heavy metals by fixing them in a non-leachable form. The migration of heavy metals can be considerably reduced by solidifying the soil, or chemically altering the metals in a non-leachable form (Peters and Shem, 1992). How different clay soils respond to immobilization of the Pb and Zn is addressed in this chapter. The immobilization of heavy metals can be affected when an acidic heavy metals solution spiked with other contaminant complexing agents is used.

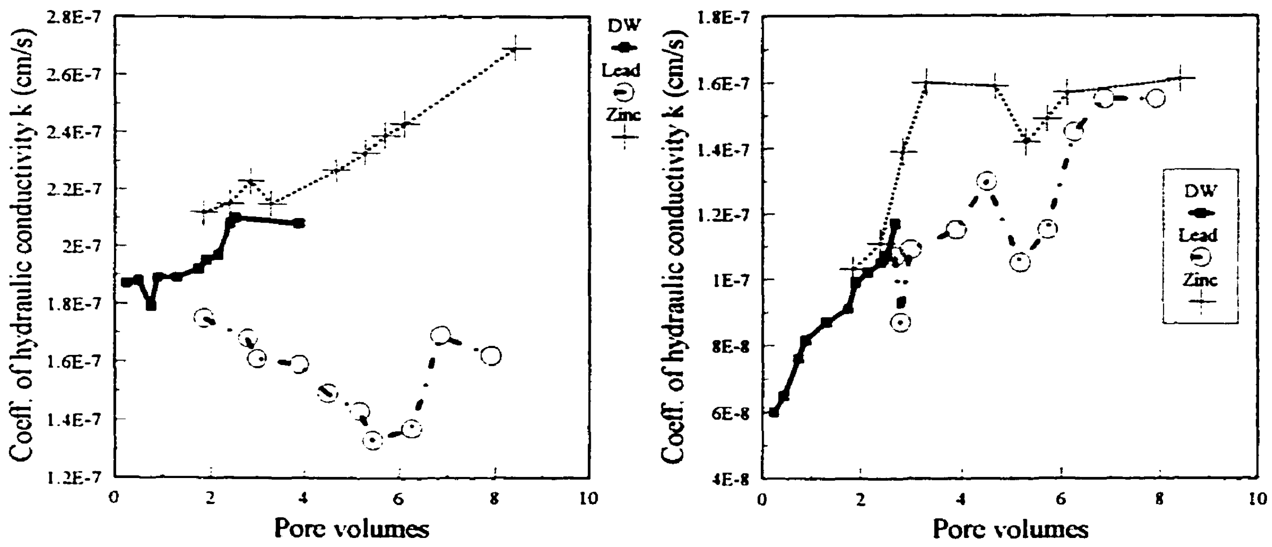
This chapter presents the results of column leaching tests for the controlled samples in which kaolinite and kaolinite mixed with silica gel and calcium carbonate (K, KS, KC, and KSC) are used as the soil material and a heavy metal solution (Pb or Zn) with a concentration of 1mmol/L (Pb or Zn) is used as a leachate spiked with NaCl at a concentration of 0.05 mol/L. The pH of the leachate solution was fixed at around 3.0 and the hydraulic pressure was monitored at 2.5 psi (2m of hydraulic head). The results of permeability tests are presented and discussed first, followed by those of chemical analyses of both leachate and test samples (total mass transfer, retention and migration profiles). Test results will often be presented in groups in order to simplify the discussion. In this fashion, the effect of soil inorganic constituents on the coefficient of hydraulic conductivity, migration and retention capability may be addressed in a more straightforward manner. The calibration of the program for parameter estimation by the experimental results is presented second, followed by the prediction of the long term migration and retention profiles of heavy metals.

## 5.2 Permeability Results

Constant head permeability tests were performed with inflow and outflow volume rates monitored. The contaminant was introduced from the top and collected at the bottom. Permeability testing using hydraulic gradients much higher than actual field conditions can cast doubt on the validity of laboratory results, however, the results of the permeability test done by Cabral and Yong (1993) and Kallur *et al.* (1995) at different gradients from 25-100 for kaolinite clay show that there are slight changes in the coefficient of the permeability. The results of the permeability test for kaolinite and kaolinite mixtures for D.W. and heavy metals solution at different pore volumes (K, KS, KC and KSC) are shown in Figure 5.1.

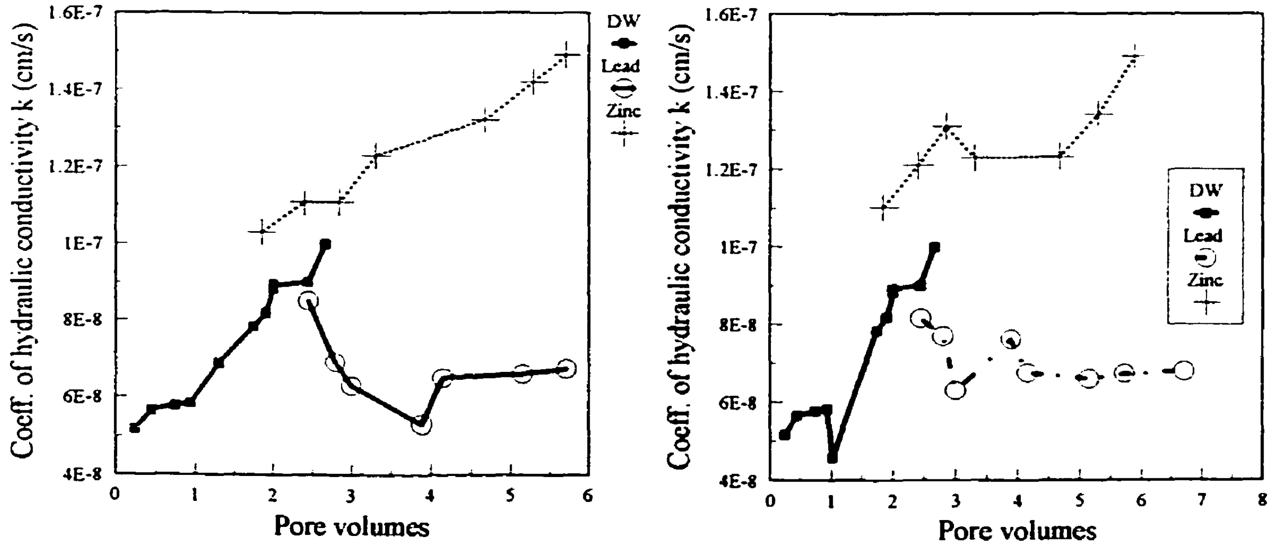
### 5.2.1 Discussion on the Hydraulic Conductivity Results

The results of coefficient of permeability, shown in Figure 5.1, indicate that the coefficient of hydraulic conductivity can be significantly influenced by the soil constituents but the introduction of the lead and zinc permeant did not affect so much the hydraulic conductivity value of the material since the permeant solution at low concentration did not affect the diffuse double layer of the clay soil material. Kaolinite soil has the least coefficient of permeability of the three other soils. This is because the addition of permeant solution with a pH of 3.00, which is above the ZPC(4.2), in kaolinite could result in the situation where the soil tends to deprotonate or surrender $H^+$ from its edges, thereby resulting in a reduction of the soil solution pH (Ohtsubo, 1994) which could result in more mobility of the ions. In all clay soils the coefficient of hydraulic conductivity of the zinc is more than the lead permeant solution. This is because Zn ions are more mobile than the Pb ions, as discussed in the batch equilibrium test.



(a) Kaolinite

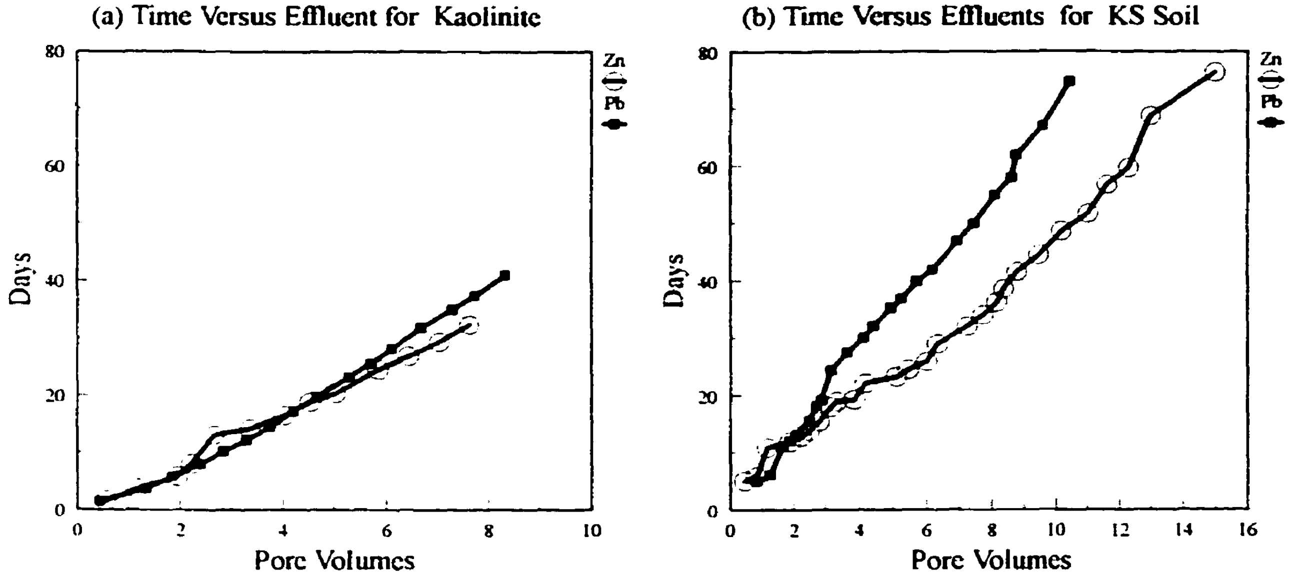
(b) KS Soil



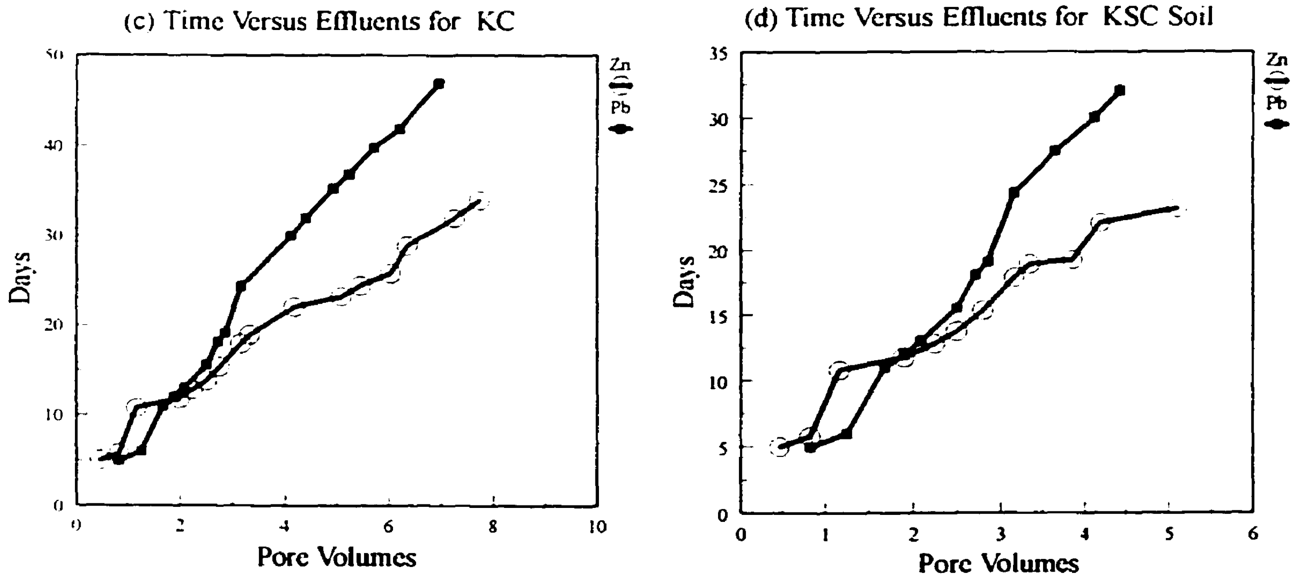
(c) KC Soil

(d) KCS Soil

**Fig. 5.1** Hyraulic Conductivity in Different Clay Soils.


(a) Time Versus Effluent for Kaolinite

(b) Time Versus Effluents for KS Soil


(c) Time Versus Effluents for KC

(d) Time Versus Effluents for KSC Soil

**Fig. 5.2** Time Versus Pore Volumes For Different Clay Soils.

As the permeant is continued and more pore volumes of effluents result, the coefficient of permeability begins to increase, as shown in the Figure 5.1. This is because at high ionic concentration solutions the thickness of the diffuse double layer decreases and consequently leads to an increase in the hydraulic conductivity (Mitchell, 1976).

In all cases, clay permeated with distilled water shows an initial decrease at first, then increases with subsequent relatively constant permeability and lower coefficient of permeability, as a result of the removal of the natural salts in the soil through leaching of the sample by distilled water. The increase in the permeability of all types of clays, leached with heavy metals at high pore volumes of effluent, can be attributed to the reduction in the diffuse double layer thickness due to replacement of the monovalent ions or exchange of calcium in carbonate soil from the solution by divalent heavy metals (Yong *et al.* 1992b).

To illustrate how fast the permeant was passed through each clay soil, a graph of time versus effluent pore volumes for each clay soil is plotted in Figure 5.2. As shown, soil constituents have a great affect on the permeability of the clay soil.

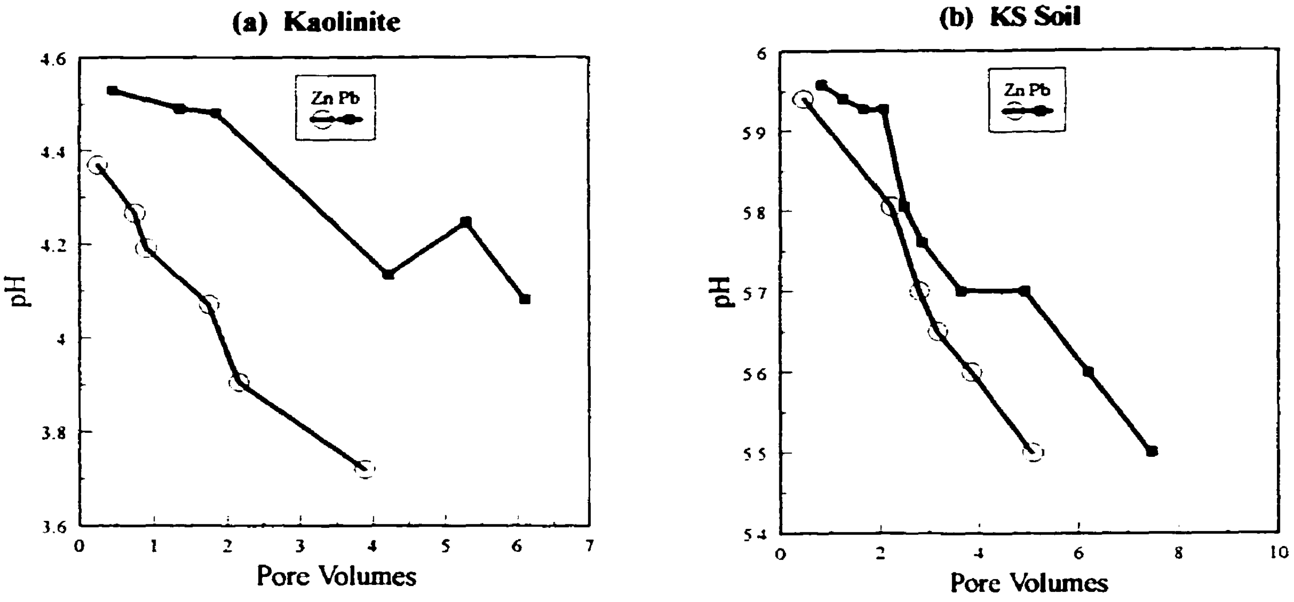
However, as shown in the Figures 5.1b and 5.2b, 5.1c and 5.2c, and 5.1d and 5.2d, the kaolinite mixtures with silica gel or calcium carbonate exhibit a coefficient of permeability almost one order less than the kaolinite. The results indicate the importance of silica gel as an additive material to clay minerals for the reduction of the permeability. Lower permeability gives a higher retardation of heavy metals transport within the landfill which agrees with previous experience with fly ash (Pluss, 1993). This is because amorphous material acts both as a coating and a cementing material (Yong *et al.*, 1992a).

## 5.3 Effluent pH Results

As described in the experimental program in Chapter 2, the pH of the permeant solution was kept constant, around 3.0, to simulate an acidic environment for the source contaminant because in the field of land disposal, not only acid rain but also the presence of acids in solid or liquid wastes in landfill can influence the soil pH. The pH of the effluents was measured after each pore volume to find out how the soil material is buffered to the acidic leachate in the input solution. The results of the effluent pH as a function of pore volume for each soil ( K, KS, KC, KSC) are shown in Figure 5.3.

### 5.3.1 Discussion on the Soil Constituent on the Effluent pH

As shown in Figure 5.3, as the pore volume increases the more $H^+$ ions are introduced into column soil and thus the pH of the soil solution decreases. The resistance of the soil to a change in pH, called soil buffer capacity (Yong, et al., 1995), is different as the column receives a continuous load of acidic heavy metals and also depends on the soil constituents. The pH of the effluent of the kaolinite soil is more affected than the three other clay soils by the increase in pore volumes. This is because kaolinite soil has low initial pH. KC soil has the highest effluent pH and soil pH profiles due to its high carbonate content (Phadungchewit, 1991).



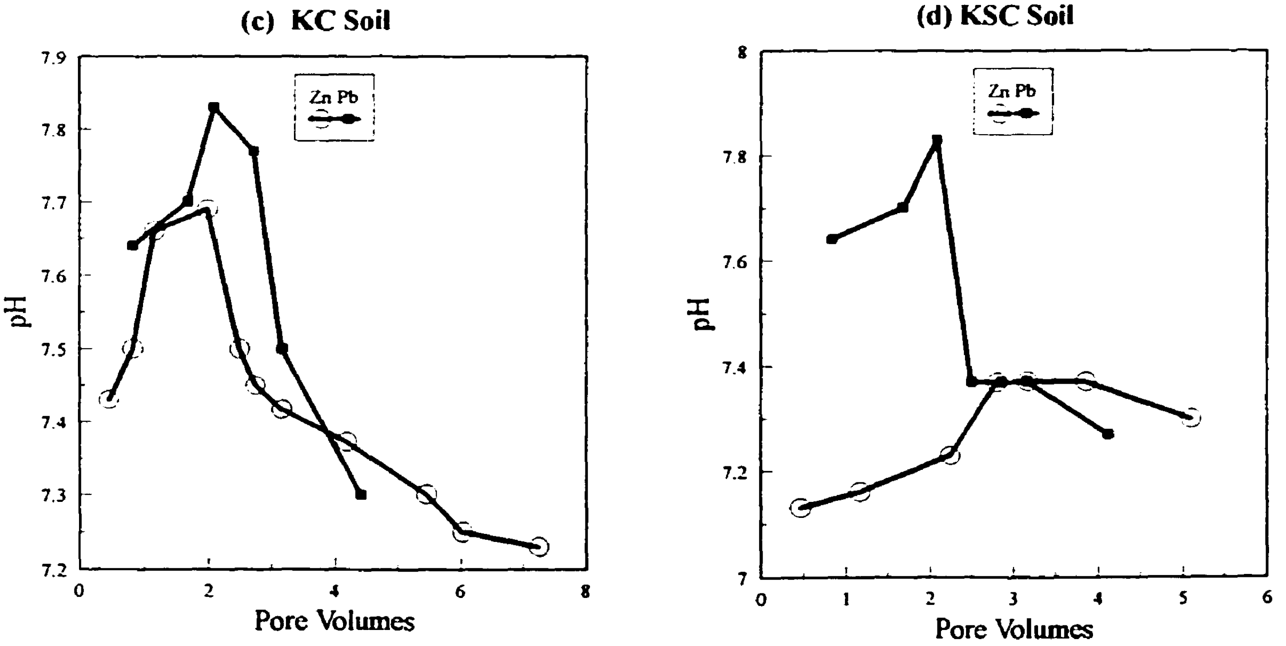


Fig. 5.3 Effluent pH Versus Pore Volumes for Different Clay Soils.

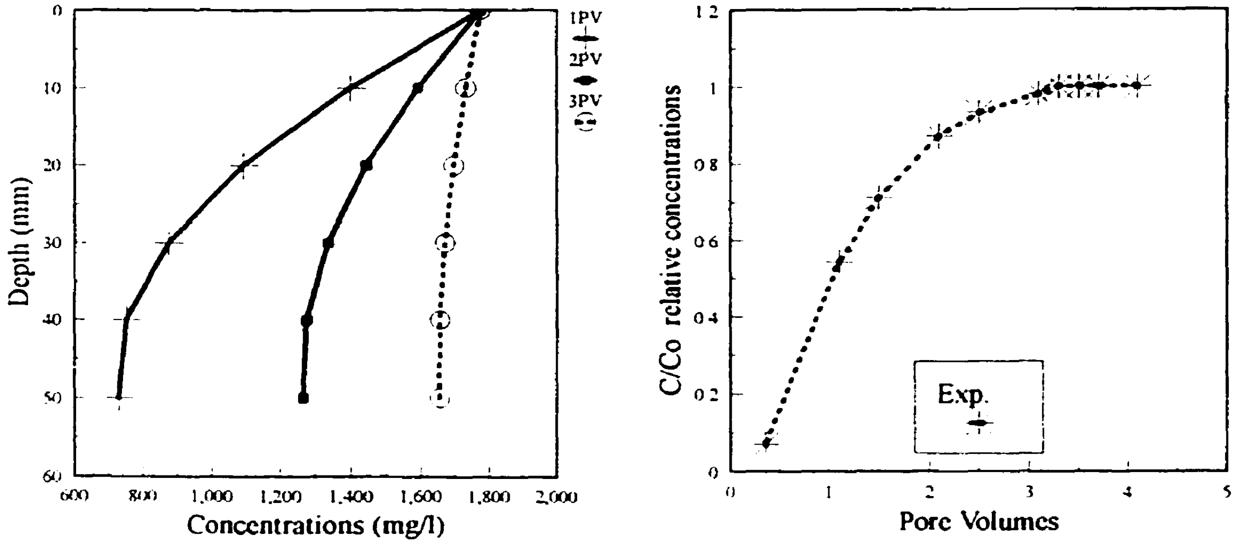
## 5.4 Migration Profiles and Breakthrough Curves for Mobile Components

The experimental migration profiles for chloride and its breakthrough curves, representing the variations of relative concentrations with effluent PVs, measured by the $AgNO_3$ titration method, and a comparison with the results of COSTCHEMCLAY for $Cl^-$ for pure kaolinite and kaolinite mixtures, are shown in Figure 5.4.

### 5.4.1 Discussion on Migration for Cl

The chloride ion is considered to be very mobile. As such, attenuation of the $Cl^-$ is low, as depicted in the figures. The kaolinite mixed with amorphous silica (KS) shows higher attenuation of $Cl^-$ with a breakthrough at 4.5 pore volumes compared to that of kaolinite at 3.5 PV. As shown in Figure 5.4, the chloride concentrations vary with the time and space. Even for chloride, which is a mobile component, its breakthrough curve did not occur until at least two pore volumes of input solution passed through the column. A breakthrough curve of the ionic species is said to have occurred when relative ( input/output) concentration is equal to 0.5. The higher the Cl concentration, the lower the degree of heavy metals adsorption. This means that the distribution coefficient, measured from the batch test using a constant concentration for the chloride, could not represent the variation of the chloride concentration with time and space in a compacted clay liner.

(a) Cl Migration in Kaolinite (b) Cl Breakthrough curve in Kaolinite



(c) Cl Migration in KS (d) Cl Breakthrough curve in KS Soil

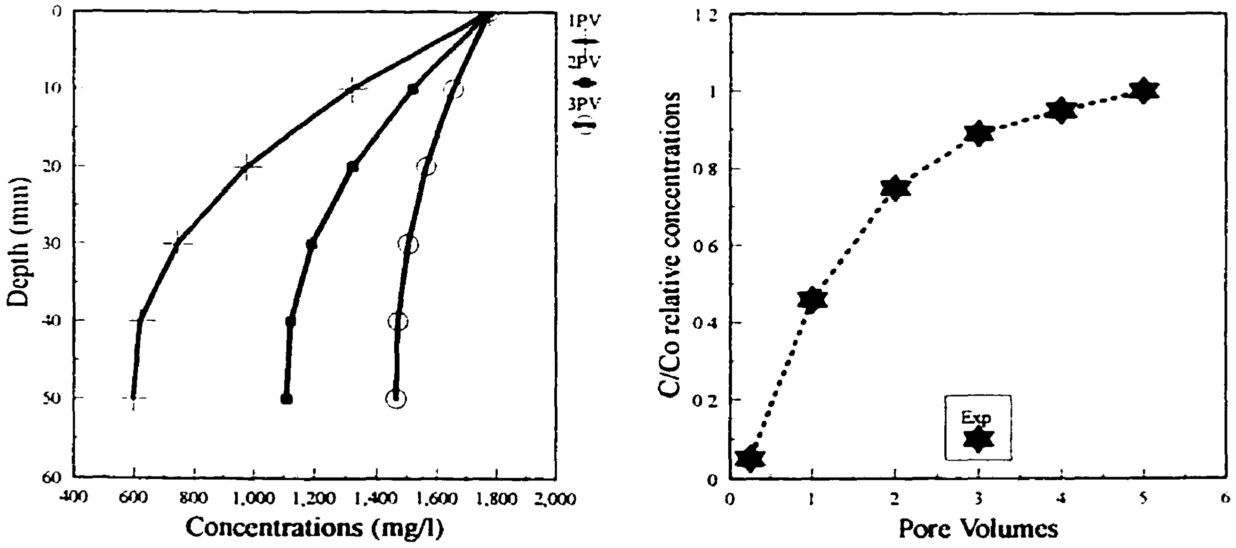


**Fig. 5.4** Time Versus Pore Volumes For Different Clay Soils.

## 5.5 Quantitative Analysis of Total Heavy Metals

Total concentration of heavy metals in any particular depth of clay soil is generally the sum of those which are sorbed by solid surfaces and in solution (soluble). The sorbed fraction consists of two basic components (Salim *et al.*, 1993): i) fixed metals which have been incorporated into the crystal lattices or mineral phases by chemisorption, solid state diffusion, or precipitation, and ii) adsorbed through exchangeable metals which are weakly bound by electrostatic forces to the organic and inorganic phases. Heavy metals which are adsorbed by the exchangeable phase or are precipitated are considered to be the most mobile, especially at low pH of the soil solution (Yong and MacDonald, 1997). On the other hand, the fixed fraction is immobile and of less toxicological concern. The chemical partitioning of heavy metals in contaminated soil is, therefore, of great significance in risk assessment and remedial investigation.

In order to determine the total amounts of heavy metals (adsorbed + precipitated + dissolved) at any particular depth in a column leached by the heavy metals, the acid digestion method recommended by ASTM (1984), was used to bring these metals into solution, and consequently measure the concentration by means of atomic adsorption spectrophotometer. To determine the vertical distribution of the total amount of each heavy metal at certain pore volumes of leachate, soil specimens were taken apart and the soil layers sectioned into 10-mm-thick slices. Trial digestion was performed using 2 grams of the bulk soil slice, representing each particular depth of the column soil (5 layers) which had been previously air-dried, ground and mixed in a ceramic mortar to ensure homogeneity. Ten millilitres of nitric acid (1:1) was added to the soil in a 250 mL conical Phillips beaker, mixed with slurry, and covered with a watch glass. The sample was heated to 95' and refluxed for 10 to 15 minutes without boiling. The sample was allowed to cool, 5 mL of concentrated nitric acid was added , the watch glass was replaced, and refluxed for 30 minutes, 2 mL of water was added as well as 3 mL of 30 % hydrogen peroxide until the general sample appearance was unchanged, then 5 mL of concentrated HCl and 10 mL of water was added and refluxed for additional 15 minutes. After the sample was cooled, its was diluted to 100 mL with water. Details of the acid digestion method can be found in the

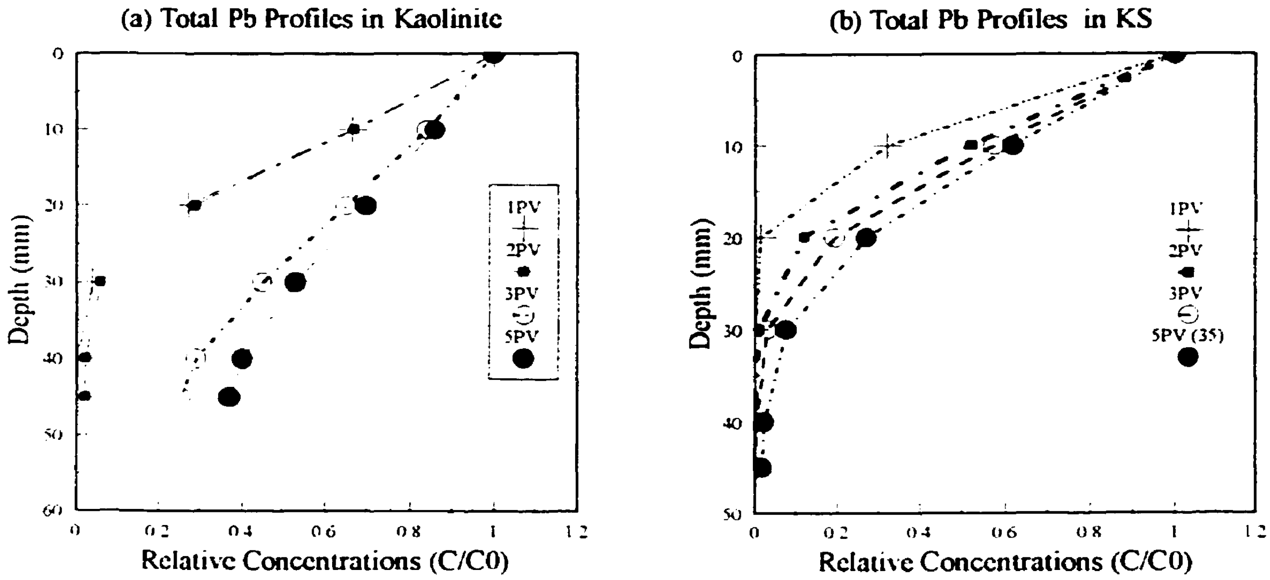
ASTM (1984). All samples were analysed in triplicate to obtain a mean value and to check precision.

### 5.5.1 Total Heavy Metal Profile Results

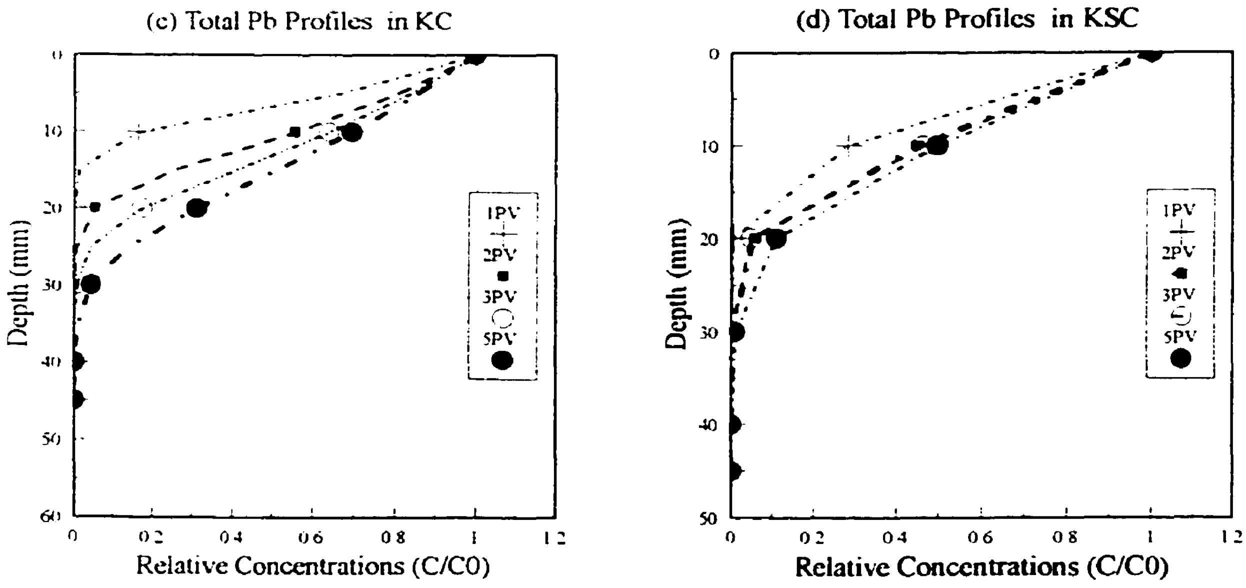
The total amounts of lead (Pb) and zinc (Zn) in each clay soil (K, KS, KC and KSC), obtained from the above methods, are presented as total lead and zinc concentration profiles in Figures 5.5a, 5.5b, 5.5c, 5.5d , 5.6a, 5.6b 5.6c and 5.6d, respectively. Triplicates were made for each one of the slices of a sample. Every point in each graph represents the average of three values. These results represent total acid-digested heavy metals (adsorbed, precipitated and dissolved, within the crystal structure of the clay minerals and other soil constituents). A simple conversion was needed to present the total heavy metals concentration from the acid digestion method in more appropriate units, i.e., grams of heavy metal retained /grams of soil, using the following formula:

$$mass\ of\ heavy\ metal\ (mg) = \frac{(supernatant\ concentration)\ x\ WDS\ x100mL}{1000mL\ x\ 2g}$$

where WDS is a weight of depth slice. To compute the concentration of heavy metal into mg/L for each slice along the soil column a simple conversion, suggested by (Mohammad, 1994), was applied.The results are plotted using total component concentrations versus depth for various leachate PVs. No $Pb^{2+}$ and very little $Zn^{2+}$ was detected in the bottom slices, especially in kaolinite mixture soils (KS, KC, KSC), leaching up to 3 PV leachate, indicating that $Pb^{2+}$ and $Zn^{2+}$ were retained at the top part of the column. The concentrations of $Pb^{2+}$ and $Zn^{2+}$ have increased with PV through the soil column as a function of leachate PV. Both metals continued to transport through the soil column as a function of leachate PV. $Zn^{2+}$ is more mobile than the $Pb^{2+}$ and less zinc was retained in all types of the soil. The kaolinite, which has a very low CEC and SSA, and does not have any significant amount of soil constituent results in the highest transport of both heavy metals compared to the three other soils, as shown in Figures 5.5a and 5.6a for lead and zinc , respectively.

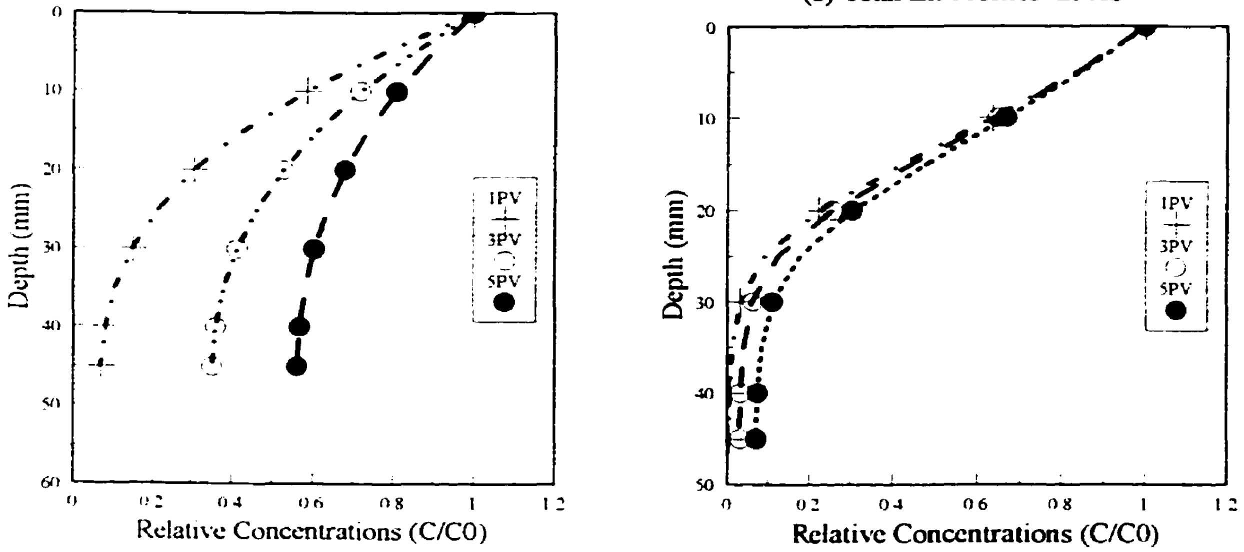

(a) Total Pb Profiles in Kaolinite

(b) Total Pb Profiles in KS


(c) Total Pb Profiles in KC

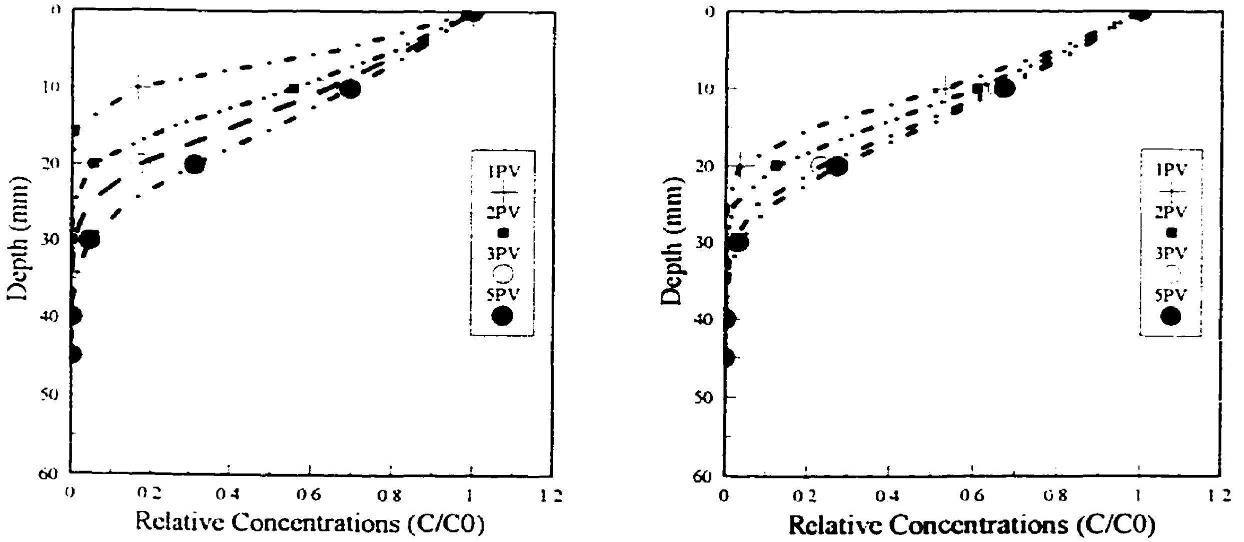
(d) Total Pb Profiles in KSC

**Fig. 5.5 Total Pb Profiles for Different Clay Soils.**



(a) Total Zn Profiles in Kaolinite

**(b) Total Zn Profiles in KS**



(c) Total Zn Profiles in KC

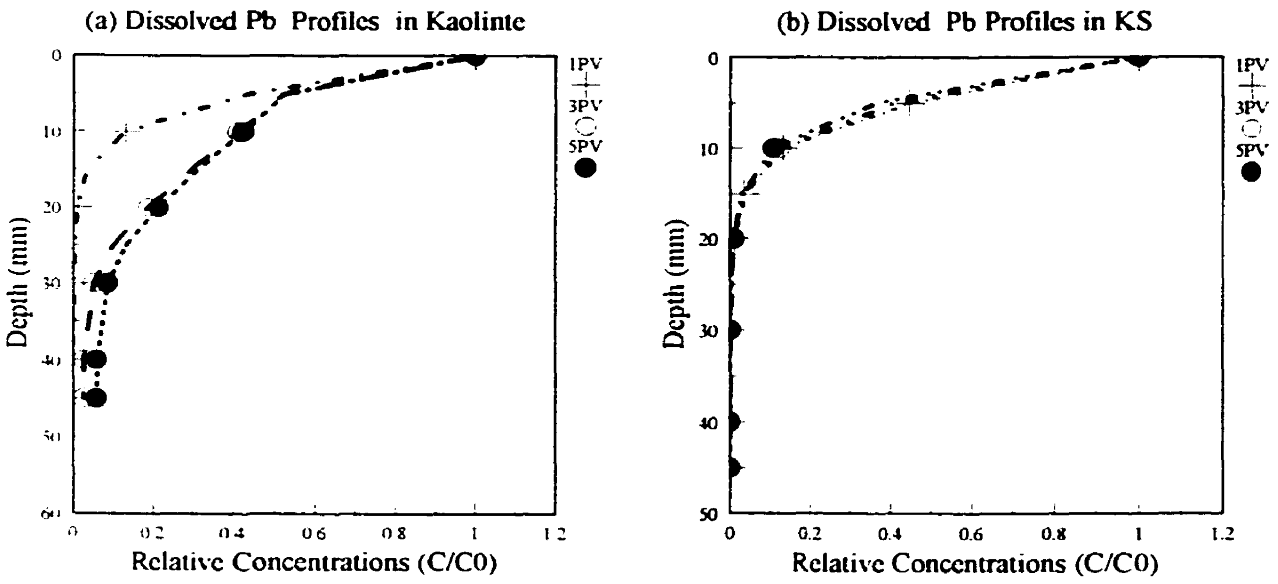
(d) Total Zn Profiles in KSC

**Fig 5.6** Total Zn Profiles for Different Clay Soils.

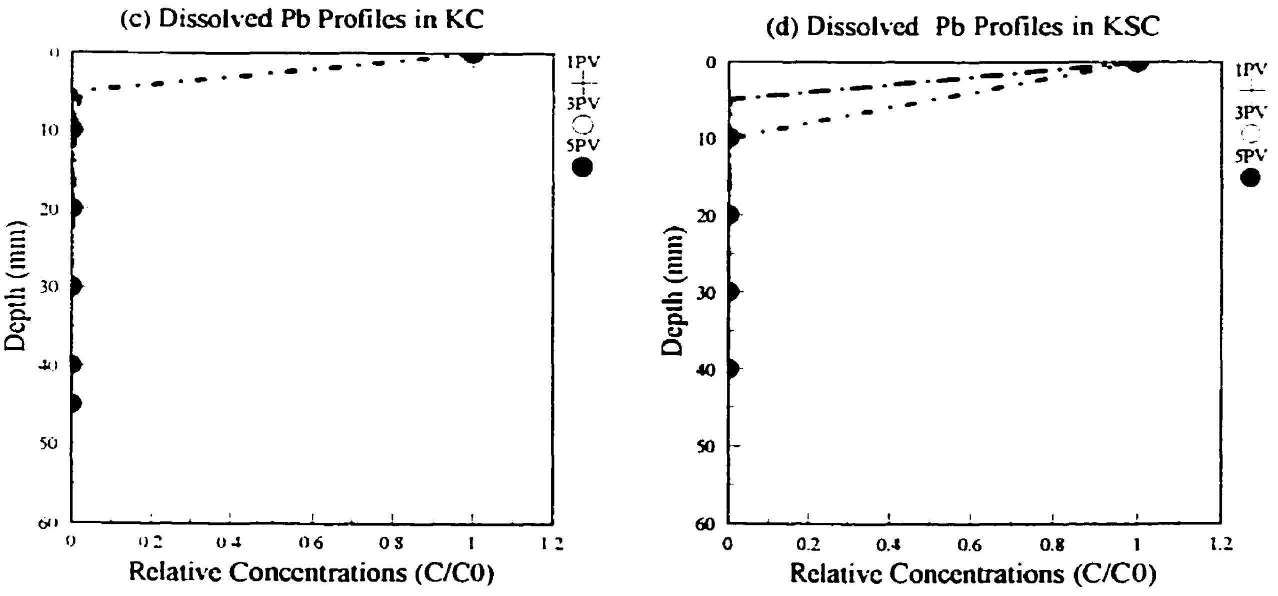
### 5.5.2 Heavy Metals Dissolved Profiles

To determine the pore fluid concentration (soluble ions) of each heavy metal at any particular depth (migration profile) of the clay soil, for each pore volume, 2 gr of sliced specimen was mixed with distilled water at a ratio of 1/10 in a 40 ml centrifuge tube. The bottles were then placed in a shaker and kept at a constant temperature of 25° C. Based on the experimental results of the supernatant concentrations and shaking time, it was determined that equilibrium concentrations were obtained after 18 h of shaking. After the shaking period, the specimens were centrifuged to separate the clay from the liquid. The supernatant liquids from the bottles were filtered, and the equilibrium concentration in the liquid phase of a constituent of interest, (C, expressed in units of mass of constituent per unit volume of liquid) were measured using atomic adsorption spectrophotometry. A simple conversion is necessary to convert the pore fluid concentration of each heavy metal in units of mg/g or g/kg of the soil.

The experimental results of migration profiles of lead and zinc for kaolinite soil and kaolinite mixtures (KS, KC, KSC) are shown in Figures 5.7a, 5.7b, 5.7c, 5.7d, 5.8a, 5.8b 5.8c and 5.8d, respectively. The results are plotted using equilibrium pore fluid concentration versus depth for various leachate PVs. No $Pb^{2+}$ and very little $Zn^{2+}$ is collected in the effluent leaching up to 3 PV leachate, indicating that $Pb^{2+}$ and $Zn^{2+}$ were retained in the soil. The concentrations of $Pb^{2+}$ and $Zn^{2+}$ in the pore fluid have increased with PV through the soil column as a function of leachate PV. Both metals continued to migrate through the soil column as a function of leachate PV. $Zn^{2+}$ is more mobile than the $Pb^{2+}$ and less zinc was retained in the soil. No lead and very little zinc migrated to the bottom slices, especially for kaolinite mixtures (KS, KC, KSC). This is because, the addition of carbonates and silica gel to the kaolinite increases the amounts of Pb removed from the solution. The efficiency of Zn removal, however, appears to be lower than that of Pb, in all types of the soils. This is because, Zn is more mobile, and has a lower selectivity for charged surfaces (Farrah and Pickering, 1977; Phadungchewit, 1990). A higher mobility and lower selectivity implies that the contaminant will not be retained as effectively by the clay particles. This may be explained by the reduced availability of free uncomplexed $Zn^{2+}$ ions for precipitation or by ion exchange as observed in the work of Yong *et al*. (1992). The fact that zinc was detected earlier than lead in the leachate collected indicates that $Zn^{2+}$ is more mobile than $Pb^{2+}$. This agrees with the previous findings of several authors, including Farrah and Pickering (1977); Phadungchewit (1990), Yong *et al.* (1993), Mohamed *et al*, 1994 and Martell and Hancock (1996). This can be attributed to the difference in the hydrated radii of $Pb^{2+}$ and $Zn^{2+}$ cations near the clay surface. The kaolinite results in the highest pore fluid concentration profiles, due to the lowest retention of both heavy metals compared to the three other soils.

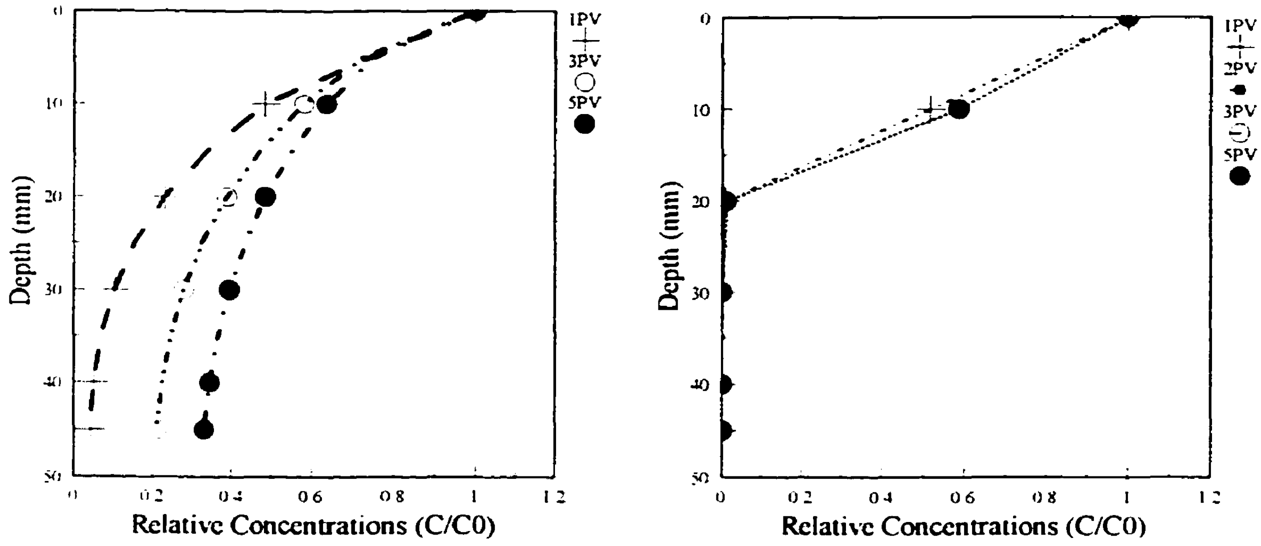

(a) Dissolved Pb Profiles in Kaolinte

(b) Dissolved Pb Profiles in KS


(c) Dissolved Pb Profiles in KC

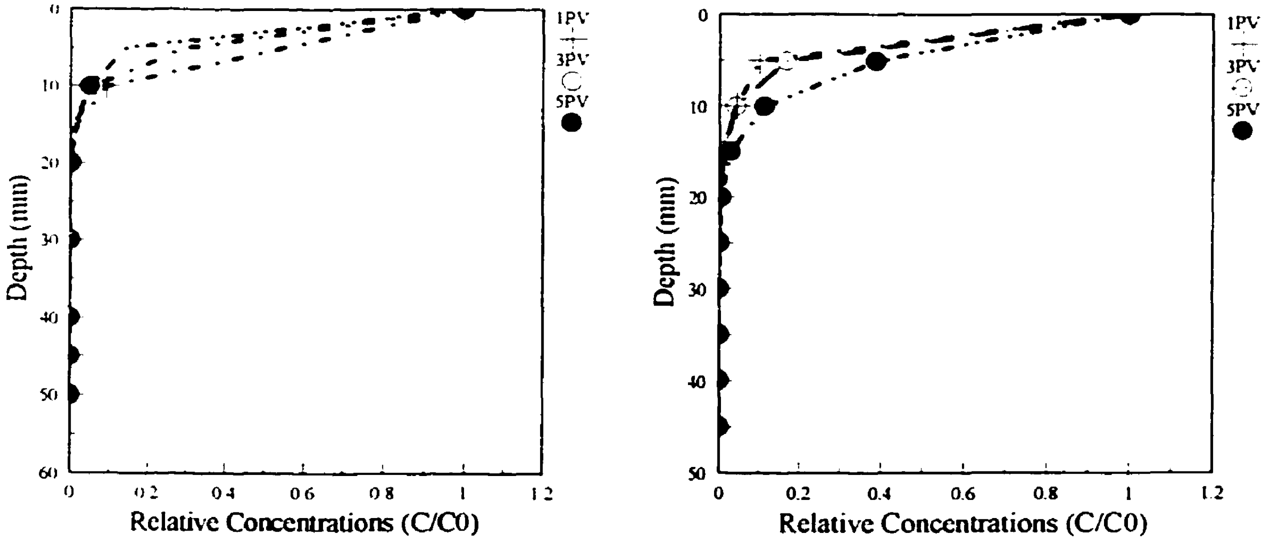
(d) Dissolved Pb Profiles in KSC

**Fig. 5.7** Pb Dissolved Profiles For Different Clay Soils.



(a) Dissolved Zn Profiles in Kaolinte

(b) Dissolved Zn Profiles in KS



(c) Dissolved Zn Profiles in KC

(d) Dissolved Zn Profiles in KSC

**Fig. 5.8** Zn Dissolved Profiles For Different Clay Soils.

### 5.5.3 Heavy Metal Adsorption and Retention Profiles

The total retention of heavy metals along the depth of the clay barrier include the adsorbed and precipitated ones . To calculate the total retention, the migrated heavy metals measured from pore concentrations (soluble ions) were subtracted from the total heavy metal measured from digestion. The concentrations of $Pb^{2-}$ and $Zn^{2-}$ were computed for unit mass of the soil [ $S=C_t - C_s$ ], where $C_t$ = the total component concentration measured by the acid digestion, and $C_s$ = the pore fluid concentration ( soluble) for each heavy metal. The unit of S is mg of constituent adsorbed/g of dry soil.

Experimentally, it is not possible to distinguish between the precipitated and adsorbed metals and since the range of concentrations of soluble heavy metals used for the leachate was low (1mmol) the heavy metals were most probably adsorbed into the clay. In other words, there was no lead or zinc precipitated into the kaolinite and very little lead was precipitated at the top part of the soil column for kaolinite mixtures, which have high soil solution pH values.

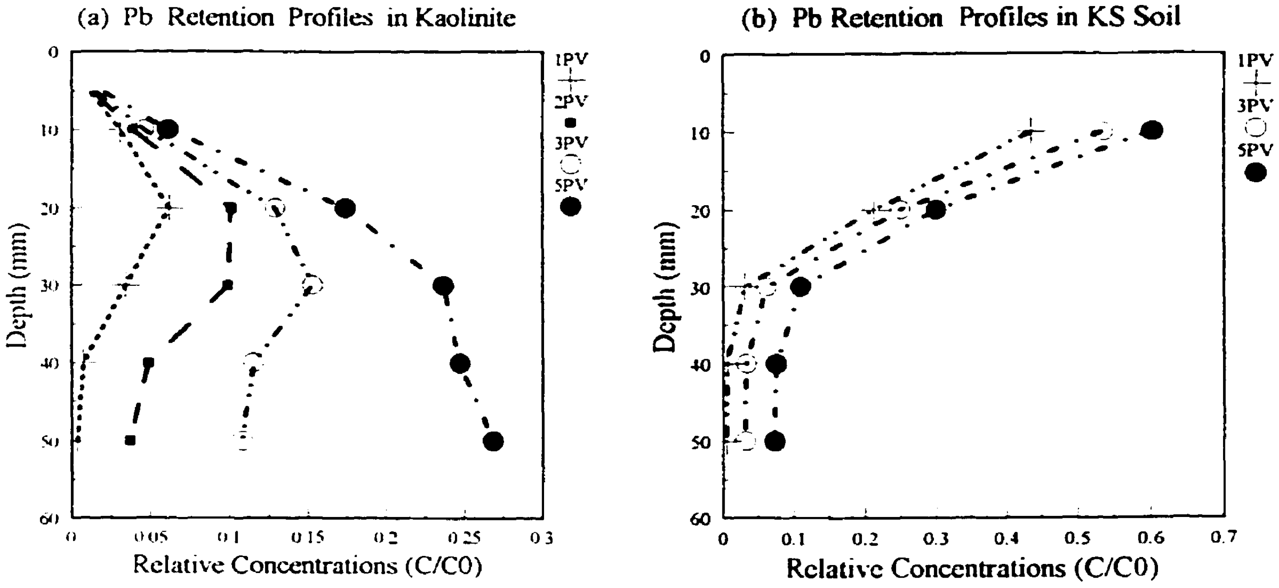
The experimental adsorption profiles of lead and zinc at 1PV, 2PV, 3PV and 5PV for kaolinite clay and kaolinite mixtures (KS, KC, KSC) are shown in Figures 5.9a, 5.9b, 5.9c, 5.9d, 5.10a, 5.10b, 5.10c and 5.10d, respectively. The kaolinite, which has a very low CEC and SSA, and does not have any significant amount of soil constituent, apparent from its clay mineral, results in the lowest retention of both heavy metals compared to the three other soils, as shown in Figures 5.9a and 5.10a for lead and zinc , respectively.

The retention increases with time and space until migrated heavy metal in each slice reaches to steady state in which the adsorption is maximum. Very little Pb and only a little Zn were adsorbed at the mid and bottom slices of the kaolinite mixtures soils since most of the lead and zinc was retained in the top slices. Retention of Pb appears to be greater than Zn by the four different soils. Macroscopically, the tendency of an ion to be sorbed is dependent on its concentration in the aqueous phase relative to the concentrations of other sorbable ions, the selectivity of the sorptive substrate for an ion relative to other ions, and the number of sites on the sorptive substrate.

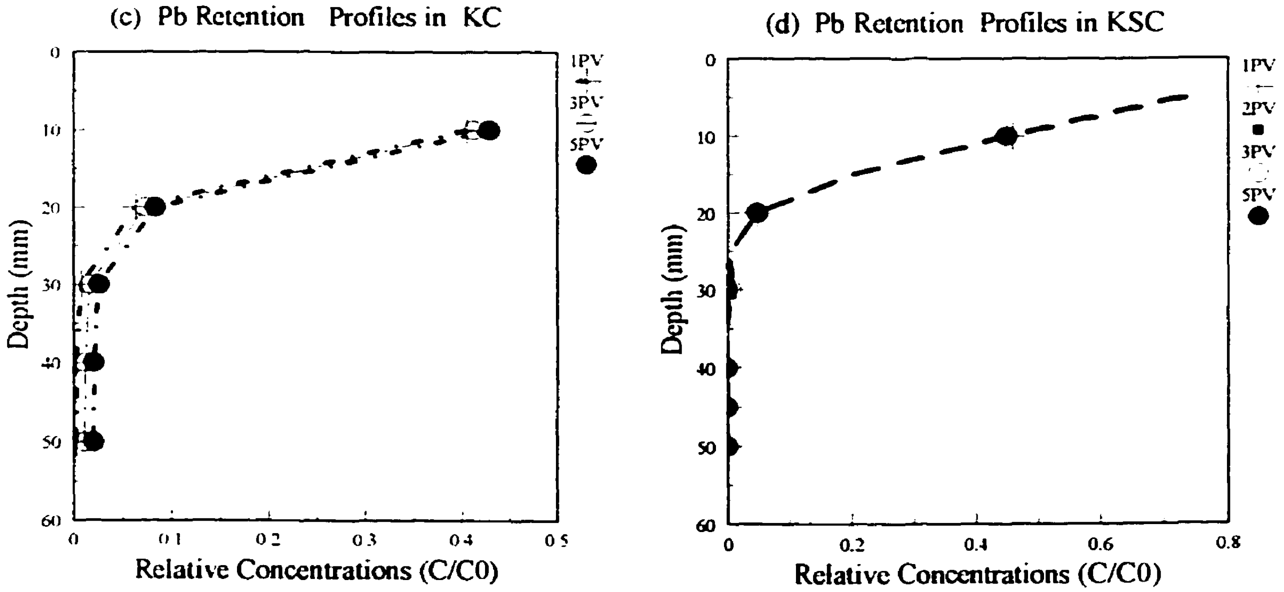
It can be seen from Figures 5.9a-d to 5.10a-d that the quantities of Pb and Zn adsorbed by the compacted clay samples are always less than quantities which characterize the adsorption isotherm of the material measured through the batch equilibrium test described in Chapter 4, using the same concentration of the each heavy metal. The differences in Pb and Zn retention are due primarily to the availability of exposed clay particle surfaces. This reasoning argues that, in soil suspensions, where all dispersed clay particles can contact the dissolved contaminant, accumulation processes are at optimum.

In the case of compacted materials, however, aggregate and cluster formation will considerably decrease the effective specific surface area, thus severely reducing adsorption. The permeant fluid will preferably flow around rather through the clay structures. The results of adsorption characteristics of compacted clay can cast doubt on the validity of the adsorption isotherm as a tool for contaminant transport models. In this fashion, the adsorption phenomena taking place in an actual situation is more realistically reproduced.

However, as these figures show, all of the heavy metals are retained in the kaolinite soil by adsorption rather than precipitation due to its low soil solution pH. Most of the heavy metals are retained in carbonated soil by precipitation (KC and KSC), which cannot be distinguished from the experimental results (Yong, and Macdonald, 1997). It is not possible to compute either the adsorption or the precipitation profiles by the $K_d$ approach (Darban *et al.*, 1997).


(a) Pb Retention Profiles in Kaolinite

(b) Pb Retention Profiles in KS Soil

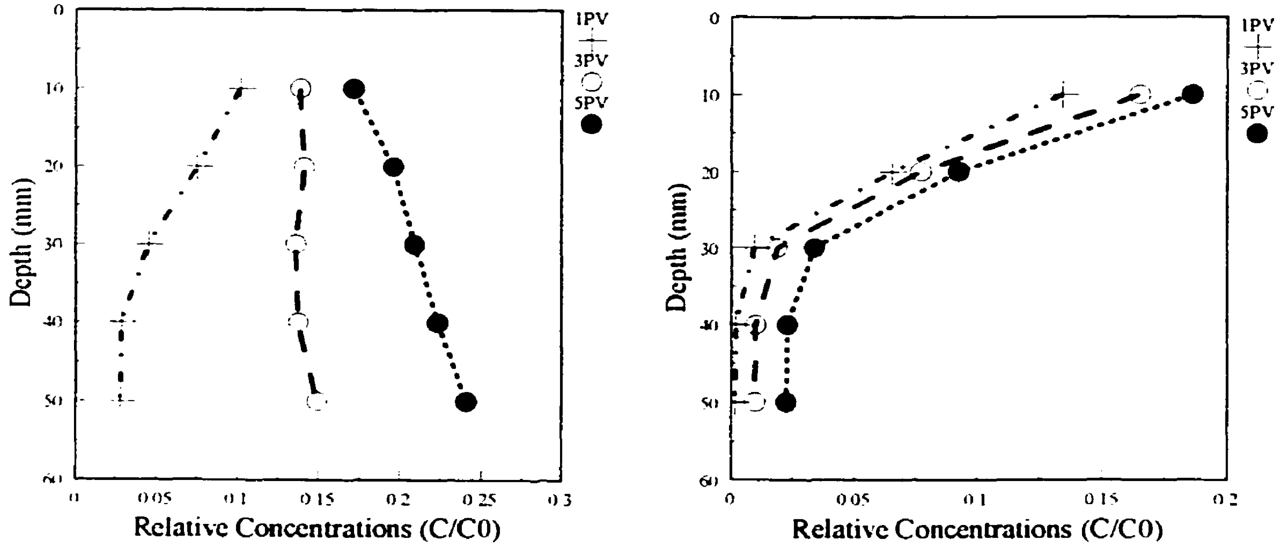

(c) Pb Retention Profiles in KC

(d) Pb Retention Profiles in KSC

**Fig 5.9** Pb Retention Profiles for Different Clay Soils.

(a) Zn Retention Profiles in Kaolinite

(b) Zn Retention Profiles in KS Soil



(c) Zn Retention Profiles in KC

(d) Zn Retention Profiles in KSC

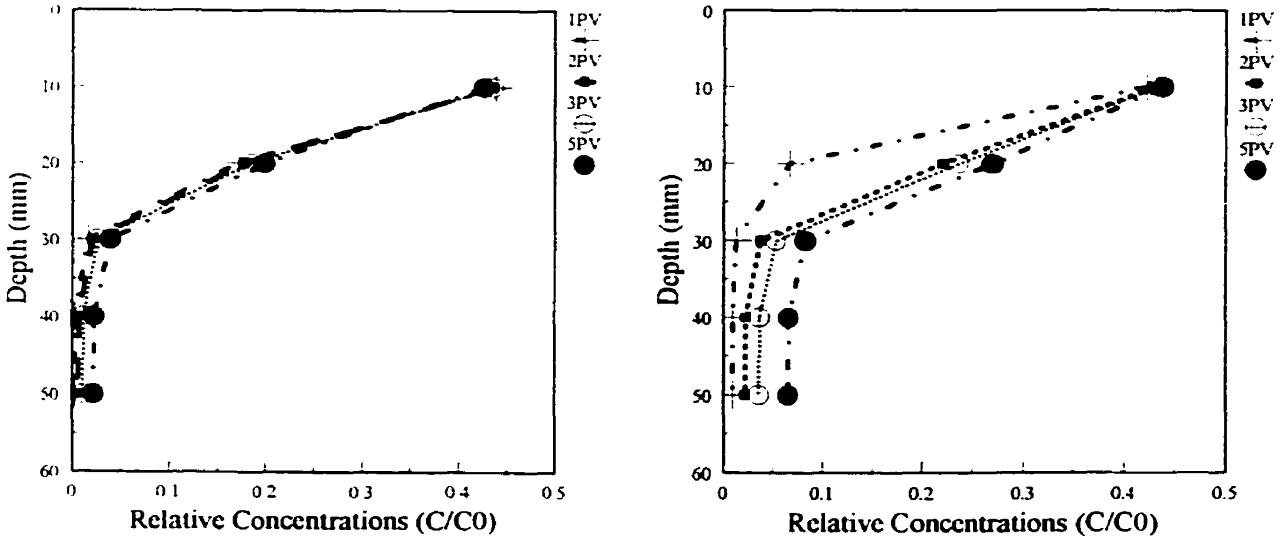


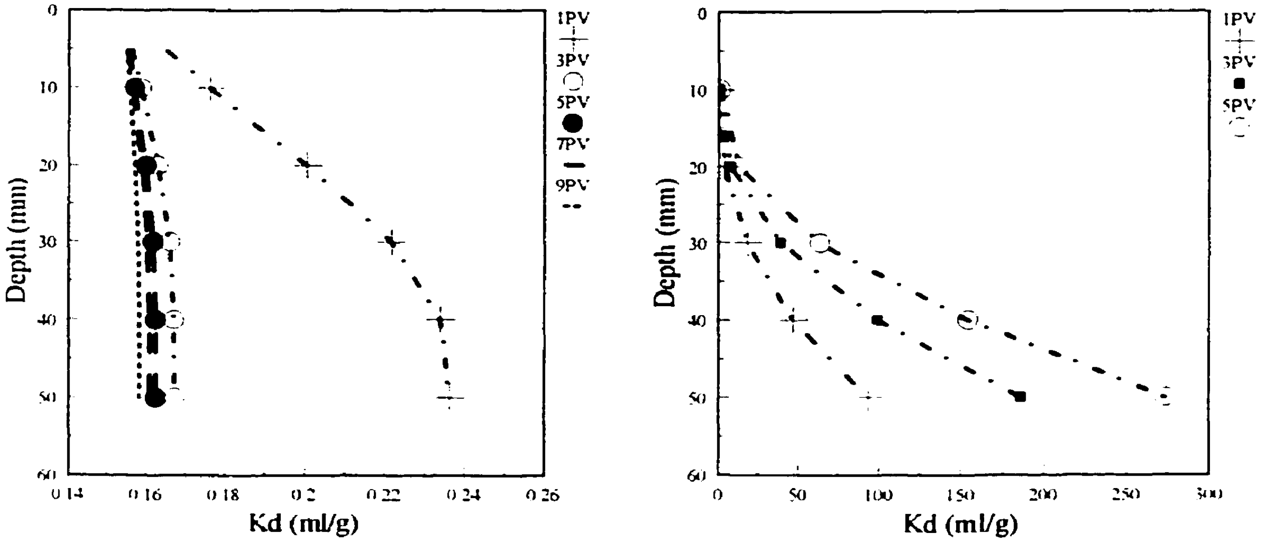
**Fig 5.10** Zn Retention Profiles for Different Clay Soils.

### 5.5.4 Partitioning Coefficient Profiles (Kd)

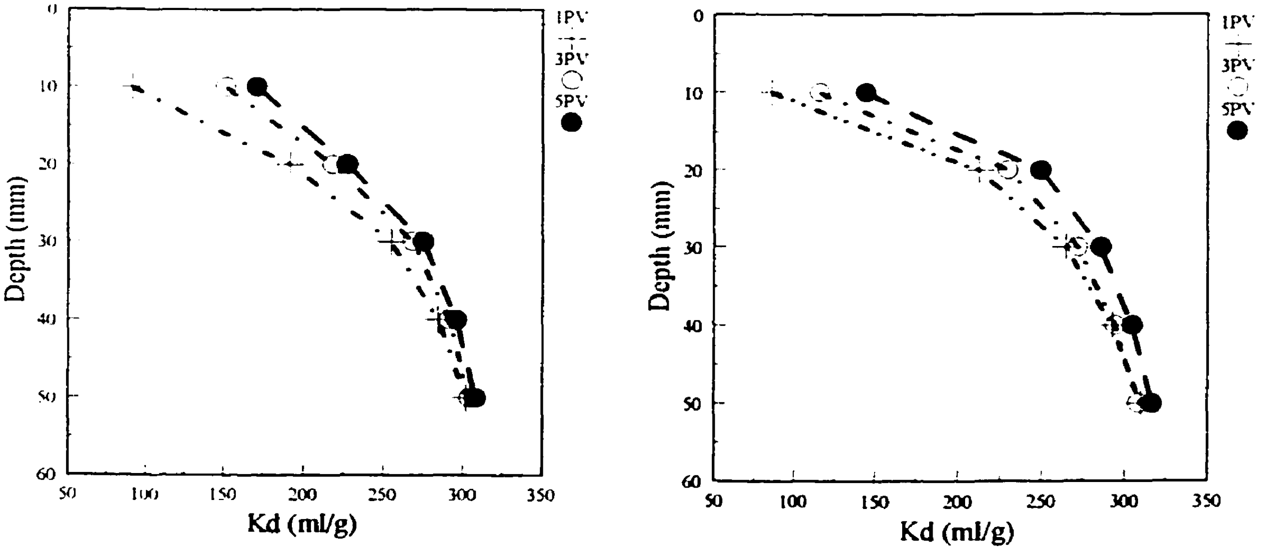
As was indicated in the introduction, most of contaminant transport models are based on a linear adsorption isotherm through batch equilibrium tests, and are most often not physically valid inasmuch as the ability of clay particles to adsorb solute ions decreases as the adsorbed amount of that solute ion increases-contrary to expectations from the linear model (Yong *et al.*, 1992b). The correct modelling of an adsorbate undergoing both transport and adsorption through a clay soil system necessitates the selection of an adsorption isotherm, or characteristic model, that best simulates the contaminant interaction. The adsorption isotherm, based on batch equilibrium tests (linear or non linear), is very far from the adsorption of the contaminant in the compacted clay in which less surface of adsorbate is exposed to contaminant and thus is expected to have less adsorption.

The Kd, representing the ratio of the adsorbed to dissolved heavy metal concentrations, is computed for each slice of the soil along the depth of the column and the results are illustrated as $K_d$ profiles in Figures 5.11a , 5.11b, 5.11c, 5.11d for lead and 5.12a, 5.12b, 5.12c, and 5.12d for zinc.

As shown in these figures, $K_d$ is dependent on the type of soil, heavy metal, and varies with time and space. In the case of kaolinite shown in Figure 5.12a and 5.13a, there is a relative drop in Pb and Zn partitioning coefficients, Kd, at the top with increasing pore volumes and it reaches to its steady state at 5 pore volumes. In the case of kaolinite mixtures (KS, KSC and KC) shown in Figure 5.11c, 5.11d, 5.12c and 5.12d, Zn and Pb partitioning coefficients were less affected by increasing pore volumes due to the precipitation of lead and zinc and higher buffer capacity of the kaolinite mixtures. It can be seen from Figures 5.11a-d to 5. 12a-d that the partitioning coefficients of Pb and Zn adsorbed by the compacted clay samples are always less than quantities which characterize the adsorption isotherm of the material measured through the batch equilibrium test, using the same concentration of the each heavy metal. The differences in Pb and Zn partitioning coefficients are due primarily to availability of exposed clay particle surfaces. In the above system since the chloride concentration and pH of the soil solution changes along the depth of the soil column and for each pore volume of effluent, as depicted in Section 5.3.1, the adsorption of the heavy metals by clay soil is changed and thus a different $K_d$ is expected. The $K_d$ increases with depth because at the top the Cl concentration is higher and the pH of the soil solution is lower, which resulted in the lower the degree of heavy metals adsorption, thus the $K_d$ values are lower. It deceases with time because as more leachate passes through the column soil the adsorption of the heavy metals is reduced due to the saturation of the clay surface area.

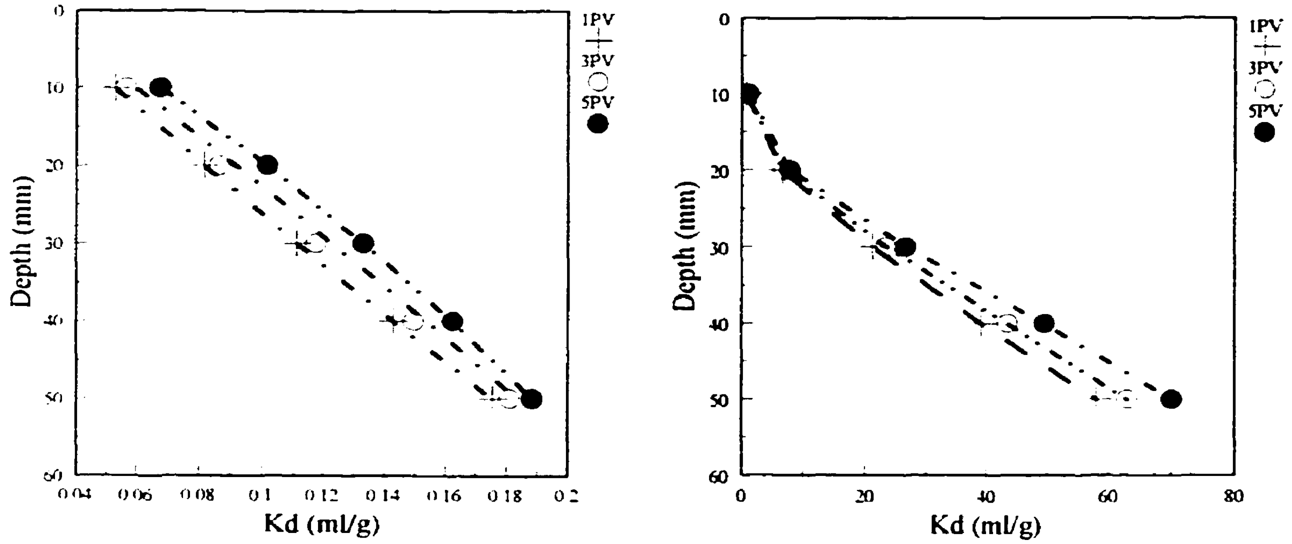

(a) Kd Profiles for Pb in Kaolinite

(b) Kd Profiles for Pb in KS


(c) Kd Profiles for Pb in KC

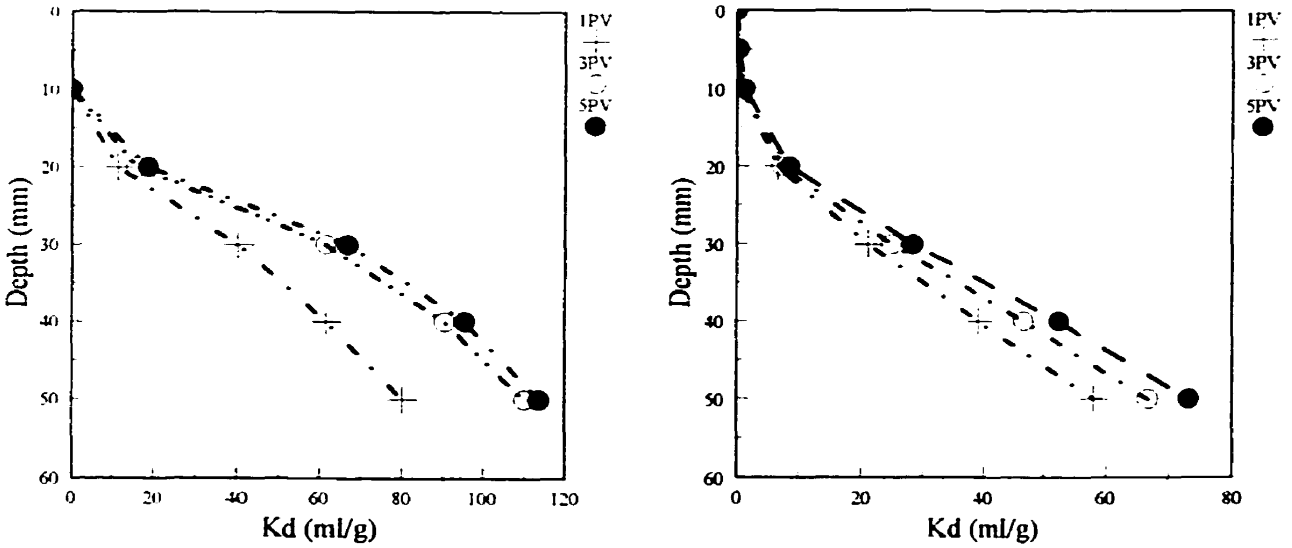
(d) Kd Profiles for Pb in KSC

**Fig. 5.11** Kd Profiles of Pb for Different Clay Soils.



(a) Kd Profiles for Zn in Kaolinite

(b) Kd Profiles for Zn in KS



(c) Kd Profiles in KC

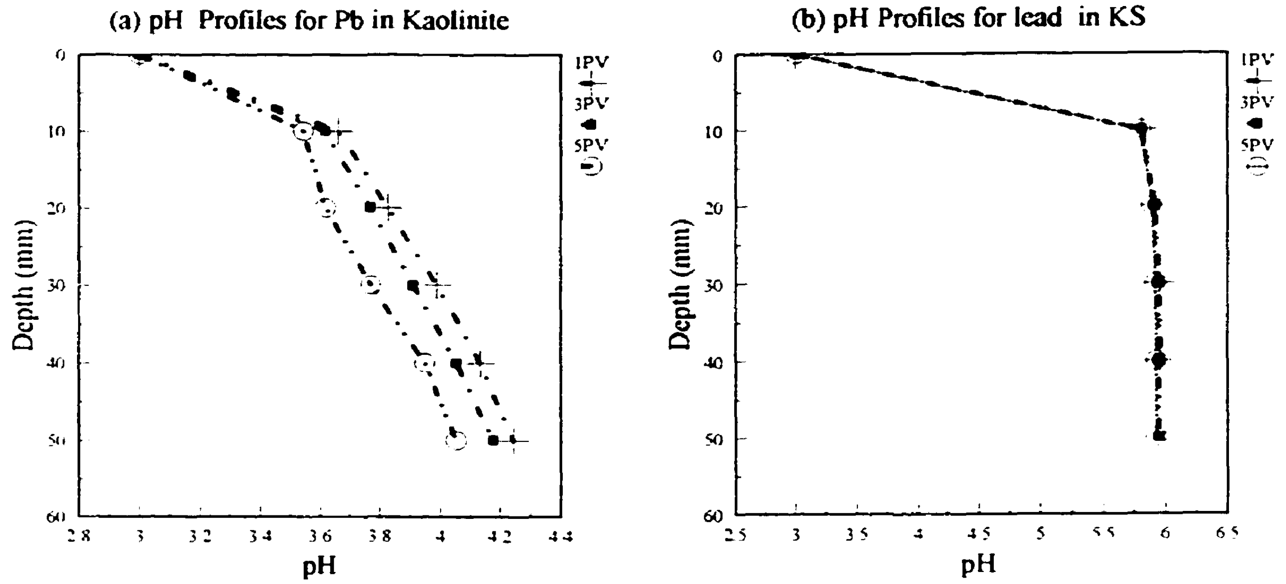
(d) Kd Profiles for Zn in KSC Soil

**Fig. 5.12** Kd Profiles of Zn for Different Clay Soils.

### 5.5.5 pH Profiles

The pH of the soil solution was measured at each pore volume, after which the recovered soil was sectioned into 10 slices and each slice was mixed with distilled water at a ratio of ½ and then allowed to reach equilibrium after being placed in a shaker. The pH profiles are illustrated in Figures 5.13 and 5.14. As shown, the pH of the soil solution varies with time and space. The pH is low at the top of the soil column due to the use of the acidic leachate and it increases with the depth and decreases as the more pore volumes of permeant passes through the clay. The kaolinite, which has a very low CEC and SSA, and does not have any significant amount of soil constituent, apparent from its clay mineral, results in the lowest pH values and least resistant to acidic input solution compared to three other soils. The addition of solutions with pH values below zero point of charge (ZPC) could result in the situation where the soil tends to deprotonate or surrender $H^-$ from its edges, thereby resulting in a reduction of the soil solution pH. Kaolinite has variable charge at the different pH levels with ZPC of 4.2 (Ohtsubo, 1994). The resulted pH is higher for lead than zinc in all types of the soils.

In the case of a kaolinite mixture with silica gel (KS), the clay soil has a very high CEC value and a pH of 6.2 has higher buffer capacity for the input solution at lower pH values. This is because silica gel has a ZPC of 2.1 (Fein, 1994). The KC soil, which has the highest carbonate content, results in the highest buffer capacity to the acidic input solution. The pH of the soil solution decreased with increase of leachate transport in the column. As shown in Figures 5.13c, 5.13d, 5.14c and 5.14d, the pH of the carbonate soil (KC, KSC) remains constant at least for the range of the experiment. The pH will be close to the pH of the leachate solution for large pore volumes of the effluent. Since the measured distribution coefficient, $K_d$, in the batch equilibrium test is based on constant pH, it will not represent the actual $K_d$ in the compacted clay barrier.



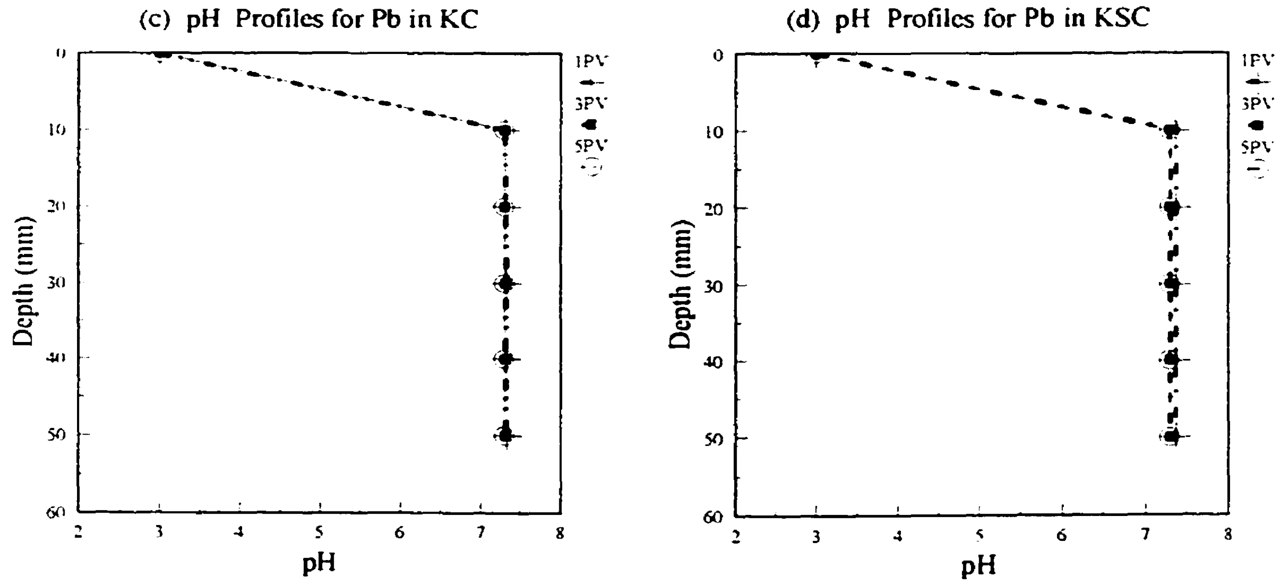
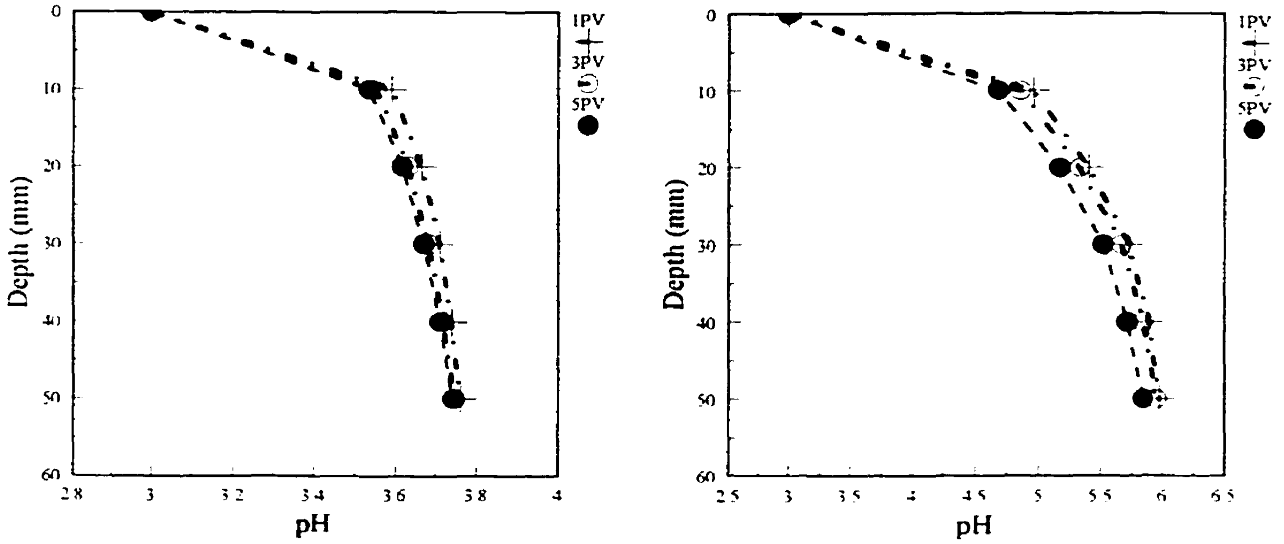
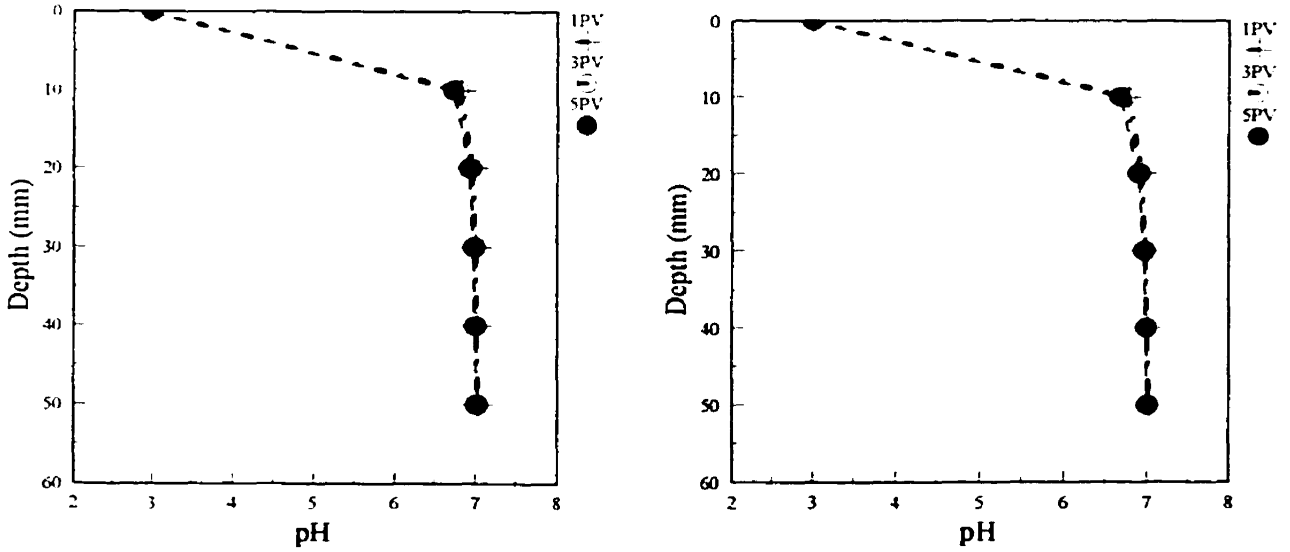


**Fig. 5.13** pH Profiles of Pb for Different Clay Soils.



(a) pH Profiles for Zn in Kaolinite

(b) pH Profiles for Zn in KS



Calculated pH Profiles for Zn in KC

(d) pH Profiles for Zn in KSC

**Fig. 5.14** pH Profiles of Zn for Different Clay Soils.

## 5.6 Model Calibration

The above experimental results were used for the calibration of the proposed model. Most of the existing transport models assume that the calculated diffusion coefficients represent average values throughout the length of the soil column, for the various individual contaminant constituents. Also, as was indicated in the introduction, existing contaminant transport models, are based on an adsorption isotherm where physico-chemical interactions are different from the adsorption of the contaminant in the compacted clay. If one recognizes that the interactions established between the contaminant and the soil cause continuous alteration in the transmissibility characteristics of the soil, the procedure which uses the constant diffusion coefficient can only provide average values since the values of C are obtained at the outlet end of the test sample. These values can be used with some certainty for cations such as Na and Ca which may reach their breakthrough concentrations at few pore volumes. However, for heavy metals which mostly will be retained in the clay these values are not applicable. Thus, whereas a representative diffusion coefficient should be calculated for individual layers in the soil column, and for each pore volume passage of effluent, so long as only outlet values of concentration are the only set of values obtained, we cannot calculate the different values of D with depth (length of the soil sample) and with the number of pore volumes of passage of leachate.

To compute the transport parameter, considering the adsorption effect, for the transient state, which is the case of heavy metals transport, and to calibrate the COSTCHESP model, a computer code called Parameter Estimation Technique (PET) has been developed (Appendix G). The program uses two main procedures to compute the unknown material parameters a, b and $k_{ch}$. The first step is to set the initial condition, i.e. initial concentrations, and compute the predicted concentration profiles at a new time step, through the COSTCHESP program based on the initial guess value of material parameters. The second step is to keep revising the material parameters until the difference between experimental and theoretical concentration profiles is minimized (Devlin, 1994). In the program, the correlation coefficient, R, which indicates the relationship between measured and calculated concentration profiles, is computed through the following equation:

$$R=\sqrt{1-\frac{\sum_{i=1}^{n}[C_{Exp.}-C_{Cal.}]^2}{\sum_{i=1}^{n}[C_{exp.}-C_{Ave.}]^2}}$$

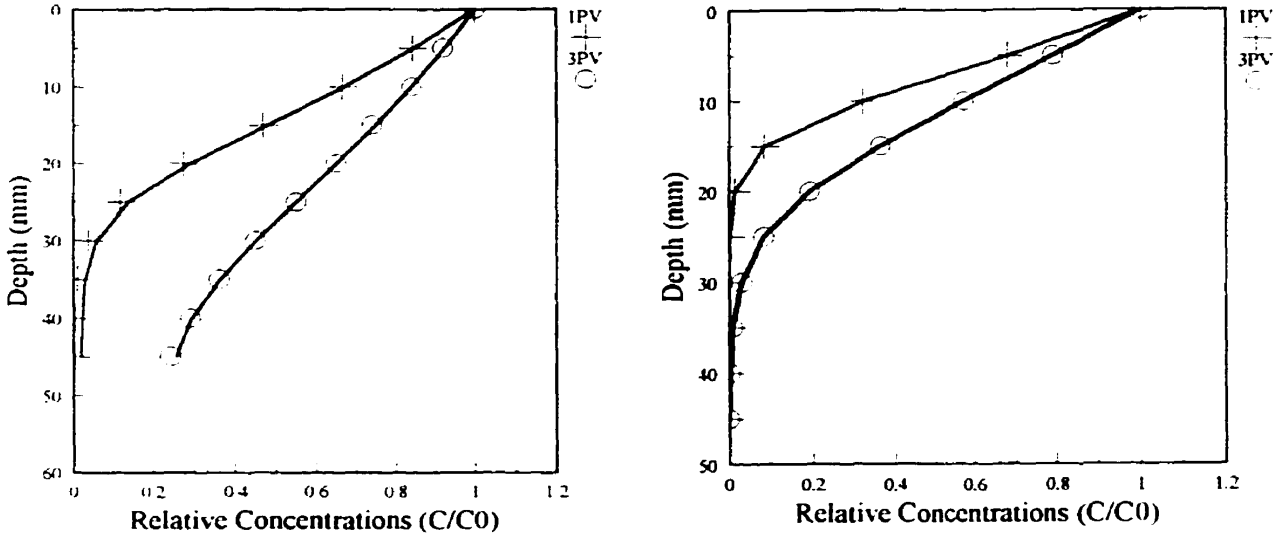
where $C_{ave}$ is an average of the measured concentration at each node for each pore volume. The PET program was used for the calculation of the diffusion parameter between 1PV and 3PV. The resulting diffusion and chemico-osmotic coefficients for lead and zinc for all types of clay soils (K, KS, KC, KSC) are tabulated in Table 5.1 and the calibrated results for the migration profiles of lead and zinc and the calculated diffusion coefficient profiles into kaolinite and kaolinite mixtures are shown in Figures 5.15a-d, 5.16a-d, 5.17a-d and 5.18a-d, respectively. The experimental results of total lead and zinc profiles for the first and third pore volumes were used for the calibration of the model. As shown, the diffusion coefficient is a function of time and space and dependent on soil constituents and its adsorption properties. The diffusion coefficient is maximum at the top of the column and minimum at the bottom. The diffusion coefficient is maximum for the kaolinite due to its low adsorption and the high hydraulic conductivity. The diffusion is lowest for KC due to its high adsorption properties. It was also shown that the diffusion coefficient increases with time and it reaches steady state. This means that diffusion coefficient may be assumed as a constant parameter for high pore volumes of the effluent, the condition which is not applicable to heavy metals transport.

Table 5.1 Resulting Diffusion and Chemico-Osmotic Coefficients from PET Program.

| **Soil Type** | **Ion** | **a ($cm^2$/day)** | **b (l/mmol)** | **$K_{ch}$ ( $cm^5$/g/day)** |
|---|---|---|---|---|
| Kaolinite | $Pb^{2-}$ | 0.1122 | 1819.16 | -10.171 |
| Kaolinite | $Zn^{2-}$ | 0.0810 | 1961.71 | -8.89 |
| KS | $Pb^{2-}$ | 0.1025 | 1411.26 | -8.81 |
| KS | $Zn^{2-}$ | 0.1325 | 1641.22 | -8.18 |
| KC | $Pb^{2+}$ | 0.1245 | 1376.17 | -8.28 |
| KC | $Zn^{2-}$ | 0.1323 | 1514.11 | -8.02 |
| KSC | $Pb^{2-}$ | 0.3231 | 1435.13 | -8.82 |
| KSC | $Zn^{2+}$ | 0.0810 | 1996.11 | -8.12 |

(a) Total Pb Profiles in Kaolinite

(b) Total Pb Profiles in KS



(c) Total Pb Profiles in KC

(d) Total Pb Profiles in KSC

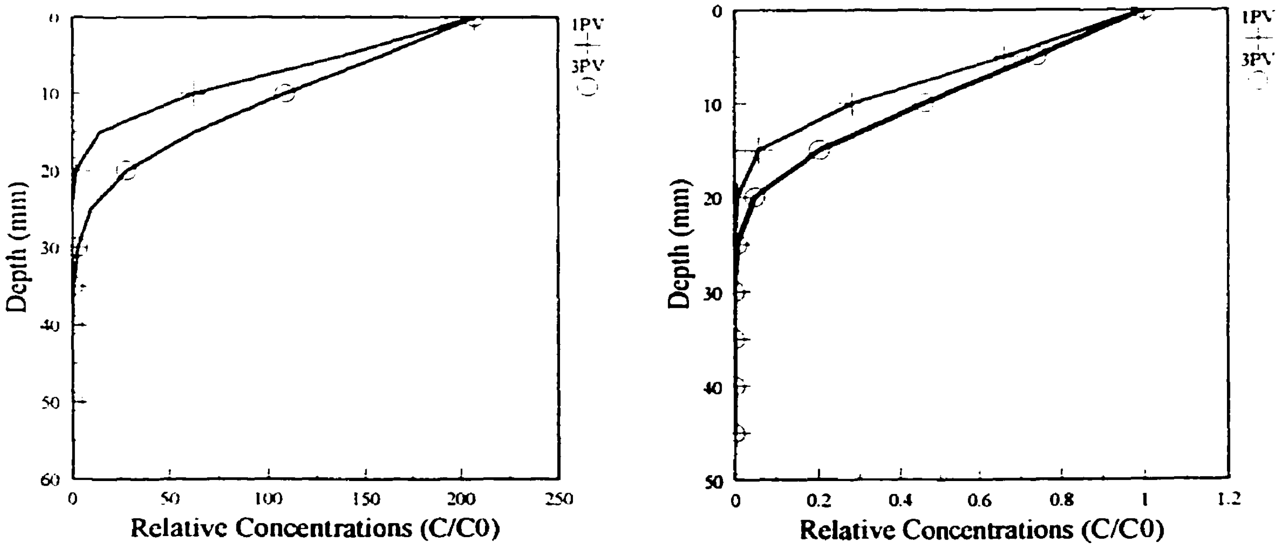


**Fig. 5.15** Calibrated Total Pb Profiles.

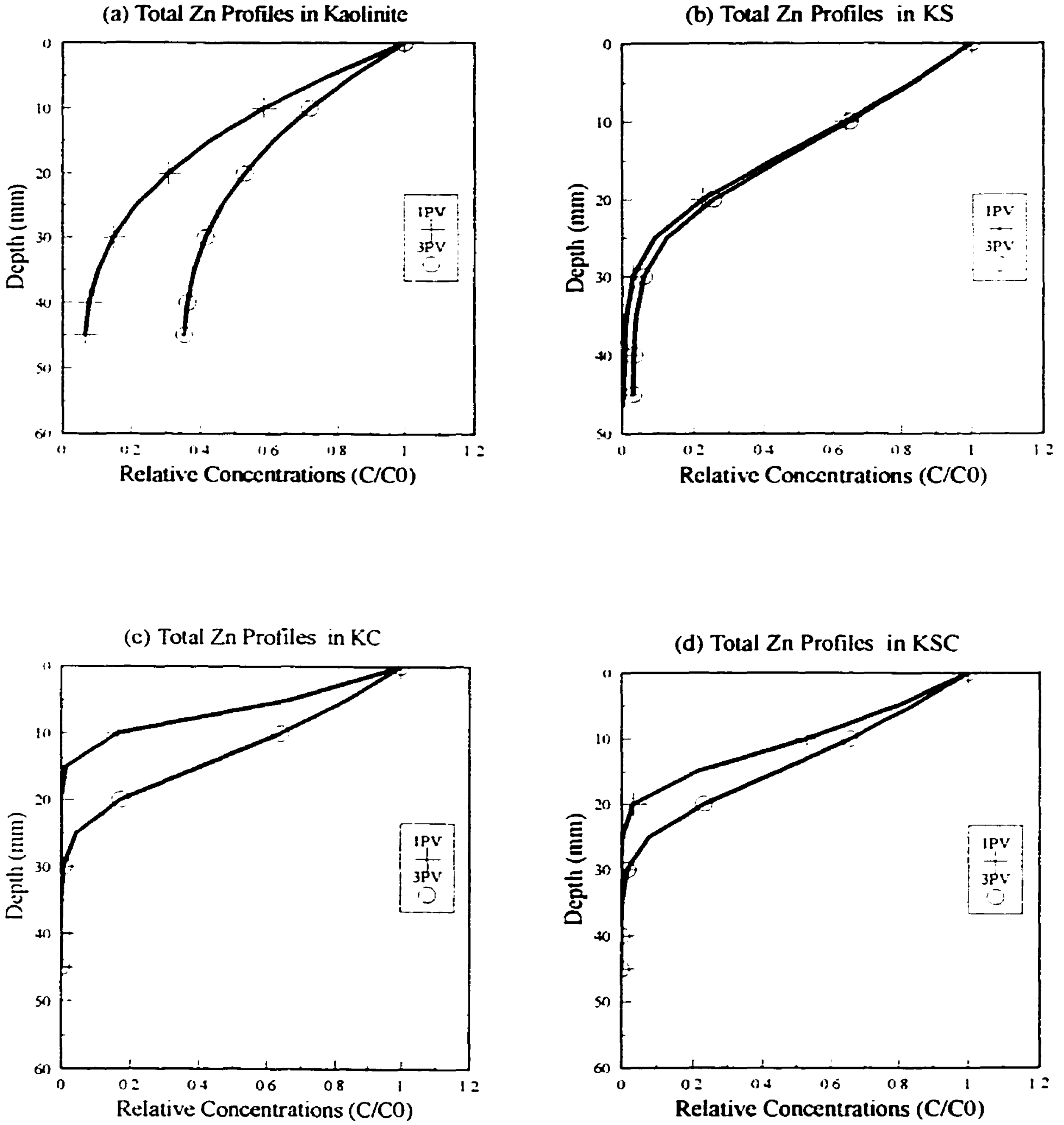
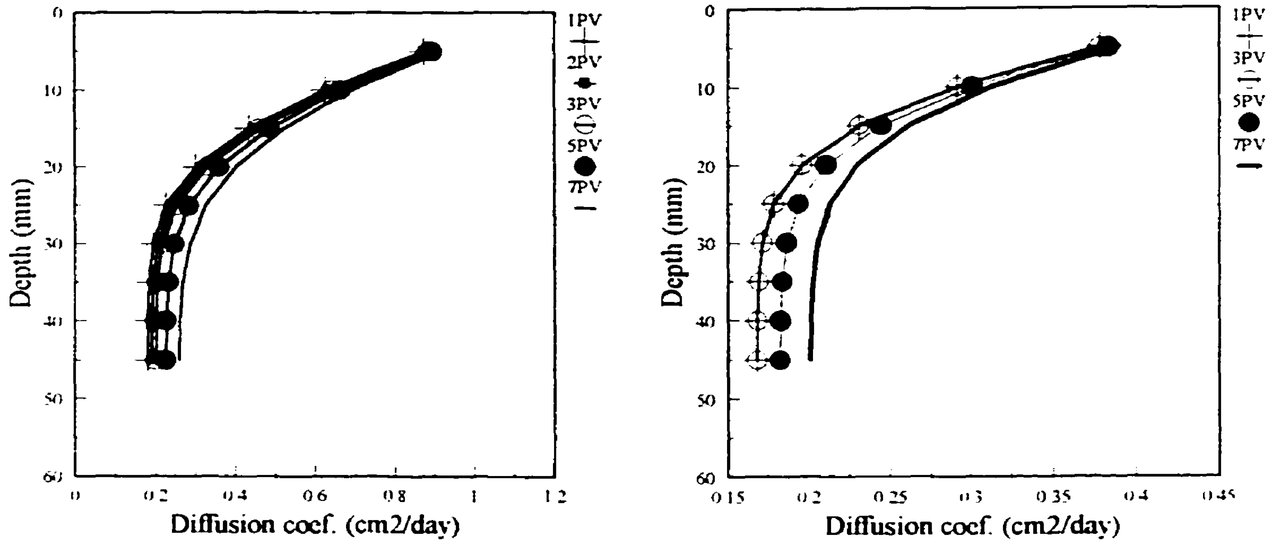


Fig. 5.16 Calibrated Total Zn Profiles.

(a) Pb Diffusion Profiles in Kaolinite

(b) Pb Diffusion Profiles in KS Soil



(c) Pb Diffusion Profiles in KC

(d) Pb Diffusion Profiles in KSC Clay

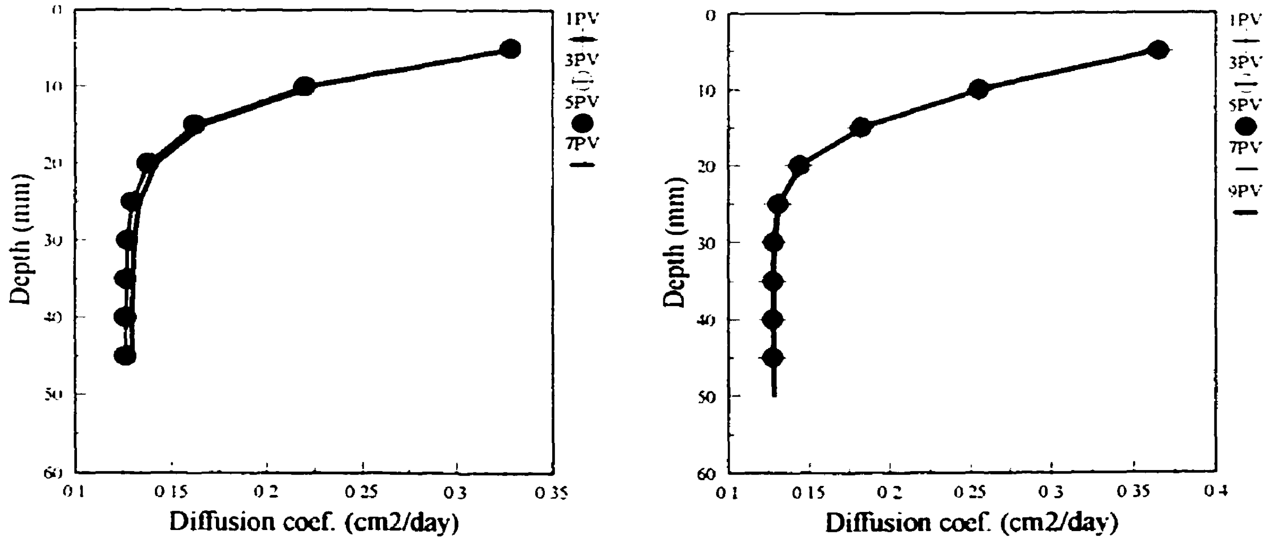
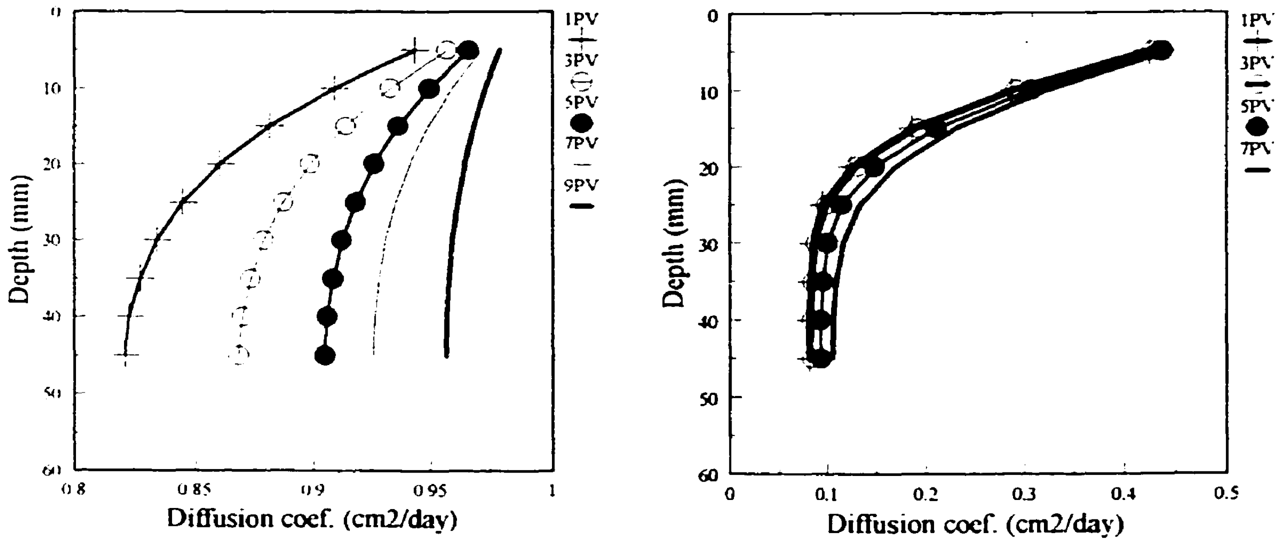
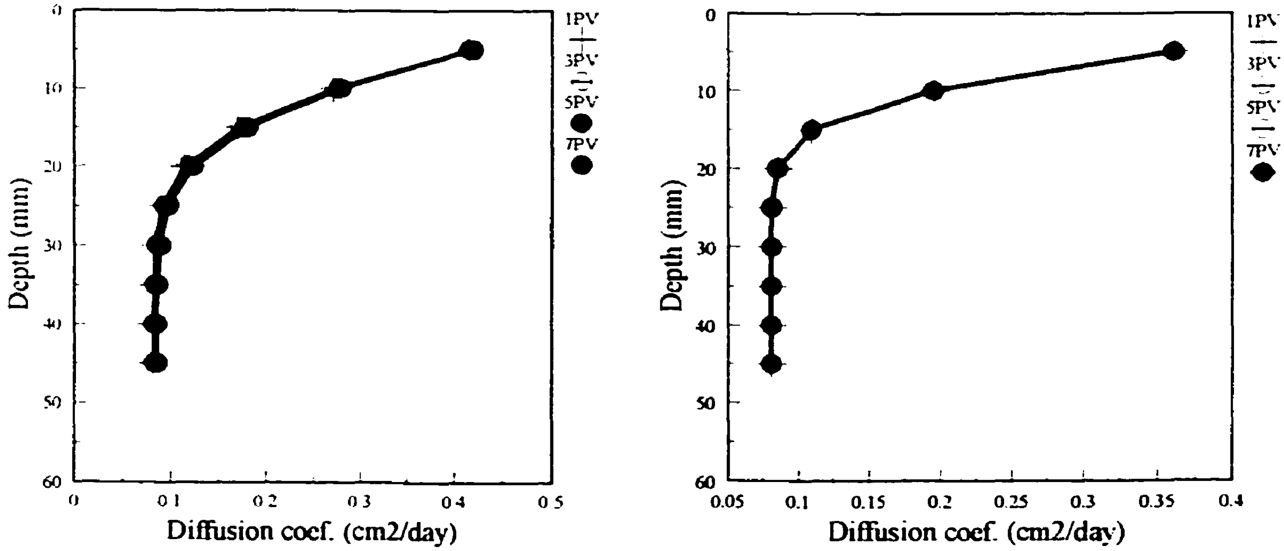


Fig 5.17 Pb Diffusion Profiles.



(a) Zn Diffusion Profiles in Kaolinite

(b) Zn Diffusion Profiles in KS



(C) Zn Diffusion Profiles in KC

(d) Zn Diffusion Profiles in KSC

**Fig 5.18** Zn Diffusion Profiles.

## 5.7 Heavy Metals Prediction

To simulate the above experimental condition by the COSTCHESP, leachate constituent concentration for each component was specified in the CHESP. CEC and SSA were also chosen as the input of the CHESP. The adsorbed parameters were initially computed from the adsorption isotherm in the batch equilibrium test and then calibrated with column leaching test experiments. To simulate the leachate pH by the model as specified in the experiment, an initial concentration of 0.001 mol/L of hydrogen ion, representing a pH of 3.0 of the influent solution, is considered. For the solid part, an initial concentration of 0.1152 mol/L of kaolinite, 0.03 mol/L of $SiO_2$ and 0.05 mol/L of $CO_3Ca$ were assumed for each layer of soil (5 layer).

The COST inputs are basically, coefficient of permeability, depth of the clay liner, depth step and time step, and diffusion parameters. The boundary condition including the hydraulic head, initial total concentration of each component and background concentrations of each component along the soil column could be easily defined. It is clear that the background concentration of the heavy metals and other components except calcium, aluminium and silicic acid, and carbonate are zero. The background concentrations of the calcium, silicic acid and carbonate could be specified, or as a zero when it is specified in the solid part (Allisson *et al.*, 1993). The typical computer input for leaching lead or zinc in different clay soils can be found in Appendix D.

Using the above calculated transport parameters, long term total lead and zinc transported, migrated (dissolved), adsorbed, or precipitated profiles and their partitioning coefficient and pH profiles into different clay soils (K, KS, KC, KSC) were predicted by the COSTCHESP program and are demonstrated in Figures 5.19a-d to 5.30a-d, respectively. The results of precipitation profiles, illustrated in Figures 5.25b-d for lead into KS, KC and KSC soil, indicate that lead was not precipitated in kaolinite soil due to its low pH. Pure kaolinite also does not have any minerals which contribute to the precipitation of lead. The same reason could be true for the Zn precipitated profiles shown in Figures 5.26c- and 5.26d for KC and KSC soil. Also, Zn has higher solubility at higher pH than the lead.

It is not possible to compute either the adsorption or precipitation profiles from the

$K_d$ approach. As shown in Figures 5.19 and 5.20, zinc appeared after the second pore volumes and lead after the third pore volume of passage of leachate in the effluent for kaolinite clay due to the low affinity of kaolinite for heavy metals retention. Whereas, for kaolinite mixtures (KS, KC, KSC) very little Pb and a little Zn was adsorbed at the mid and bottom of the column. Zinc appeared in KS clay after three pore volumes of output and after 5 pore volumes for KSC and KC. Lead appeared, in KS soil, after 7 pore volumes of effluent and for KSC and KSC after 9 pore volumes. The equivalent $K_d$ was calculated by the program and as shown in Figures 5.27 and 5.28, demonstrates the variation of $K_d$ with time and space. As can be seen from the $K_d$ profiles, it decreases with time as more leachate is passed through the column soil. When soil will not adsorb any more lead or zinc, the partitioning coefficient will be equal to zero. From the results of the pH profiles shown in Figures 5.29 and 5.30, it may be concluded that the pH of the soil varies with time and space. The pH decreases as the pore volumes pass through the column and is lowest at the top part of the soil and highest at the bottom of the column. The pH of the soil column will reach to the influent pH when the soil buffer capacity is zero or there is no resistance from the soil to acidic pH.

Using the $K_d$ approach for the prediction of the heavy metals provides only the migration profiles, based on the batch equilibrium test at constant pH which is not the case in column leaching with variable pH. Figures 5.31a-d and Figure 5.32a-d demonstrate the predicted results of lead and zinc in different clay soils using average $K_d$ values computed through the compacted clay soils. Higher or lower $K_d$ values provide under or over estimates of the predicted results of lead and zinc concentrations. Nevertheless, using the average $K_d$ values computed through the column test may yield more reasonable values than isotherms constructed with soil suspensions. The present results raise some very interesting points about the widespread use of constant partitioning coefficients.

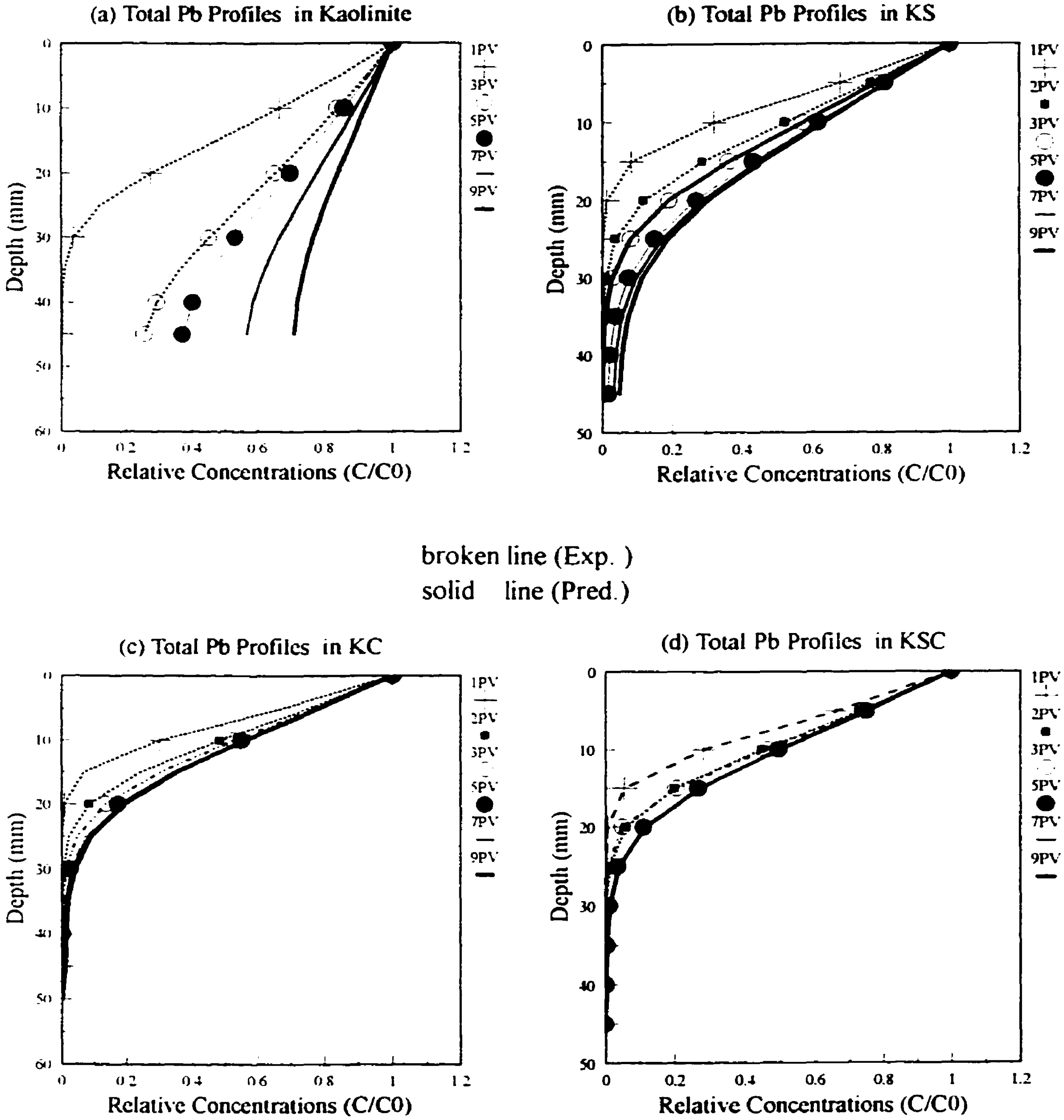
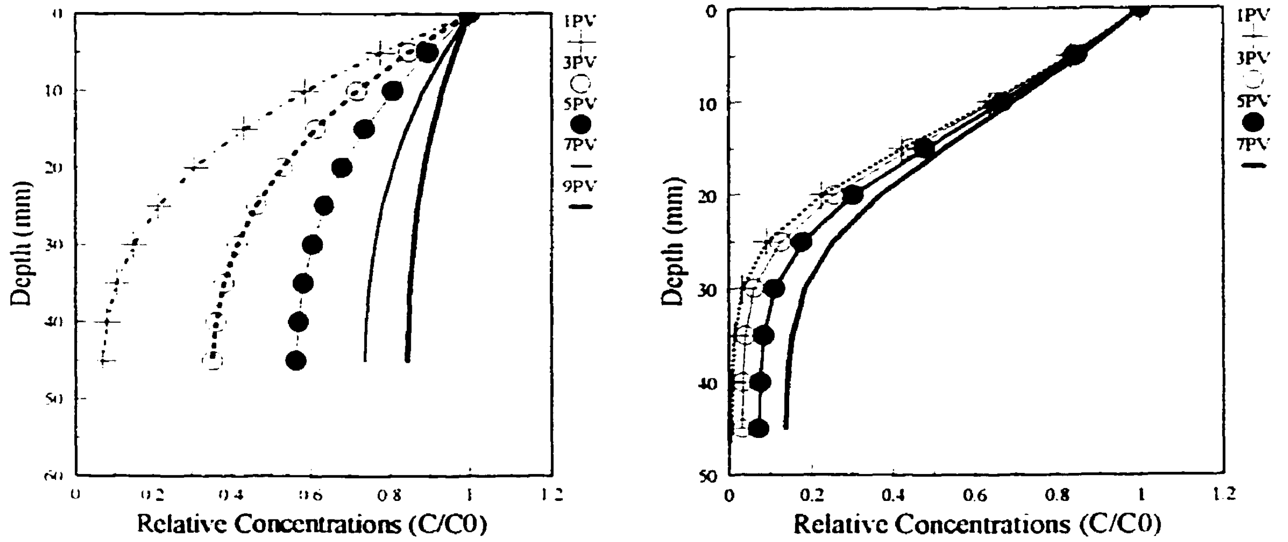


Fig. 5.19 Total Pb Profiles.

(a) Total Zn Profiles in Kaolinite

(b) Total Zn Profiles in KS



broken line (Exp. )
solid line (Pred.)

(c) Total Zn Profiles in KC

(d) Total Zn Profiles in KSC

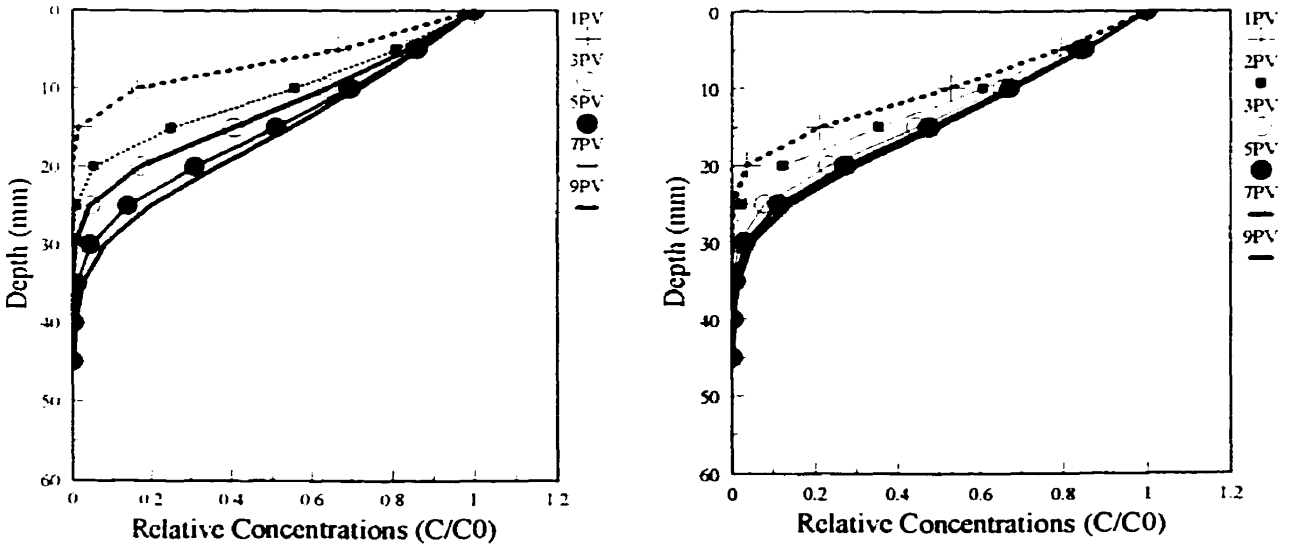
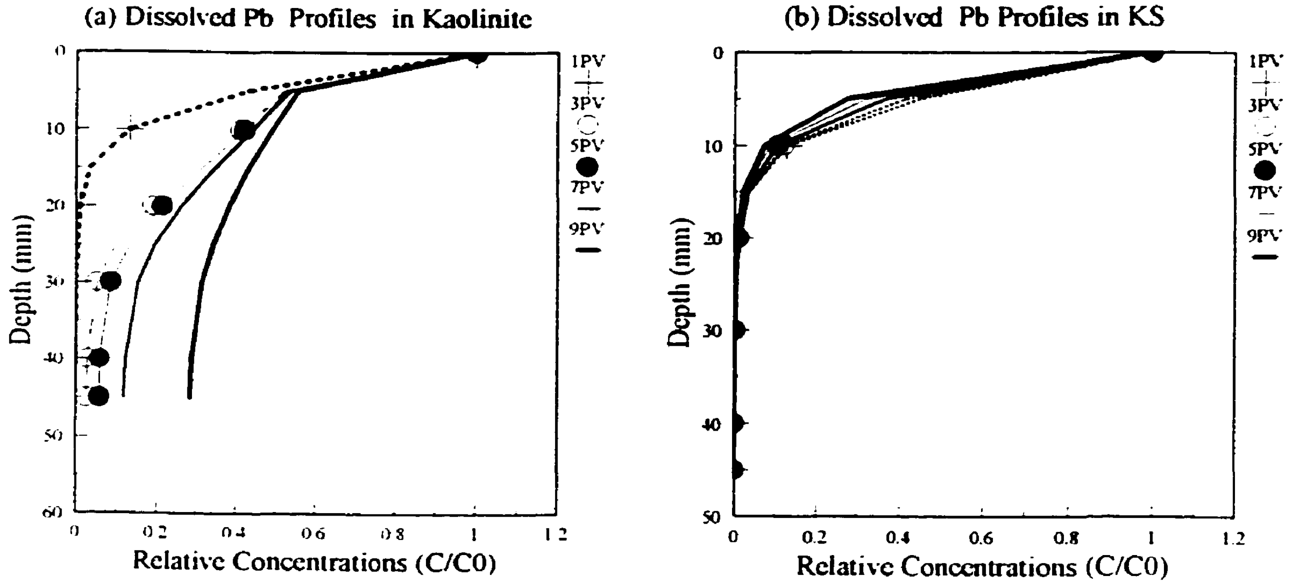
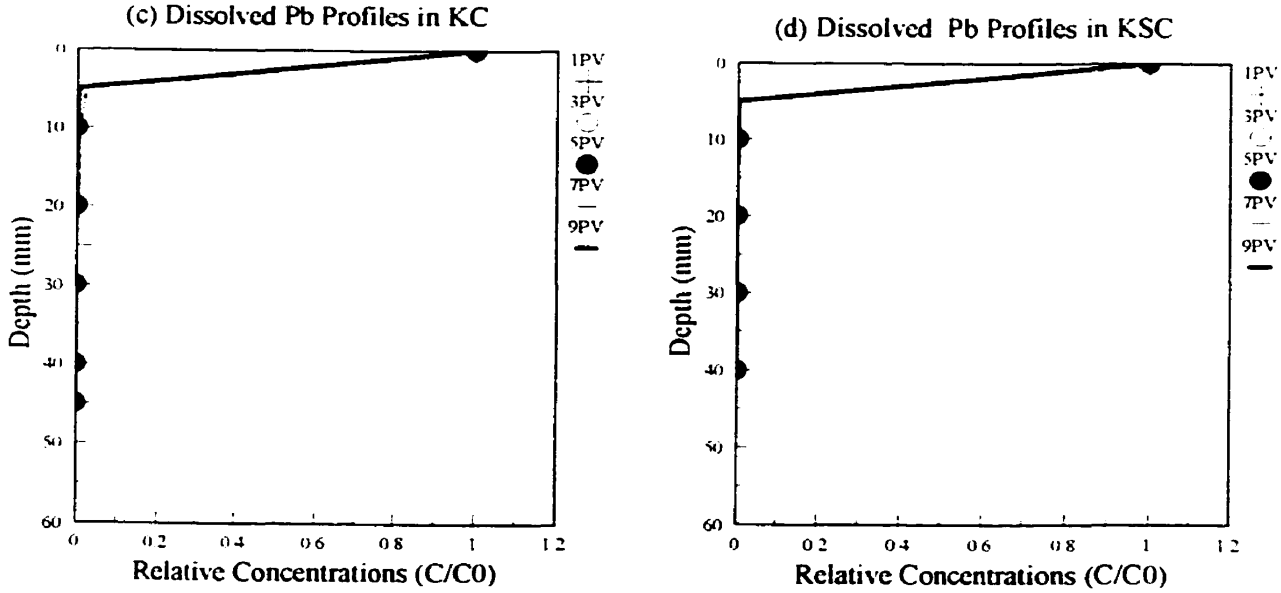


**Fig. 5.20** Total Zn Profiles.


(a) Dissolved Pb Profiles in Kaolinite

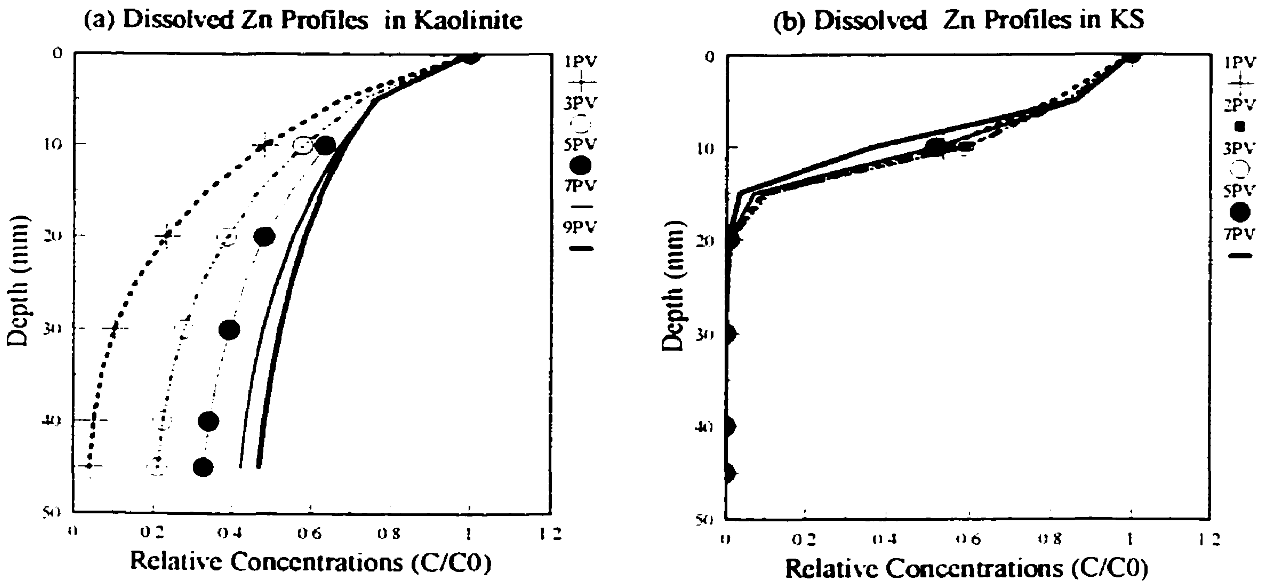
(b) Dissolved Pb Profiles in KS

broken line (Exp. )
solid line (Pred.)


(c) Dissolved Pb Profiles in KC

(d) Dissolved Pb Profiles in KSC

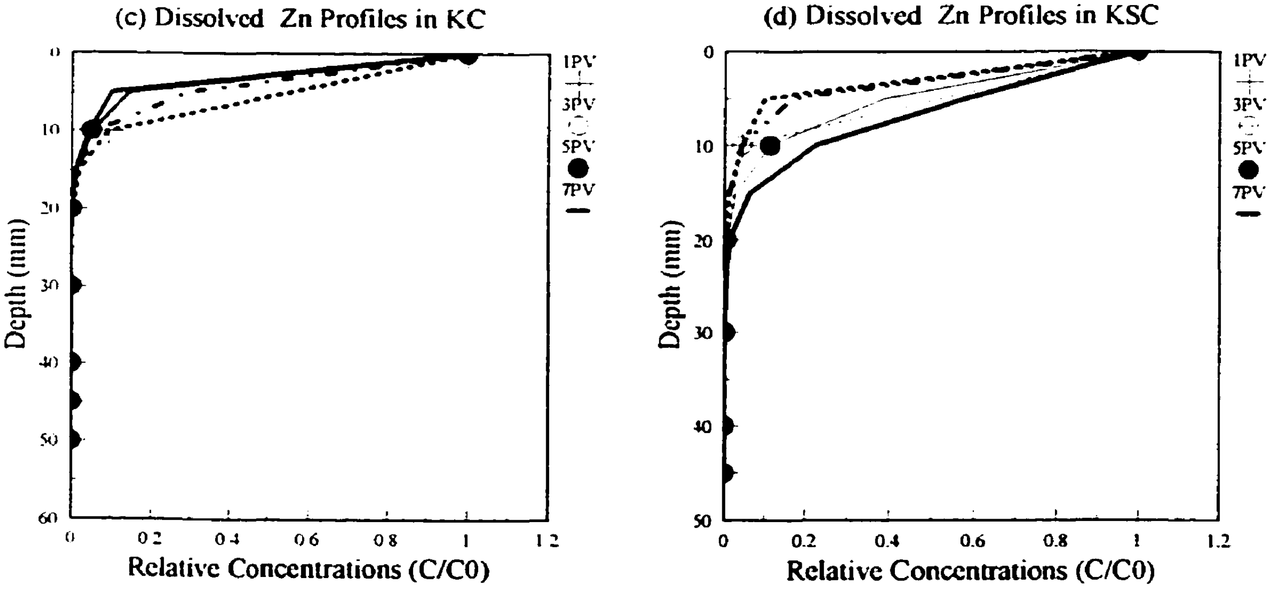
**Fig. 5.21** Pb Pore Fluid Profiles.



(a) Dissolved Zn Profiles in Kaolinite

(b) Dissolved Zn Profiles in KS

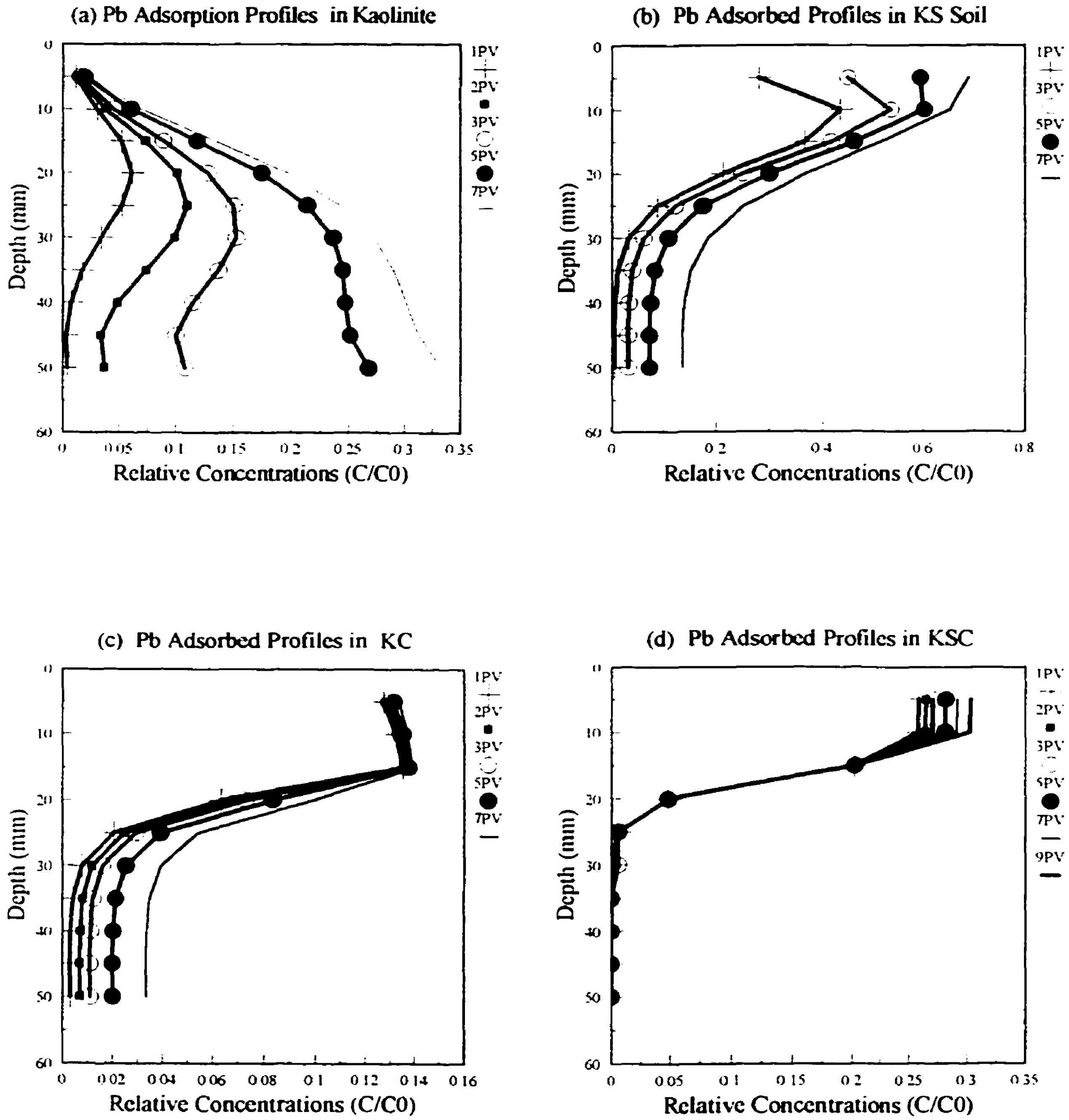
broken line (Exp. )
solid line (Pred.)



(c) Dissolved Zn Profiles in KC

(d) Dissolved Zn Profiles in KSC

Fig. 5.22 Zn Pore Fluid Profiles.



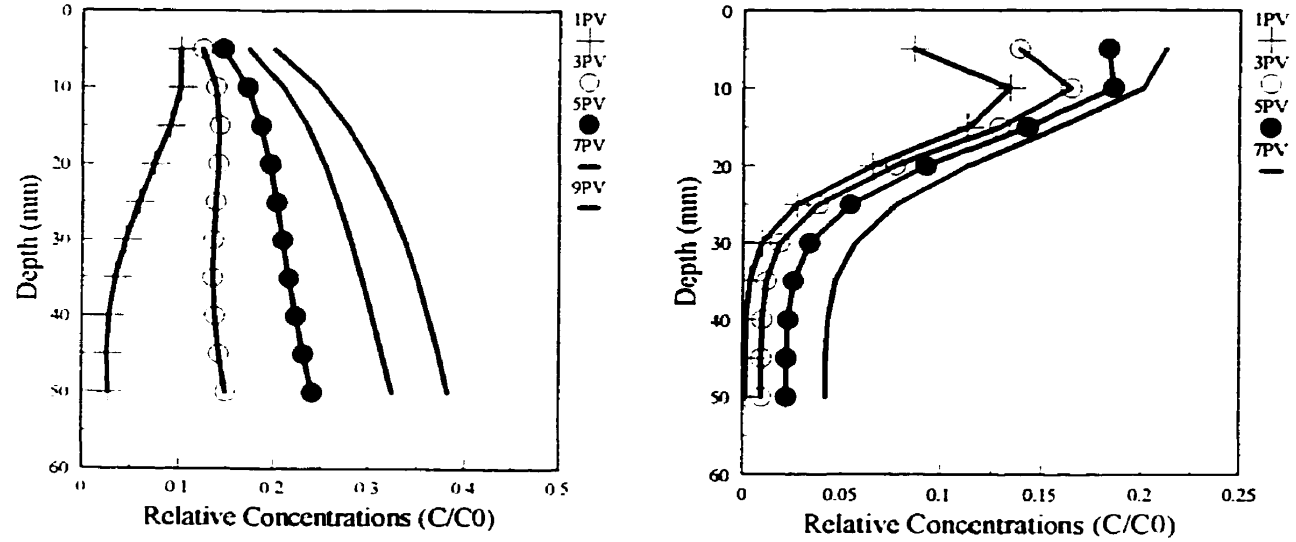
(a) Pb Adsorption Profiles in Kaolinite

(b) Pb Adsorbed Profiles in KS Soil

(c) Pb Adsorbed Profiles in KC

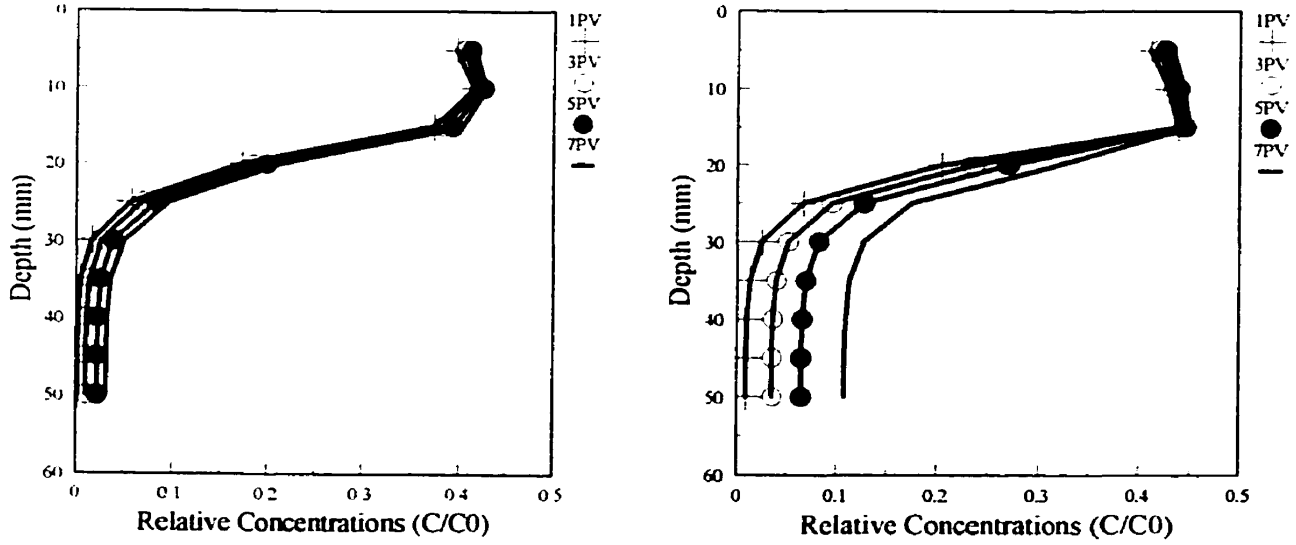
(d) Pb Adsorbed Profiles in KSC

**Fig. 5.23** Predicted Adsorbed Pb Profiles.



(a) Zn Adsorption Profiles in Kaolinite

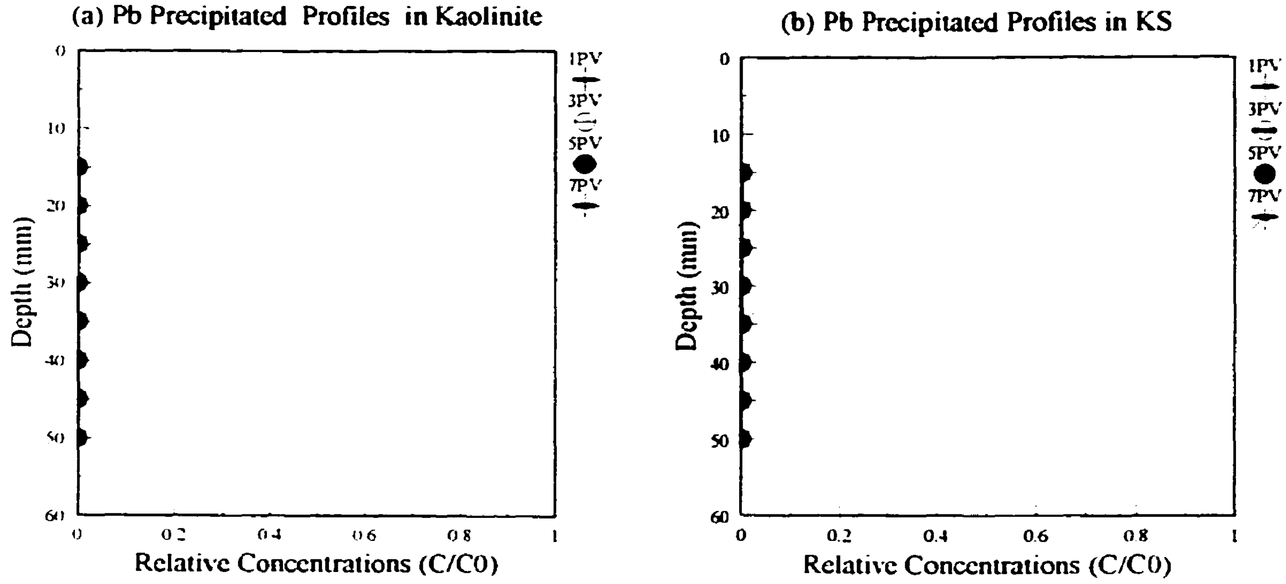
(b) Zn Adsorbed Profiles in KS Soil



(c) Zn Adsorbed Profiles in KC

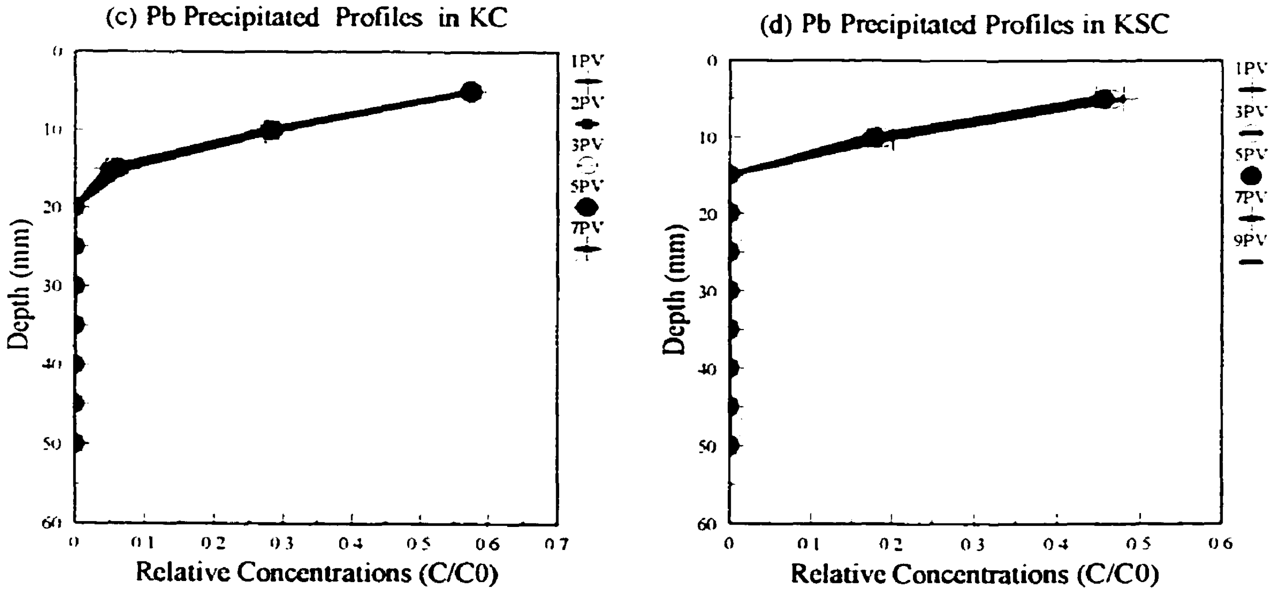
(d) Adsorbed Zn Profiles in KSC

Fig. 5.24 Predicted Adsorbed Zn Profiles.



(a) Pb Precipitated Profiles in Kaolinite

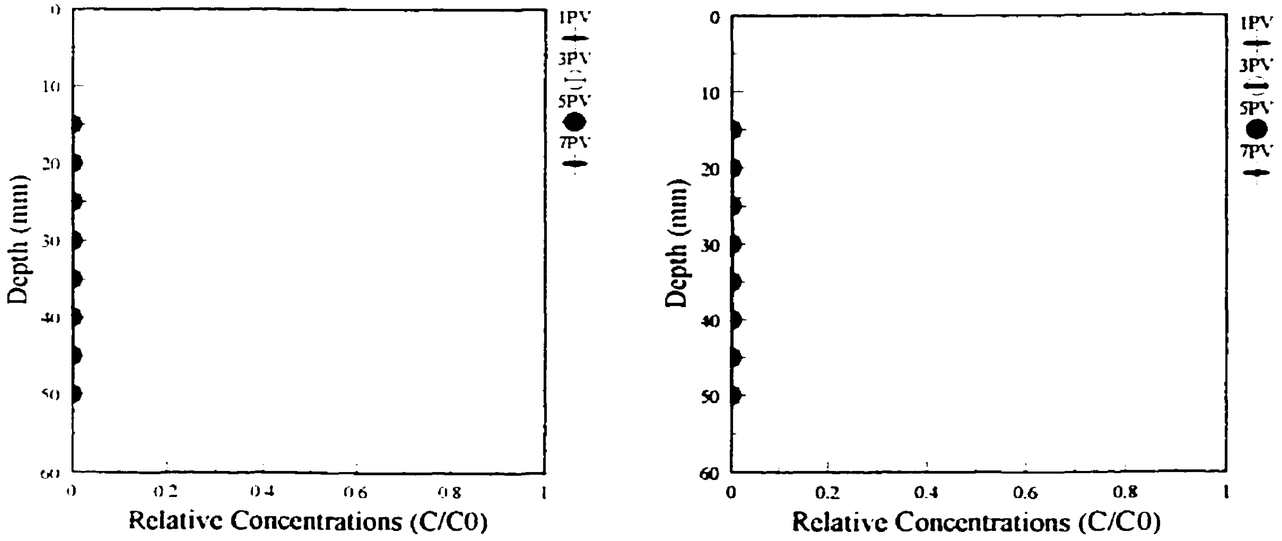
(b) Pb Precipitated Profiles in KS



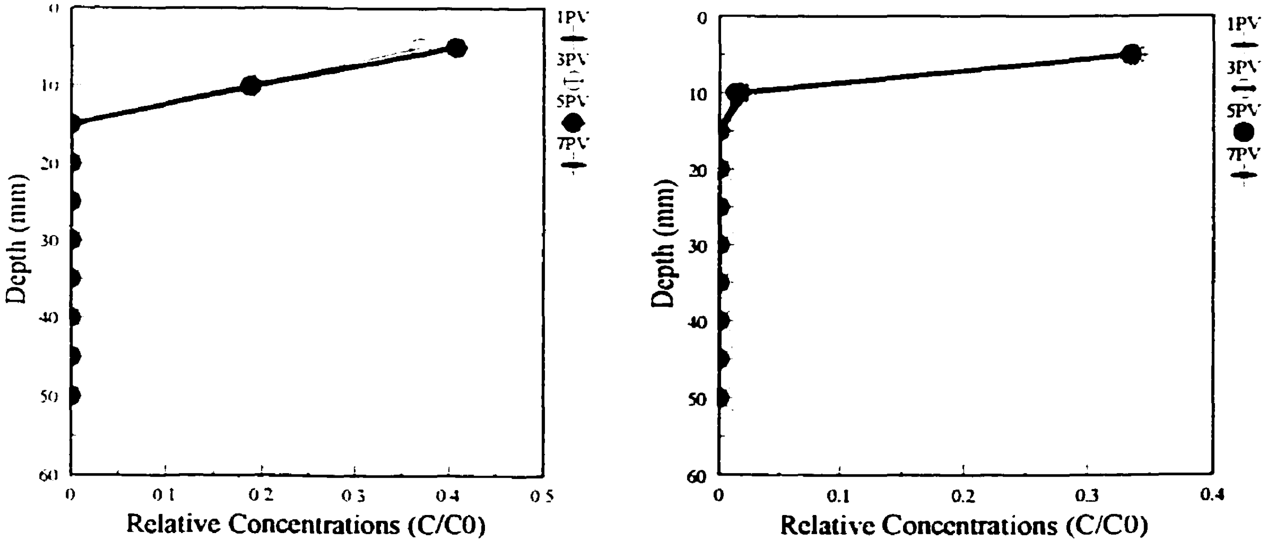
(c) Pb Precipitated Profiles in KC

(d) Pb Precipitated Profiles in KSC

**Fig. 5.25** Predicted Pb Precipitaed Profiles.


(a) Zn Precipitated Profiles in Kaolinite

(b) Zn Precipitated Profiles in KS


(c) Zn Precipitated Profiles in KC

(d) Zn Precipitated Profiles in KSC

**Fig 5.26** Zn Predicted Precipitaed Profiles.

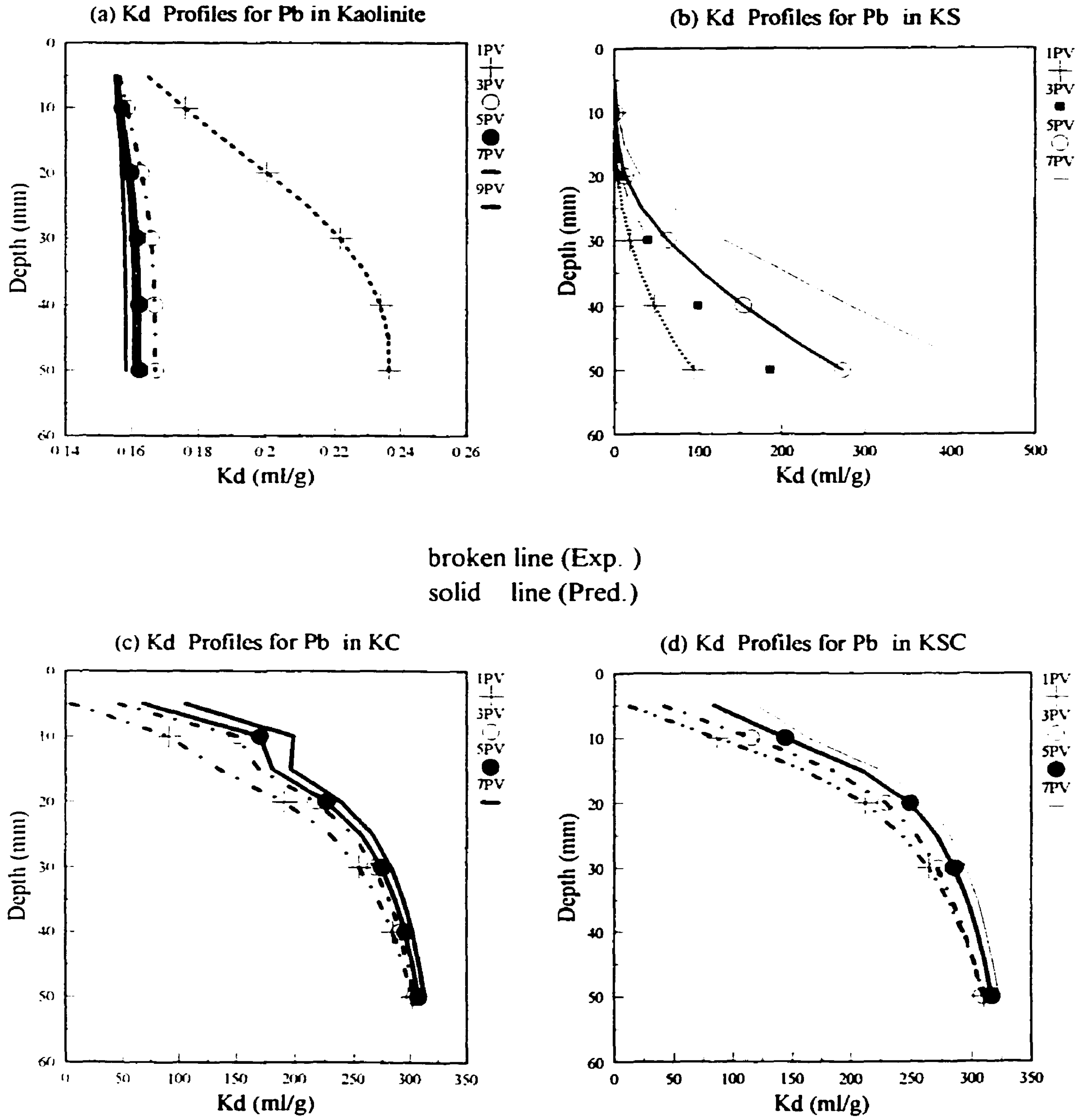
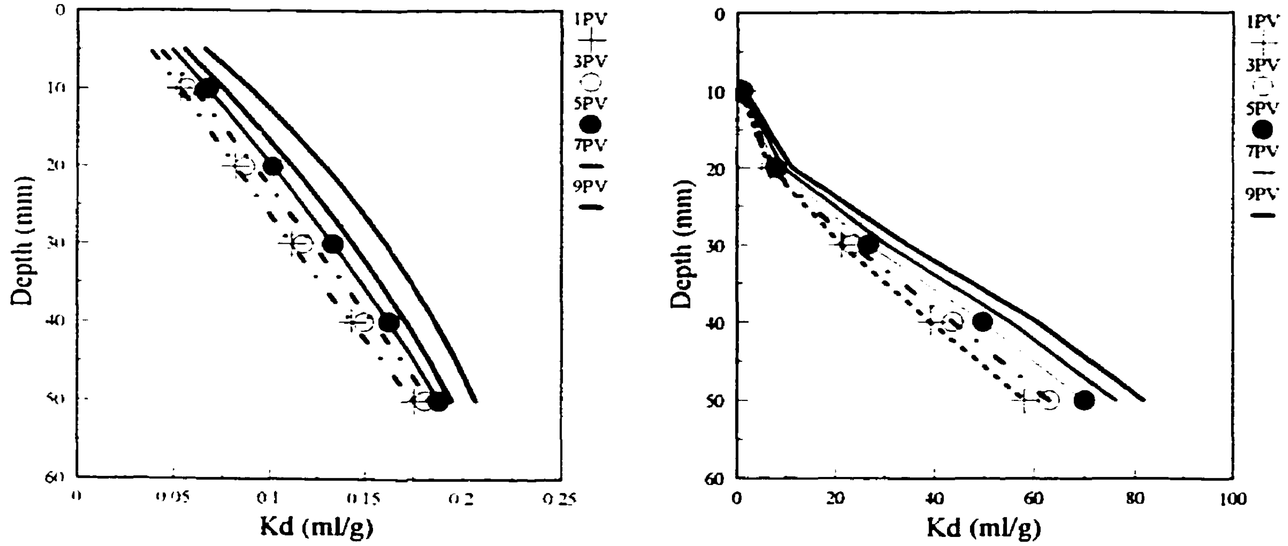


**Fig. 5.27** Kd Profiles for Lead.



(a) Kd Profiles for Zn in Kaolinite

(b) Kd Profiles for Zn in KS

broken line (Exp. )
solid line (Pred.)

(c) Kd Profiles in KC

(d) Kd Profiles for Zn in KSC Soil

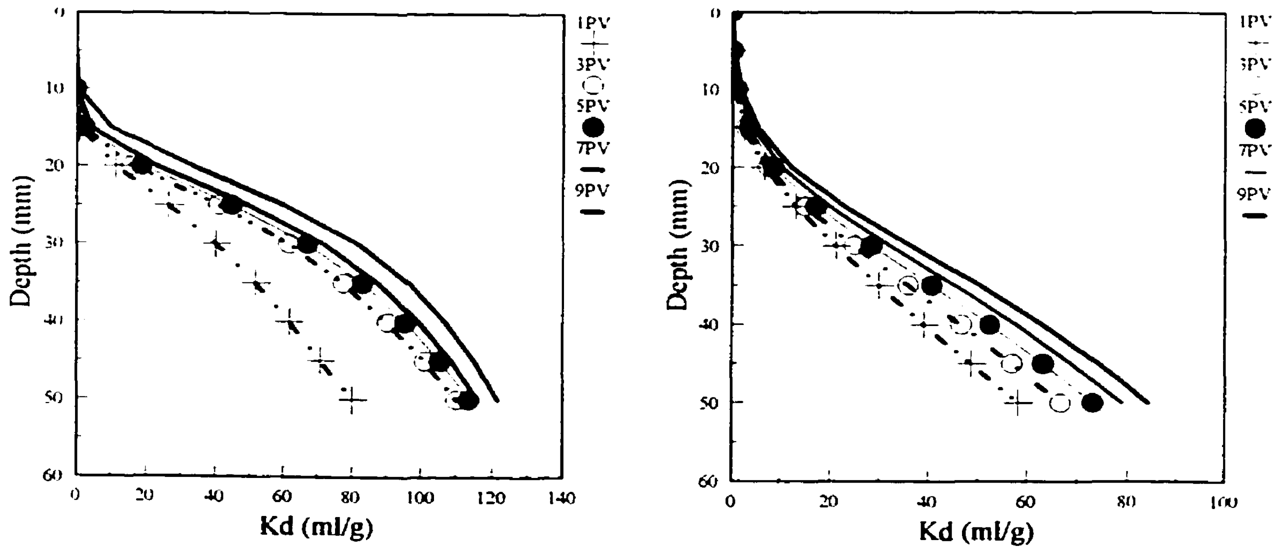
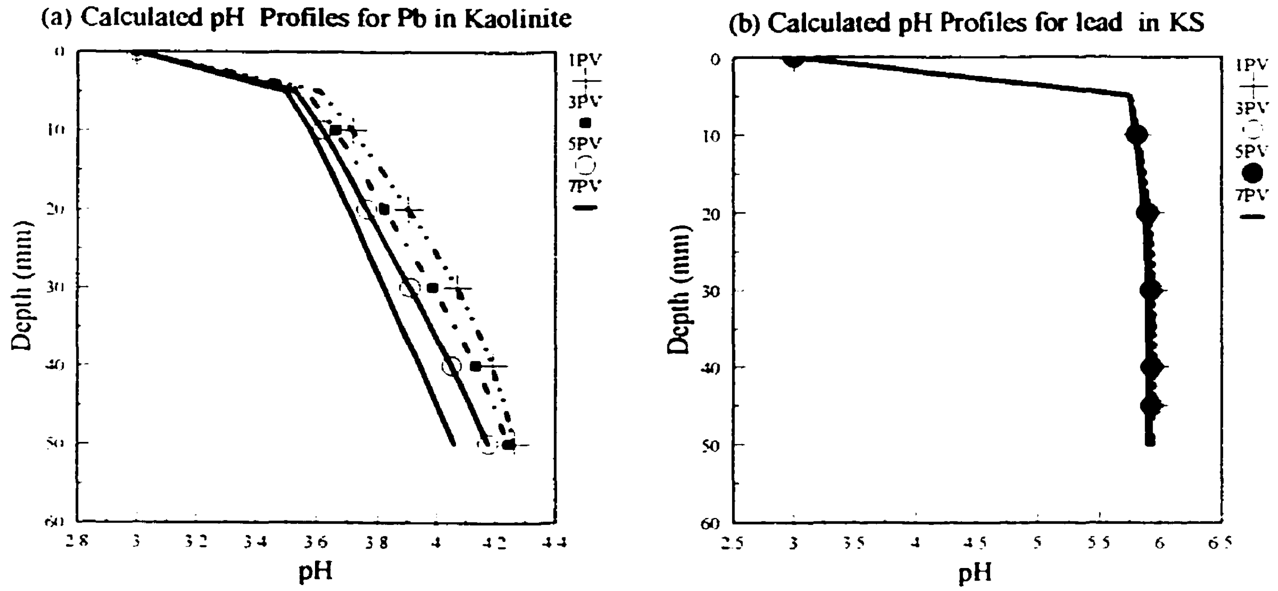
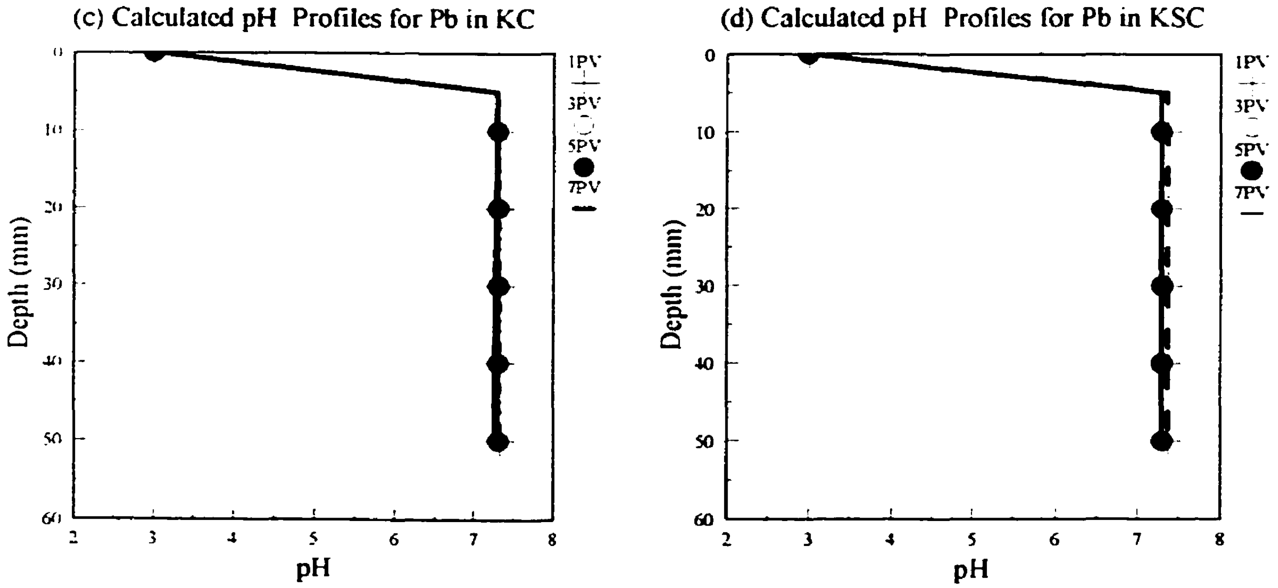


Fig. 5.28 Predicted Kd Profiles for Zn.


(a) Calculated pH Profiles for Pb in Kaolinite

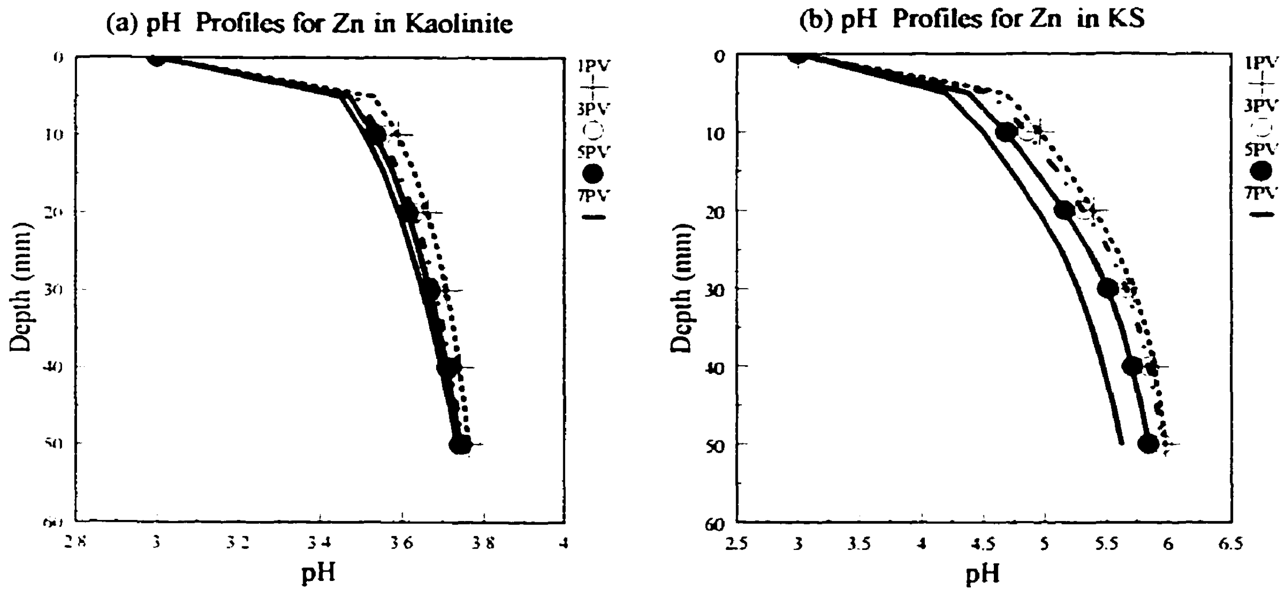
(b) Calculated pH Profiles for lead in KS

broken line (Exp.)
solid line (Pred.)


(c) Calculated pH Profiles for Pb in KC

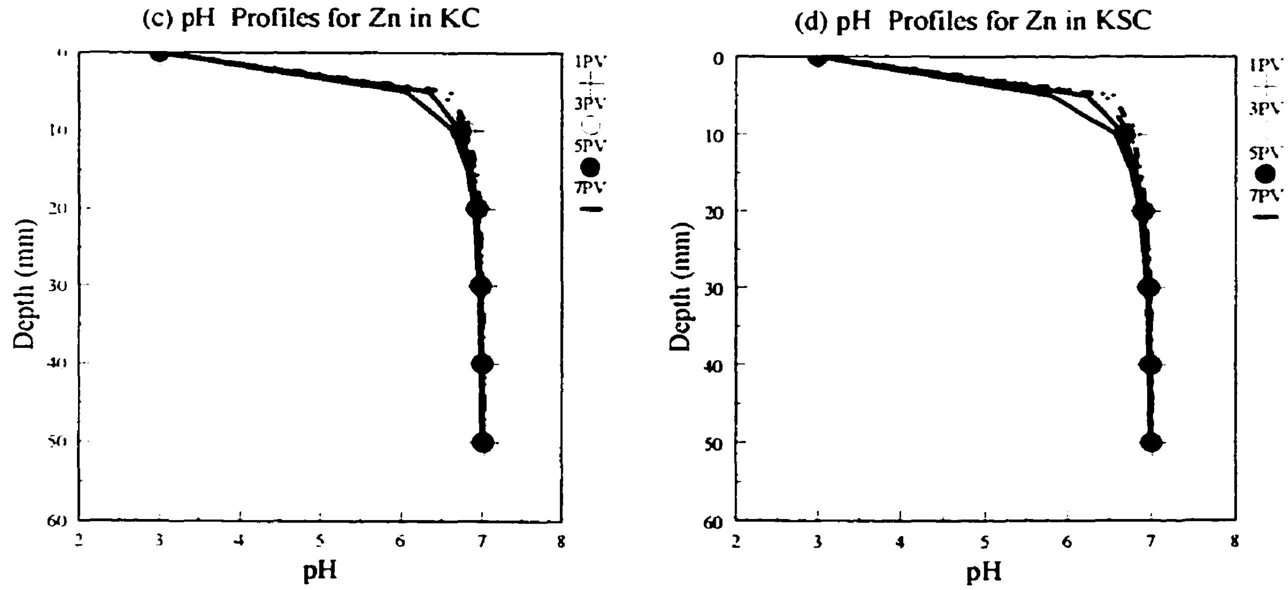
(d) Calculated pH Profiles for Pb in KSC

**Fig. 5.29** Predicted pH Profiles for Lead.


(a) pH Profiles for Zn in Kaolinite

(b) pH Profiles for Zn in KS

broken line (Exp. )
solid line (Pred.)

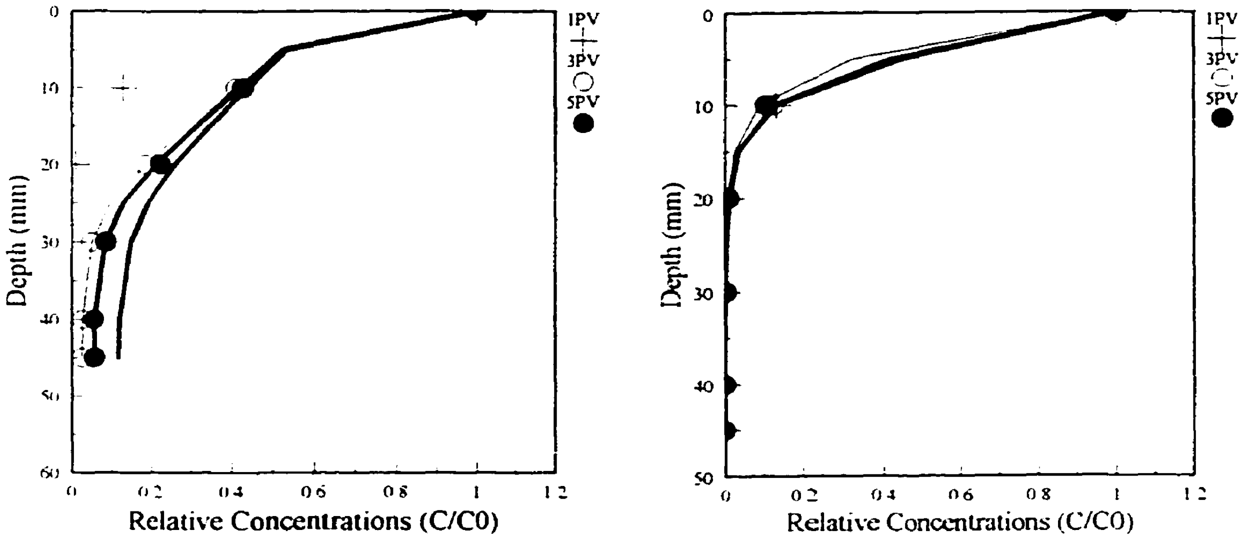

(c) pH Profiles for Zn in KC

(d) pH Profiles for Zn in KSC

**Fig. 5.30** Predicted pH Profiles for Zinc.

(a) Kaolinite (Kd=0.22 ml/g)

(b) KS Soil (Kd=110 ml/g)



(c) KC Soil (Kd=220 ml/g)

(d) KSC Soil (Kd=175 ml/g)

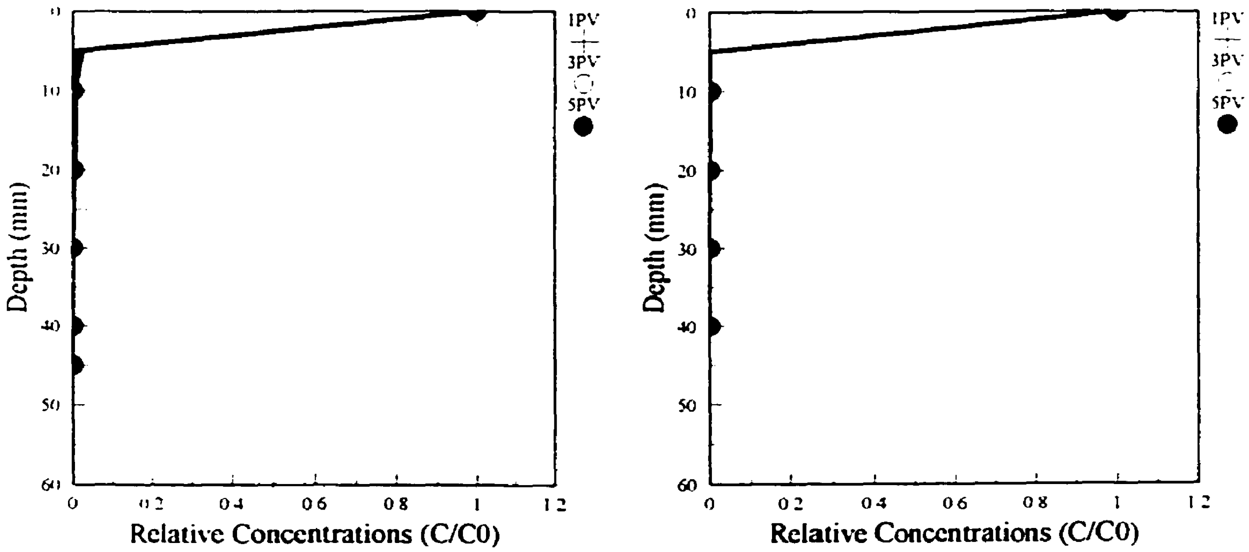
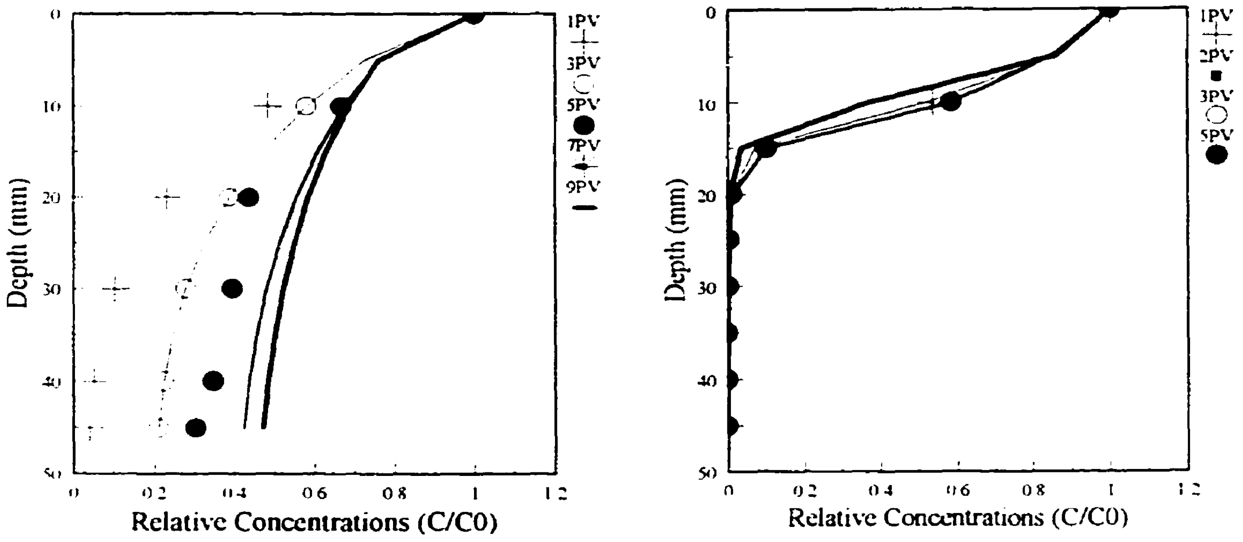
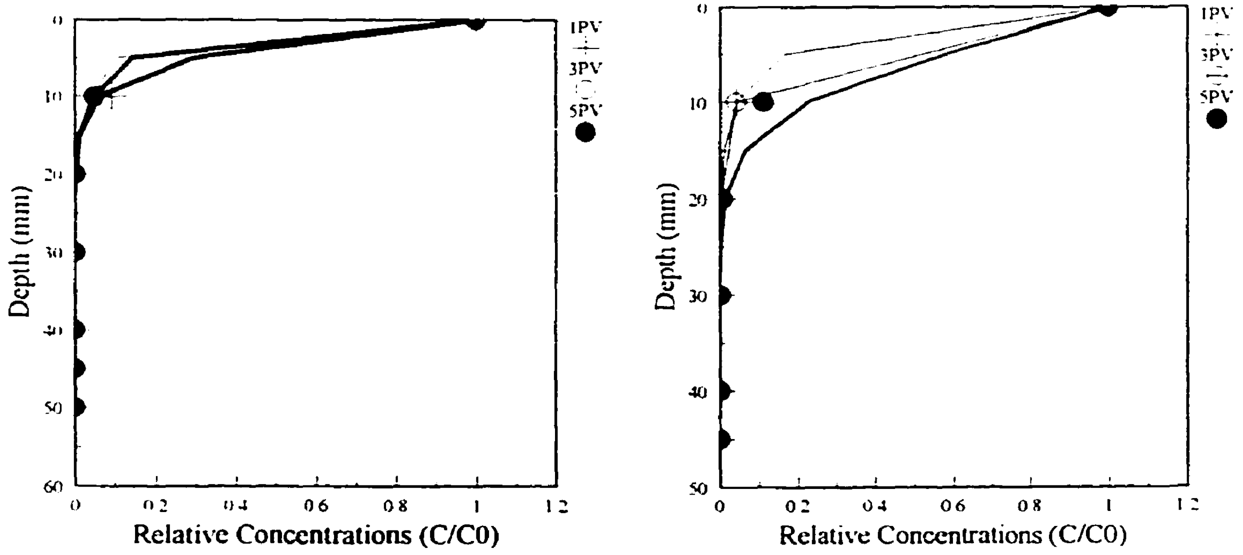


**Fig. 5.31** Predicted Pb Pore Fluid Profiles Using Kd Approach.


(a) Kaolinite (Kd = 0.12 ml/g)

(b) KS Soil (Kd= 22 ml/g)


(c) KC Soil (Kd=35 ml/g)

(d) KSC Soil (Kd= 27 ml/g)

**Fig. 5.32** Predicted Zn Pore Fluid Profiles Using Kd Approach.

## 5.8 Heavy Metals Speciation

Speciation analysis of an element in a water sample has been defined as, the determination of the concentrations of the different chemical forms of the element which together make up its total concentration in the sample. For a metal ion it is well known that the individual chemical forms include; dissolved forms, such as simple inorganic complexes, including the aquacomplex or free metal ion, organic complexes, and elements adsorbed on the inorganic fraction of the soil. The total concentration of these metals is not the most important point when it comes to understanding the metals' effect on the environment. The key concept in this case is the speciation of the metal. Small changes in the speciation of a trace metal, even at fixed total concentration, can strongly modify its toxicity and its over-all mobility in an aquatic system. Most studies on the toxicity of heavy metals towards aquatic life have shown that usually free (hydrated) metal ions are the most toxic forms. The direct measurement of each one of these forms, in general, is very difficult if not impossible. The COSTCHEMCLAY provides a good estimation of the forms of the heavy metals which are released to the groundwater. Typical results of the all components in the solution and all speciation forms of the components for leaching lead solution in Kaolinite soil for the last node along the column after 7 pore volumes is demonstrated in Table E1 to E4 in Appendix E. Typical results of the all components in the solution and all speciation forms of the components for leaching zinc solution in kaolinite and KSC soil for the last node along the column after 7 pore volumes is demonstrated in Table E5 to E14 in Appendix E. As illustrated in Table E10 some zinc was retained by the precipitation mechanism which is not distinguishable experimentally from precipitation.The possible complex formation of zinc with chloride, nitrate and hydroxides is also demonstrated in Table E10. The possible precipitation of zinc is in hydroxide and carbonate forms. The precipitation depends on the type of heavy metal, heavy metal concentration, pH of the solution, other contaminants in solutions (Yong *et al.*, 1995). The possible complex formation of zinc with carbonate, chloride, and hydroxides is also demonstrated.

## 5.9 Summary

The effect of the multi-component on the transport of heavy metals ( lead and zinc) into different clay soils has been discussed in this chapter through the results of column leaching tests, using kaolinite and kaolinite mixed with silica gel and calcium carbonate (K, KS, KC, and KSC) as the soil material and a heavy metal solution (Pb or Zn) spiked with NaCl as leachate. From the experimental results, it is evident that the amount of heavy metals retained in each type of soil depends, not only on the other contaminants in the solution but also, on the soil solution pH, CEC, SSA, soil constituents, and type of the heavy metal. It is also concluded that a dissolved inorganic complexing agent could change the mobility of heavy metals along the clay liner.

The partitioning coefficient was reduced from the bottom to the top of the column and from low to high pore volumes. It is because the concentration of the complexing agent increases and the migration of lead is less to the bottom than the top part of the soil. In other words, the $K_d$ is time and space dependent, and it varies with the type of the soil. The model was able to simulate both solute transport and geo-chemical reaction of heavy metals with other contaminants and soil compositions in the clay barrier system. It also provides the distribution of heavy metals concentration (adsorbed, precipitated, and dissolved ) along the depth of clay liner. Using the $K_d$ approach for the prediction of the heavy metals provides only the migration profiles, based on the batch equilibrium test at constant pH which is not the case in column leaching with variable pH. The prediction results show good accord between the values predicted and the values measured. It was also concluded that using an average diffusion coefficient, as in most of the existing transport models, is not a good assumption for the various individual contaminant constituents, regardless of soil composition and other contaminants in solution.

The results confirm that the distribution coefficient ($K_d$) is a function, not only of the contaminant and a given material, but also of a given leachate chemistry and the physicochemical-chemical properties of the soil liner material. Thus, the $K_d$ approach for the prediction of pollutants such as heavy metals is not a proper approach for the design of clay barrier systems.

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# Chapter 6

# COSTCHESP Simulation of a Natural Clay Barrier

## 6.1 General

In the previous chapter, the coupled solute transport of a single heavy metal at low concentration, spiked with chloride in artificial soil, with different soil constituents was simulated. The effect of chloride concentration and pH on the distribution coefficient in the case of a batch equilibrium test for composite heavy metals at low and high concentrations has been discussed in Chapter 4. It was shown that pH, chloride and heavy metals concentrations contribute most to the retention of the heavy metals/distribution coefficient in clay soil. It was also concluded that a high chloride concentration increases the mobility of heavy metals. Whereas, at high pH, of the soil solution (above 6) the mobility is reduced for high level concentrations of heavy metals, due to precipitation processes. In this chapter, the multi-component transport of heavy metals is simulated by COSTCHESP, using a composite solution of heavy metals (lead and zinc) spiked with chloride as a leachate and natural clay as a barrier. The concentrations of chloride, lead and zinc are almost five, and 20 times, respectively, higher than the previous cases for artificial soil.

## 6.2 Application

The experimental data used in this study was previously reported by Mohamed *et al.* (1994). The soil was characterized as having moderately high specific surface areas of 90-206 $m^2/g$, low CEC of about 10-20 meq/100g, maximum dry densities of 1.83-1.84 $Mg/m^3$, and low permeabilities of $10^{-9}$ m/sec for the compacted samples.

The leachate used was produced in an actual landfill site receiving only municipal solid wastes. Since the initial heavy metal concentrations in the leachate were very low, leachate was spiked with $Pb^{2+}$ and $Zn^{2+}$ to increase the heavy metal concentrations. The pH of the reconstituted leachate was reduced to 1.33. The chemical compositions of the reconstituted leachate are as shown in Table 6.1.

**Table 6.1** Input Chemical Compositions of the Reconstituted Leachate (Mohamed et al., 1994)

| | | | | |
|---|---|---|---|---|
| $Na^+$ | 346 | ppm | $Pb^{2+}$ | 1372.2 |
| $K^+$ | 164.8 | | $Zn^{2+}$ | 1141.6 |
| $Mg^{2+}$ | 43.8 | | $Cl^-$ | 5258.4 |
| $Ca^{2+}$ | 95.4 | | pH | 1.33 |

The mineralogical analysis reveals that the soil contains 15% of carbonate and 21% of brucite (MgO). Leaching was carried out under a constant applied air pressure of 12.0 or 15.0 psi, i.e., equivalent to a water head of 8.4 or 10.6 m depending on the sample height. This resulted in a similar hydraulic gradient of 97. During the leaching process, effluent was collected every 0.5 PV (pore volume) and analysed. At the end of the 1 PV, 3 PV and 5 PV series, the soil samples were extruded, cut into 10 mm thick slices, and analysed for pore fluids contents (soluble ions) and exchangeable cations. Detailed analytical procedures were reported by Mohamed et al. (1994).

### 6.2.1 Prediction

In the above mentioned case the experimental results were reported in terms of pore fluid concentration profiles instead of total component concentration. In the COSTCHESP formulation the dependent variable was changed from total component concentration to total aqueous component concentration. In this case iterations between COST and CHESP continue until the difference between two consecutive total aqueous concentrations converges to the tolerance value, as shown in Figure 6.1. To simulate the above experimental condition by the COSTCHESP, leachate constituent concentration for each component was specified in the chemical equlibrium speciation program. CEC and SSA were also chosen as the input of the CHESP. The adsorbed parameters were initially computed from the adsorption isotherm in the batch equilibrium test and then calibrated with column leaching test experiments. To simulate the leachate pH by the model, as specified in the experiment, an initial concentration of 0.0467 mol/L of hydrogen ion, representing a pH of 1.33 of the influent solution, is considered. For the solid part, an initial concentration of 1.52 mol/L of MgO and 1.15 mole/L of $CO^3Ca$ were assumed for each layer of soil (10 layers).

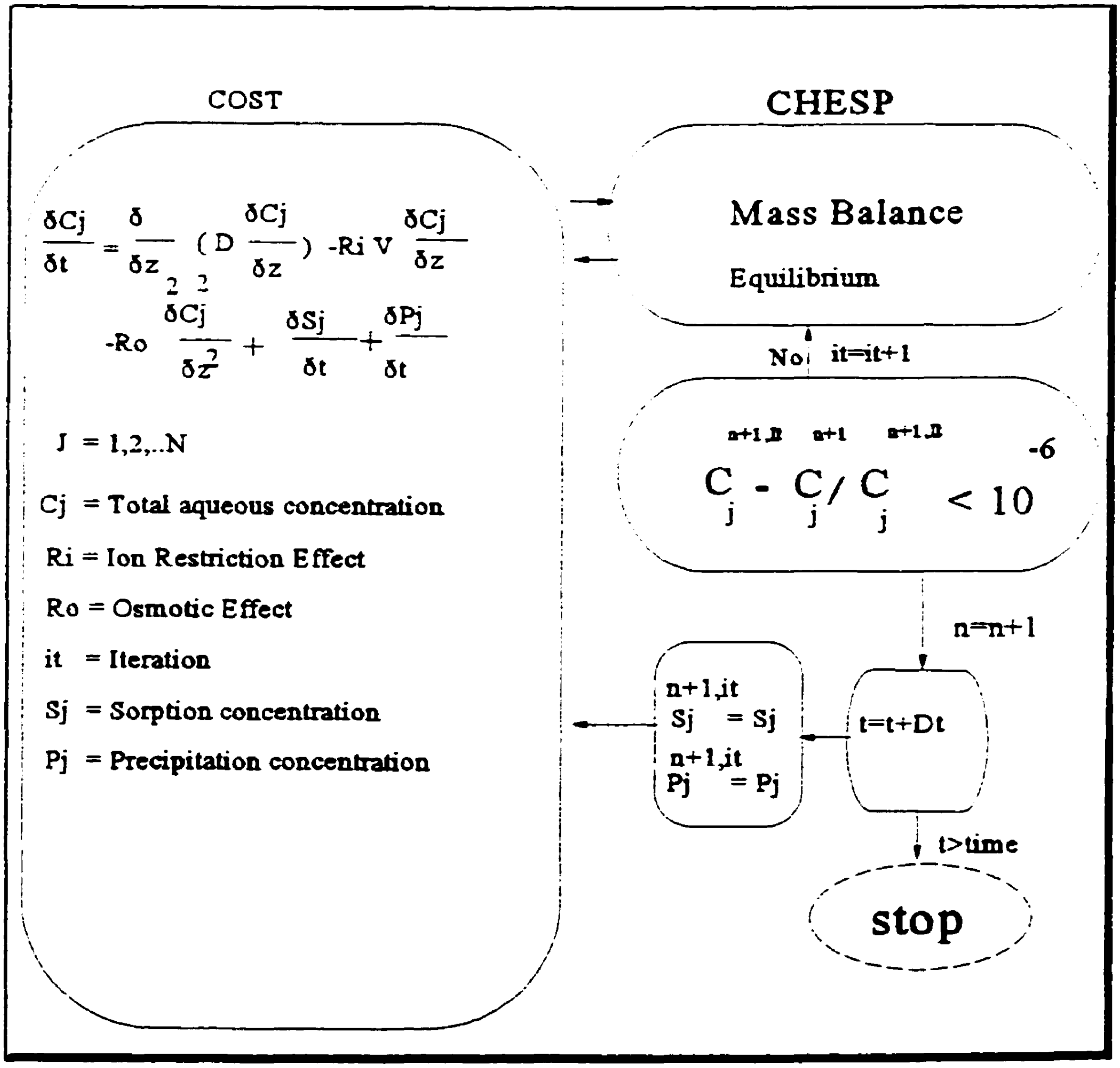


**Figure 6.1** COSTCHESP for Predicting Total Aqueous Concentrations.

The input of the CHESP which was produced by PRECHESP program is demonstrated in Section D.2. in Appendix D. As shown, all possible adsorption of the cations in the leachate solution on clay soil were simulated. $SOPb^-$, SOPbOH, $SOZn^-$, SOPb, SOZnOH, SOK, SONa,...represents adsorbed species for the simulation. The COST inputs are basically, coefficient of permeability (0.0148 cm/day), depth of the clay liner (120 mm), depth step (10 mm), time step (0.1 day), required times for 1 PV (2.45 days), 2 PV (5.0 days), 3 PV (7.79 days), 5 PV (18.25 days) and transport parameters (diffusion coefficient and chemico-osmotic coefficient). The transport parameters are determined by the parameter estimation technique (PET) as described in section 5.6. The program uses two main procedures to compute the unknown material parameters a, b and $k_{ch}$ . The first step is to set the initial condition, i.e. initial concentrations, and compute the predicted concentration profiles at a new time step, through the COST program based on the initial guess value of material parameters. The second step is to keep revising the material parameters until the difference between experimental and theoretical concentration profiles is minimized. The PET program was used for the calculation of the diffusion parameter between 1PV and 3PV. The resulted diffusion and chemico-osmotic coefficients for lead and zinc for all types of clay soils (K, KS, KC, KSC) are tabulated in Table 5.1 using the total aquoues concentration The boundary conditions including the hydraulic head (1060 cm), initial total concentrations and background concentrations of each component along the soil column can be easily defined. It is clear that the background concentration of heavy metals and other components, except calcium, magnesium, and carbonate are zero. The background concentrations of calcium, magnesium and carbonate can be specified based on the effluent concentrations. The initial concentrations of all components are the same as specified in the leachate solution, shown in Table 6.1.

The PET program was used to calculate the diffusion parameter between 1PV and 3PV and then the computed diffusion parameters were used for the prediction of migration, adsorption, precipitation, pH of the soil solution and $K_d$ profiles from the COSTCHESP model for higher pore volumes of effluent. The resulting diffusion and chemico-osmotic coefficients for lead, zinc and chloride are shown in Table 6.2.

**Table 6.2** Resulting Diffusion and Chemico-Osmotic Coefficients from PET Program.

| **Ion** | **A ($cm^2$/day)** | **B (L/mol)** | **$K_{ch}$ ($cm^5$/g/day)** |
|---|---|---|---|
| $Pb^{2+}$ | 0.325 | 141.26 | -6.81 |
| $Zn^{2+}$ | 0.323 | 154.11 | -6.82 |
| $Cl^-$ | 7.1 | 0.0 | -0.1 |

## 6.3 Cl Migration Profiles

Using COSTCHESP the calculated diffusion coefficient, migration, and precipitation profiles of Cl ions and their breakthrough curves are shown in Figures 6.2a, 6.2b, 6.2c and 6.2d. The chloride ion is considered to be a very mobile and non-interacting anion (conservative contaminant). As is shown, $Cl^-$ ions were not adsorbed along the soil column and increased as more permeant passed through the soil, reaching the breakthrough curve at 3PV of influent. Since the concentrations of $Cl^-$ in the leachate were significant (5258.4 ppm) some of chloride ions were precipitated as $Cl^2Pb$ along the soil column. The precipitated chloride decreases with depth and increases with time and most of the chloride was precipitated at the top of the column soil. This is due to the increase in total chloride concentrations with time There is good agreement between the predicted and experimental results. The breakthrough curves for chloride are less than unity due to the precipitation of Cl ions in soil column.

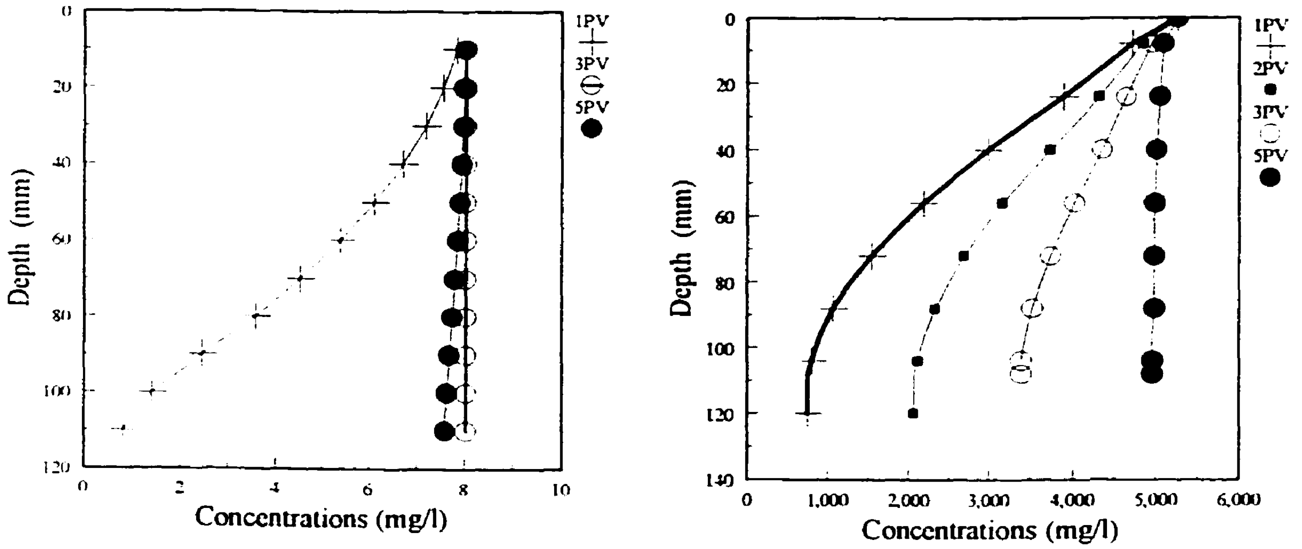
From the computed diffusion profiles for chloride, shown in Figure 6.2d, it may concluded that even for chloride ions which are very mobile, the diffusion coefficient is not a constant parameter. It varies with time and space but does reach its steady state very fast. The computed diffusion for chloride ions at steady state are almost the same as reported in the literature. Yong and Warith (1990) computed the chloride diffusion equal to 0.33 ($cm^2$/day) using a finite difference method from experimental results of column leaching tests with a gradient of 25. Mohamed et al. (1994) calculated the diffusion coefficient of 7.53

using a square root method from column leaching. The difference in the calculated diffusion parameters is due to the difference in hydraulic gradient and chloride concentrations.

It should also be noted that the precipitated chloride concentration profiles shown in Fig. 6.2d, could not be measured by the experiment (Yong and MacDonald, 1997).

(a) Cl Diffusion Profiles in Natural Clay

(b) Cl Migration Profiles in Natural Clay



(c) Cl Breakthrough Curve

(d) Cl Precipitation Profiles in Natural Clay

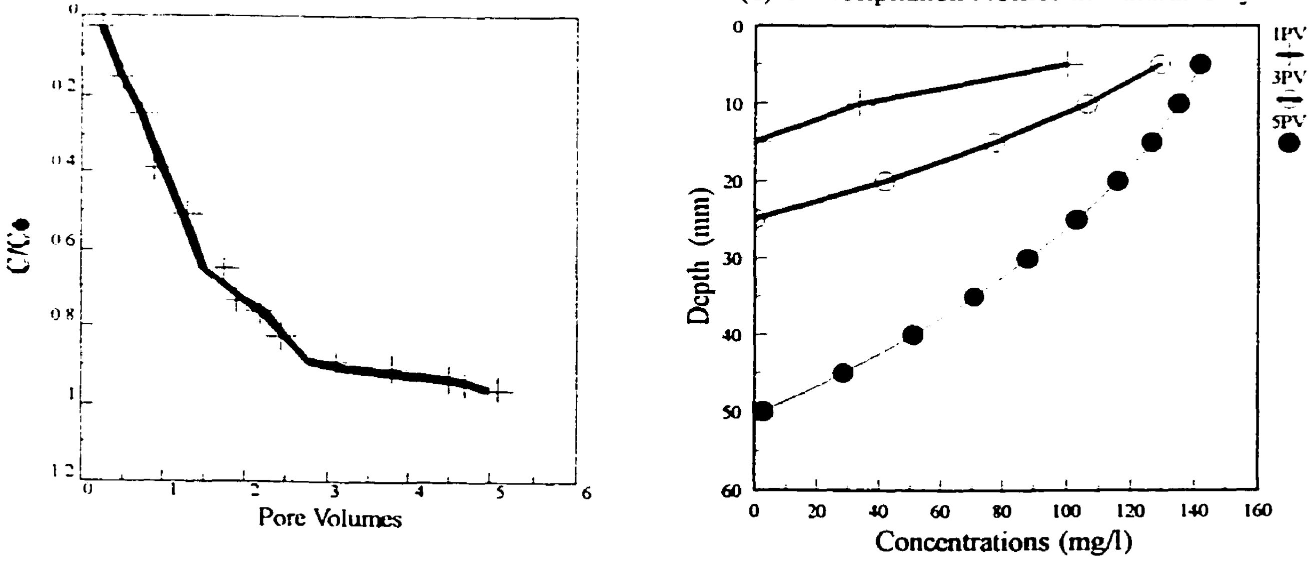


**Fig. 6.2** Chloride Diffusion, Migration, Precipitation Profiles and its Breakthrough Curves Natural Clay.

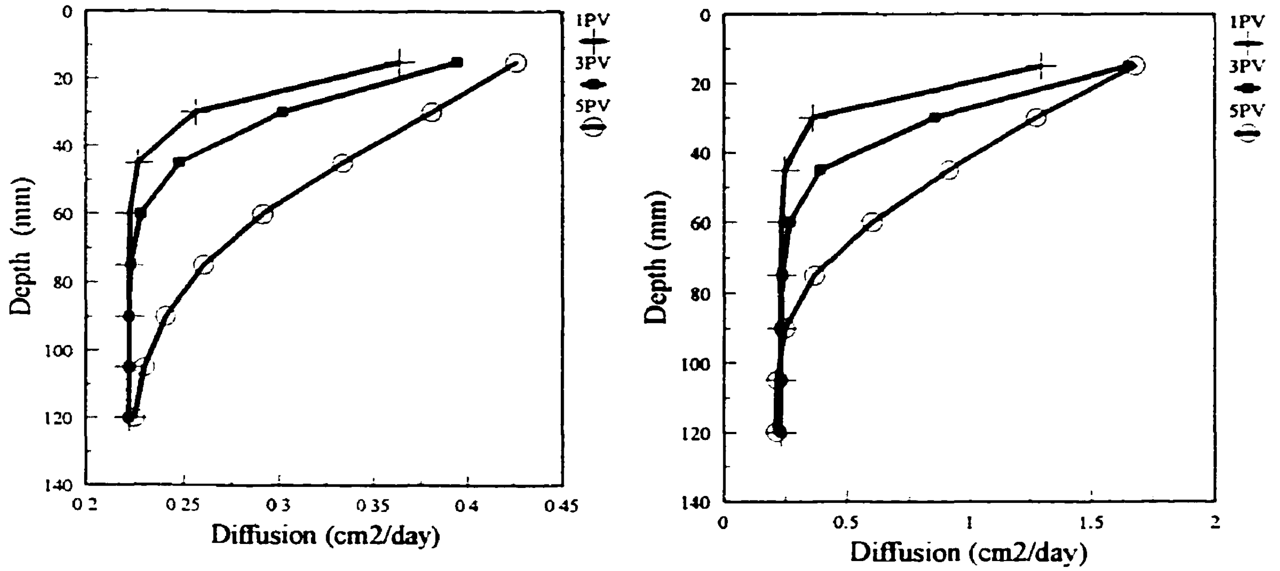
## 6.4 Pb and Zn Migration Profiles

As mentioned above, the diffusion parameters computed from the PET program were used for the prediction profiles of heavy metals. The computed diffusion coefficient profiles for lead and zinc and their related calibration curves are shown in Fig. 6.3a-d.The experimental results of pH variations with depth after 1PV show that dissolution of calcite and hydroxide forming from the brucite (MgO) cause significant changes in solution pH (pH 5.4 at the top and 7. for the remainder of the soil column).

The predicted results for 1PV, 3PV and 5PV migration profiles of lead and zinc, computed from the COSTCHESP are shown in Figures 6.4a and 6.4b for Pb and Zn, respectively. As these figures show, very little $Pb^{2+}$ or $Zn^{2+}$ is collected in the effluent leaching, indicating that $Pb^{2+}$ and $Zn^{2+}$ were retained by the soil. The dissolved (pore fluid) concentrations of $Pb^{2+}$ and $Zn^{2+}$ have increased with PV through the soil column as shown in Figures 6.4a and 6.4b. Similar results are obtained for $Zn^{2+}$ migration through the soil column except that the rate of movement of $Zn^{2+}$ is higher than that for $Pb^{2+}$. Using the $K_d$ approach for the prediction of the heavy metals provides only the migration profiles, based on the batch equilibrium test at constant pH which is not the case in column leaching with variable pH. Figures 6.4c and Figure 6.4d demonstrate the difference between the predicted results of the lead and zinc concentrations using $K_d$ approach with the experimental results. Using higher or lower $K_d$ values provide under or over estimates the predicted results of lead and zinc concentrations. However, using the average $K_d$ values computed through the column test may yield more reasonable values than isotherm constructed with soil suspensions. The present results raise some very interesting points about the widespread use of constant partitioning coefficient through batch equilibrium tests. The COSTCHESP has the capability of investigating the partitioning of the heavy metals along the depth of clay liner at different pore volumes.

(a) Pb Diffusion in Natural Clay

(b) Zn Diffusion in Natural Clay



(c) Calibrated Pb Migration Profiles

(d) Calibrated Zn Migration Profiles

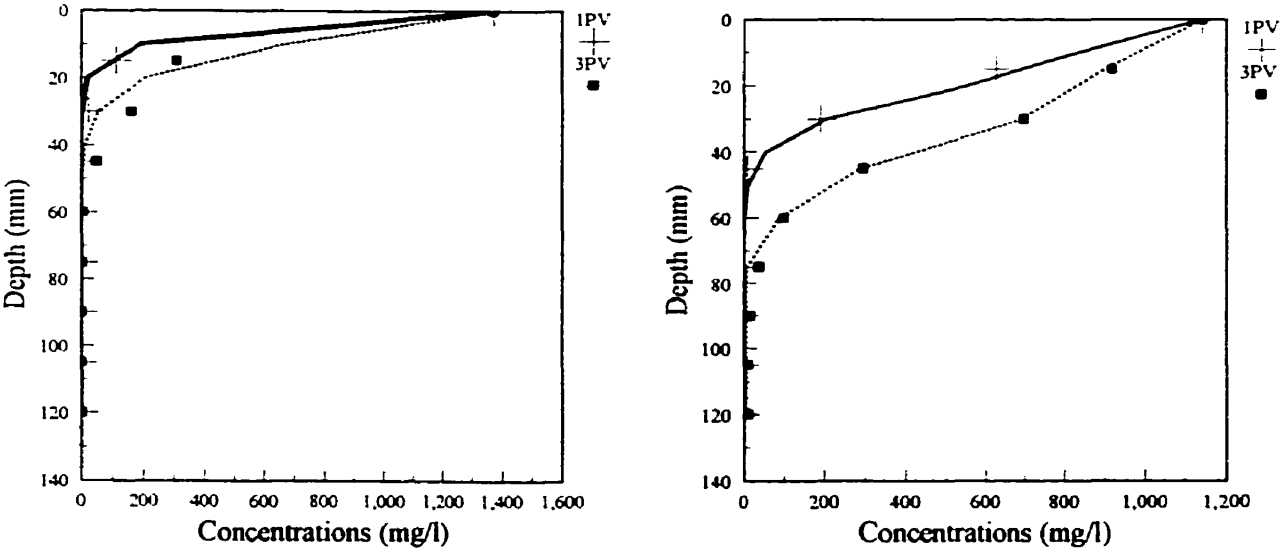


**Fig 6.3** Heavy Metals Diffusion Coefficients and the Calibration Curves.

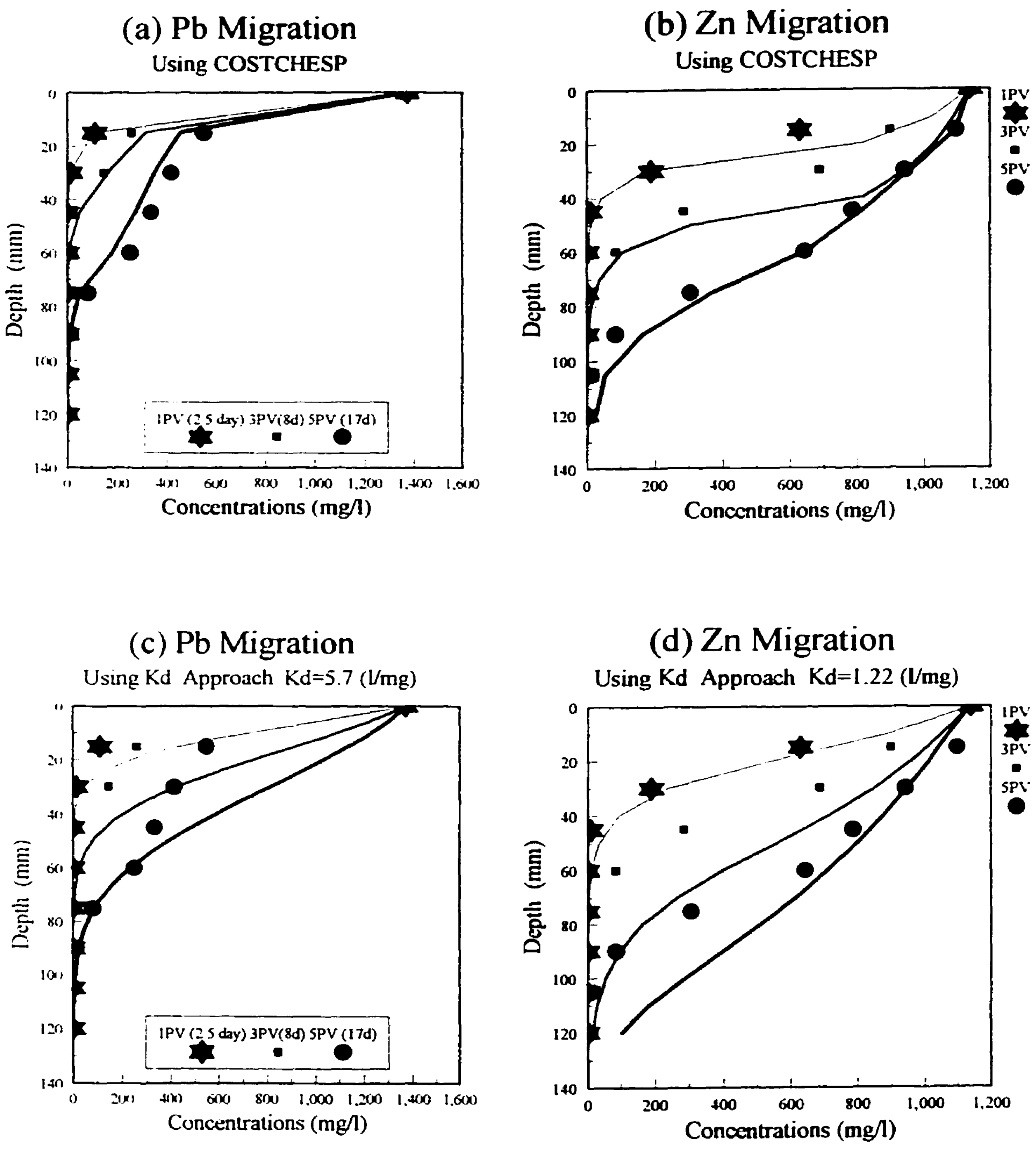


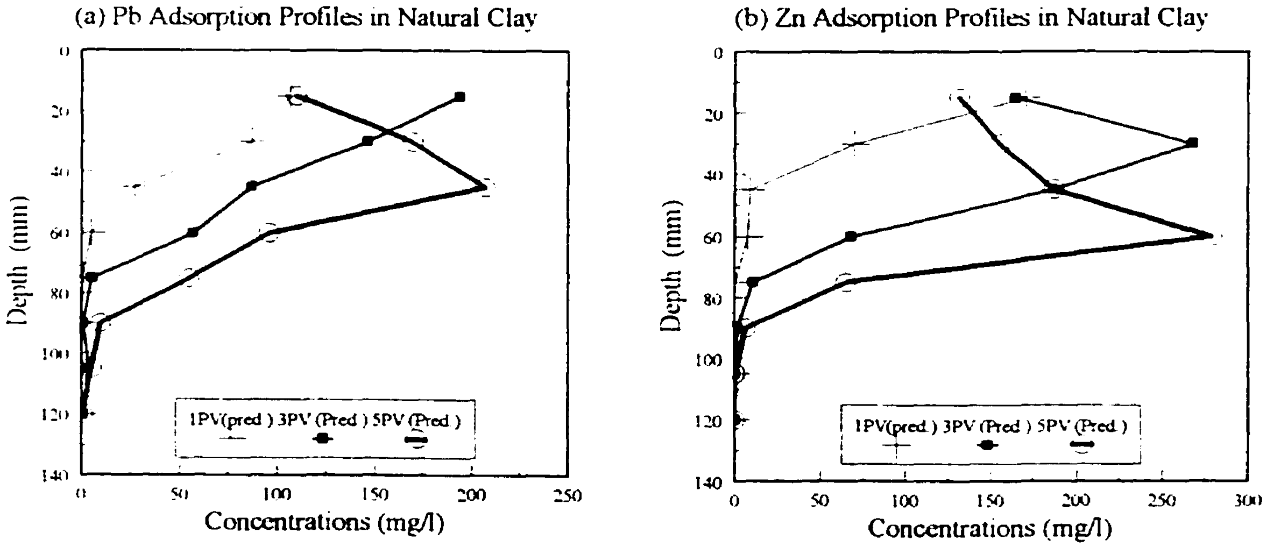
**Fig. 6.4** Predicted Pb and Zn Migration Profiles in Natural Clay.

### 6.4.1 Pb and Zn Adsorption Profiles

The predicted results of lead and zinc adsorption profiles are plotted in Figures 6.5a and 6.5b, regarding adsorbed concentration versus depth for various leachate PVs. The retention of Pb and Zn may be explained by precipitation, and adsorption. The experimental adsorption profiles show that 65% of Pb and 55% of Zn were retained in the top part of (approximately 15 mm) the soil. No $Pb^{2+}$ and very little $Zn^{2+}$ were adsorbed at the bottom of the soil column until 3PV of leachate was collected. The concentrations of $Pb^{2+}$ and $Zn^{2+}$ adsorbed increased with PV through the soil column as a function of leachate PV.

As more leachate passes through the column the adsorption decreases at the top of the column and increases at the bottom due to low soil solution pH at the top and high soil solution pH at the bottom. Both metals continued to adsorb through the soil column until the available site was occupied by the cations, then the adsorption rate decreased and desorption of the heavy metals began. This phenomenon may start after 5 pore volumes or more, depending on the type of soil, its CEC and SSA and the type and concentration of the heavy metals or other components in the solution.

The fact that zinc was detected earlier than lead in the leachate collected indicates that $Zn^{2+}$ is less adsorbed than the $Pb^{2+}$. This agrees with previous findings of several authors including Farrah and Pickering (1979); , Yong et al. (1993), Mohamed et al, 1994 and Martell and Hancock (1996). This can be attributed to the difference in the hydrated radii of $Pb^{2+}$ and $Zn^{2+}$ cations near the clay surface. This situation confirms the observation concerning the exchange mechanism of cations of equal charge as generally inversely proportional to the hydrated radii or proportional to the unhydrated radii of cations (Yong et al., 1992b). If one predicts the order of soil retention based on the unhydrated radii, one obtains a preference adsorption of $Pb^{2+}$, i.e., adsorption of $Pb^{2+}$ (0.12 nm)> $Zn^{2+}$ (0.074 nm) as indicated in the previous chapter, which agrees generally with the experimental results.Macroscopically, the tendency of an ion to be sorbed depends on its concentration in the aqueous phase, relative to the concentrations of other sorbable ions, the selectivity of the sorptive substrate for an ion relative to the other ions, and the number of sites on the sorptive substrate (Miller and Benson, 1983 ). Given similar concentrations of sorbable ions in the aqueous phase, the selectivity of $Pb^{2+}$ is higher than the selectivity of $Zn^{2+}$. According to the hard-soft acid base theory, the predicted preferential adsorption regarding metal ion softness is $Pb^{2+}$ (3.58) >$Zn^{2+}$ (2.34), which agrees with experimental results. Metal ion softness is a function of the ionization potential charge of the metal ion and the ionic radius (Mohamed *et al.*, 1994). It also should be noted that it is not possible to predict the adsorbed profiles of contaminant through the $K_d$ approach.


(a) Pb Adsorption Profiles in Natural Clay

(b) Zn Adsorption Profiles in Natural Clay

**Fig 6.5** Predicted Heavy Metals Adsorption Profiles in Natural Clay.

### 6.4.2 Pb and Zn Precipitated Profiles

The predicted results of lead and zinc precipitated profiles are plotted in Figures 6.6a 6.6b, using precipitated concentrations versus depth for various leachate PVs. Since the effluent pH remained close to the original soil pH (around 6.0) most of the heavy metals are retained on the soil by precipitation (especially lead) rather than adsorption by soil which cannot be distinguished from the experimental results (Yong and McDonald, 1997). Figures 6.6a and 6.6b also show that lead precipitated more than the zinc since lead begins to precipitate at lower pH and lead has lower solubility than the zinc at equal concentrations. $Pb^{2+}$ precipitates as hydroxide ($PbOH_2$), carbonate ($PbCO_3$) and $Cl_2$ Pb.Using the $K_d$ approach for the prediction of contaminant transport purposes, it may not be possible to compute the precipitation profiles of the contaminant. Higher attention of both heavy metals by the soil could decrease the hydraulic conductivity of the clay soil due to precipitation of heavy metals and closure of the pores as indicated by Sposito (1984).

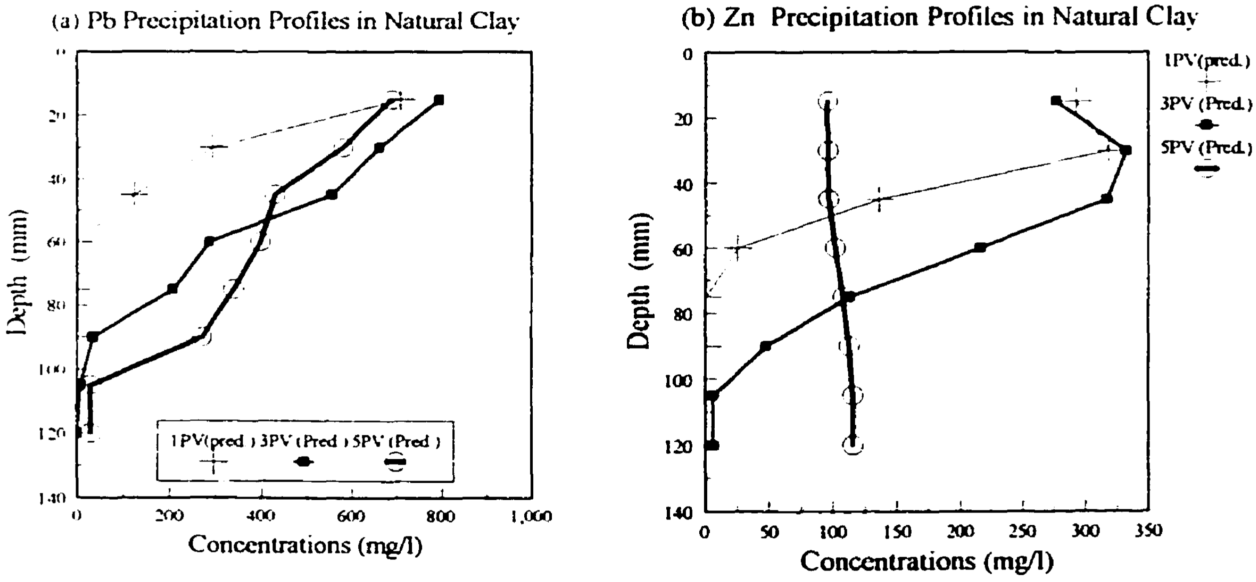


**Fig 6.6** Predicted Heavy Metals Precipitation Profiles in Natural Clay.

## 6.5 pH Profiles

The predicted pH variation versus depth for various leachate PVs is shown in Figure 6.7. As shown, the pH of the soil is the least at the top of the soil column and decreases as more solution passes through the column soil. This is because the permeant is an acidic solution with a pH of 1.33, which is lower than the pH of the soil column used in the experiment. The resulting high pH value of soil solution along the column is due to the dissolution of calcite and hydroxide forming from the brucite (MgO), causing significant changes in solution pH (pH 5.4 at the top and above 6. for the remainder of the soil column) The acidic permeant causes the reduction in the soil pH. It becomes close to the permeant solution after long period of times. These results can cast doubt on the validity of $K_d$ determined through the batch equilibrium test since it is often computed at constant pH.

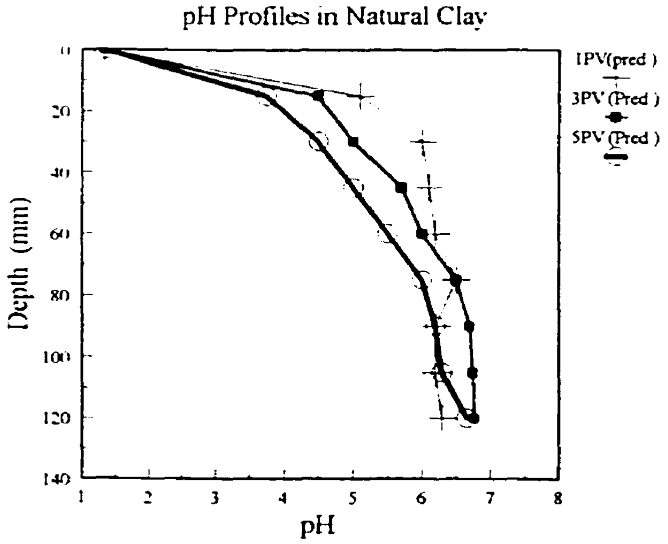


Fig 6.7 Predicted pH of the Soil Solution Profiles in Natural Clay.

## 6.6 $K_d$ Profiles

The predicted $K_d$ profiles are plotted in Figures 6.8a and 6.8b, using the partitioning coefficient versus depth for various leachate PVs. As shown, the partitioning coefficient, $K_d$ varies with time and space. It increases with depth because less soluble heavy metals were transported through the depth of the column soil. With increasing time of leaching, or as more pore volume of the leachate passes through the soil, $K_d$ decreases. The $K_d$ values of lead are more than the zinc's. These results also indicate the $K_d$ values in the column test are always less than in the batch equilibrium test. This is because the batch results are based on soil suspension in a soil solution ratio of 1/10 which results in a higher surface area exposed to heavy metals. While in the column test, the physico-chemical interaction of the leachate with compacted soil is far different. The $K_d$ value for kaolinite is the least when compared to the three other soil materials.

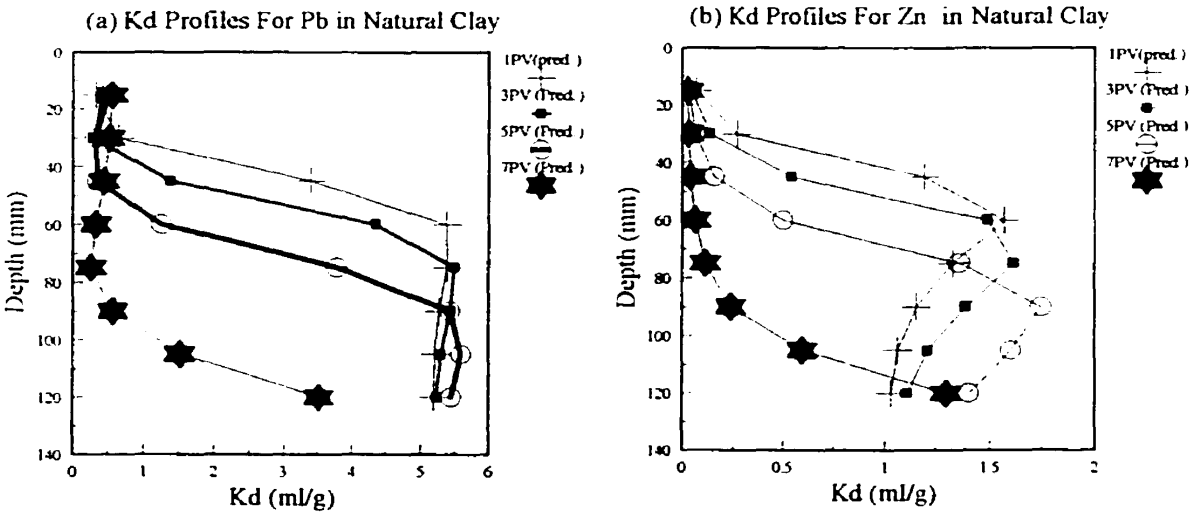


**Fig 6.8** Predicted Heavy Metals Kd Profiles in Natural Clay.

## 6.7 Heavy Metals Speciation

The COSTCHESP provides a good estimation of the forms of the heavy metals which are released to the groundwater. For lead and zinc and all other metals metal ions it is well known that the individual chemical forms include; dissolved forms, such as simple inorganic complexes, including the aquacomplex or free metal ion, organic complexes, and elements adsorbed on the inorganic fraction of the soil. The total concentration of these metals is not the most important point when it comes to understanding the metals' effect on the environment. The key concept in this case is the speciation of the metal. Small changes in the speciation of a heavy metal, even at fixed total concentration, can strongly modify its toxicity and its over-all mobility in an aquatic system. Most studies on the toxicity of heavy metals towards aquatic life have shown that usually free (hydrated) metal ions are the most toxic forms. The direct measurement of each one of the these forms, in general, is very difficult if not impossible. Typical results of the all components in the solution and all speciation forms of the components for the last node along the column after 5 pore volumes is demonstrated in Appendix E.2.1. As illustrated, most of the lead and zinc were retained by the precipitation mechanism, in the forms of hydroxides, chloride or carbonate, which are not distinguishable experimentally from adsorption. The details of speciation results for the last node at five pore volumes of effluent and the computer output and input can be found in Appendix E.2 and Appendix D.2, respectively.

## 6.8 Summary

In this chapter, the multi-component transport of heavy metals in natural soil was simulated by COSTCHESP. From the results of adsorbed or partitioning coefficient profiles, it is evident that the amount of heavy metals retained depends not only on the other contaminants in the solution but also, on the soil solution pH, soil constituents, and type of the heavy metal. It is also concluded that a inorganic ligand could change the mobility of heavy metals along the clay liner.

The partitioning coefficient was reduced from the bottom to the top of the column and from low to high pore volumes. It is because the concentration of the complexing agent increases and the migration of lead is less to the bottom than the top part of the soil. In other words, the $K_d$ is time and space dependent. The model was able to simulate both solute transport and geo-chemical reaction of heavy metals with other contaminants and soil compositions in the clay barrier system. It predicts the distribution of heavy metals concentration (adsorbed, precipitated, and dissolved ) along the depth of clay liner with time.The prediction results show good accord between the values predicted and the values measured. It was also concluded that using an average diffusion coefficient, used in most of the existing transport models, is not a good assumption for the various individual contaminant constituents, regardless of soil composition and other contaminants in solution.

The results confirm that the distribution coefficient ($K_d$) is a function, not only of the contaminant and a given material, but also of a given leachate chemistry and the physicochemical-chemical properties of the soil liner material. Thus, the $K_d$ approach for the prediction of pollutants such as heavy metals is not a proper approach for the design of clay barrier systems. It was shown that attenuation of both heavy metals (lead and zinc) and especially lead was governed by precipitation which could not be predicted by traditional approachs or may not be distinguished from adsorption in the experiment. The results indicated that both $K_d$ and diffusion coefficient are space and time dependent and may not be assumed as a constant parameter. These results can also cast doubt on the validity of $K_d$ determined through batch equilibrium test since it often computed at constant pH.

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# Chapter 7

# Adsorption of Heavy Metals with EDTA

## 7.1 General

The effect of an acidic heavy metals solution spiked with a inorganic complexing agent on the migration and immobilization of heavy metals using different clay soils has already been discussed. As shown, in the batch equilibrium test, the retention or immobilization of heavy metals can be significantly affected when an acidic heavy metals solution spiked with an organic complexing agent such as EDTA (ethyleneediaminetetraacetic acid) is used. This chapter presents the experimental results of the migration and distribution of lead into different clay soils, using the column leaching test, and then the long term migration of heavy metals is predicted by COSTCHESP through calibration with experimental results.

## 7.2 The Effect of Complexing Ligand on the Mobility of Heavy Metals

The effectiveness of complexing ligands depends not only on the choice of the chelating agent used, but also on the stability and absorbability of the complexes formed and on the pH of the system (Castellan, 1996). The control parameters applied in an application would be, the type and concentration of the complexing agent, the presence of other cations, and the pH of the system. EDTA has been justified by many researchers ( Raghavan *et al.*, 1989; Mohamed and Trasente, 1996) as a complexing agent and was used in this study to investigate how EDTA affects the mobility of the heavy metals in different clay soils. EDTA has a relatively low solubility in water, therefore, it is usually used in an aqueous solution in the form of its disodium salt, Na-EDTA. The molecular weight of Na-EDTA is 452.21 g, and it has a solubility of 10.8g in 100 $cm^3$ at 22°C. Trasente's (1995) research indicated that

EDTA at a pH level of 4.50 and a minimum concentration of 0.01 mol/L had the maximum effectiveness for removal of heavy metals from clay soil in the batch equilibrium test. Thus, lead as a heavy metal with a concentration of 1mmol/L spiked with EDTA at a concentration of 0.01 mol/L and pH level of 4.5 was used as a leachate in the column leaching test. EDTA is available in two forms: $H_4Y$ $Na_2H_2Y$ x $2H_2O$, or $Na_4$ $H_4Y$ x $2H_2O$. The notation Y refers to the fully deprotonated form of EDTA. Since the tetra sodium form is most soluble in water, this form of EDTA was chosen for this study. The initial pH of the EDTA at a concentration of 0.1 mol/L is 10.75. The pH of the samples was reduced by adding nitric acid.

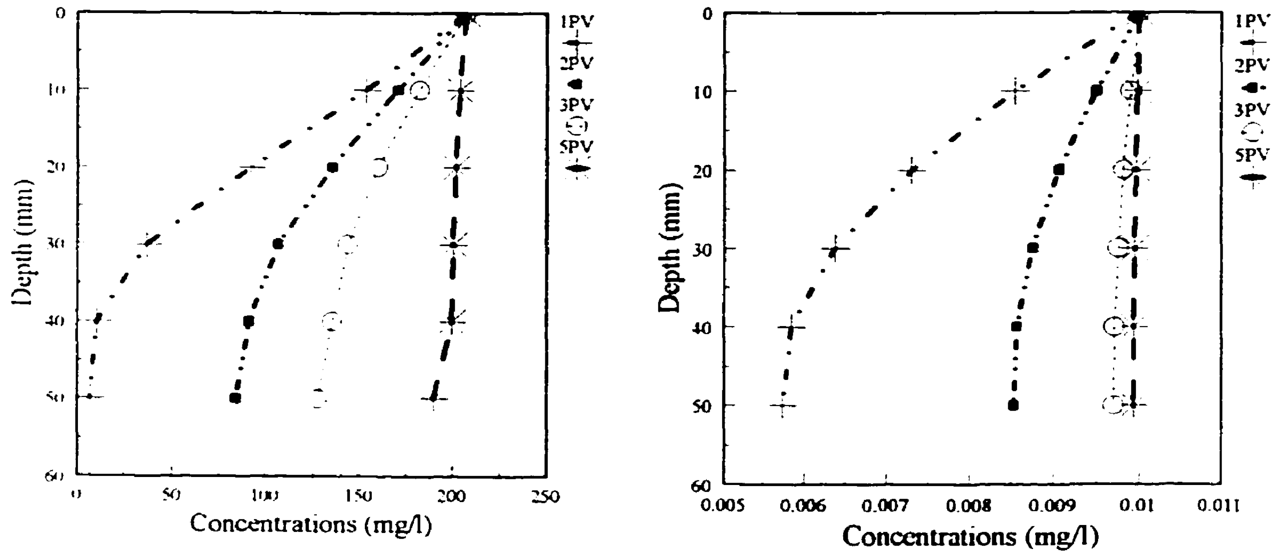
### 7.2.1 Kaolinite Results

The experimental results of the total lead concentration profiles, measured by the acid digestion method as described in Chapter 5, and EDTA concentration profiles and their breakthrough curves are shown in the Figures 7.1a-d, respectively. The dissolved (pore fluid concentration) and adsorbed lead concentration profiles, pH profiles and the computed partitioning coefficient profiles, $K_d$ , are also shown in Figure 7.2a-d.

The transport of lead has also been shown to be a complex function of the presence of other components in the solution. In the presence of a conservative complexing component such as EDTA, the mobility or transport of lead increased significantly (Peters and Shem, 1992). In the case of a lead solution spiked with chloride leached into kaolinite, the appearance of lead in the effluent took 20 days. Whereas in the case using EDTA, lead appeared after 6 days in the first pore volume of the effluent.

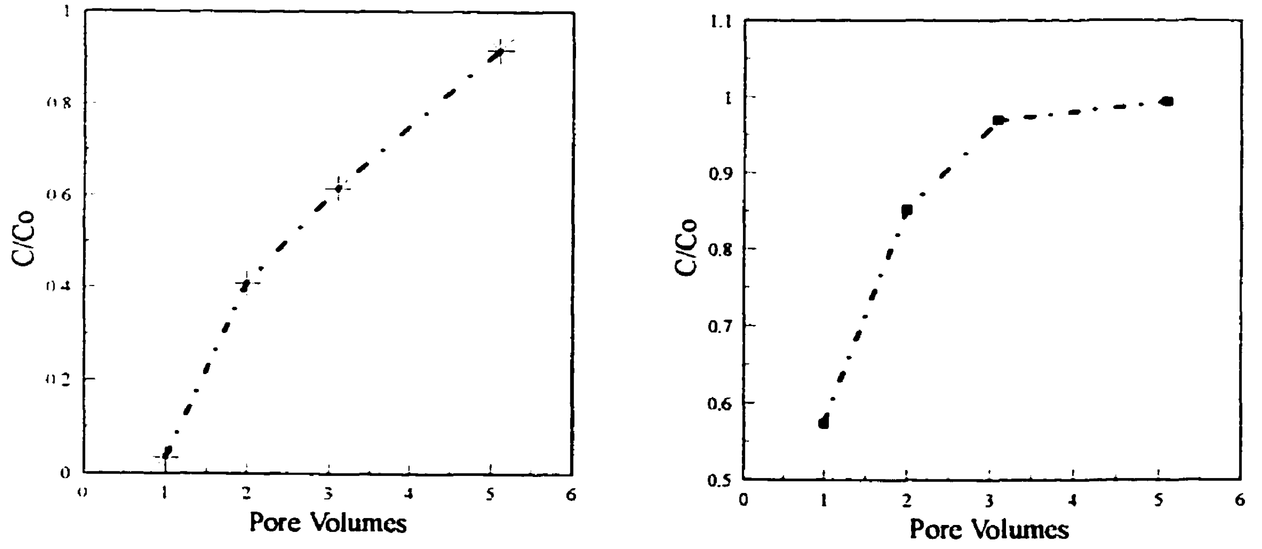
The adsorption of lead was decreased in the presence of EDTA as shown in the Figure 7.2b. The adsorption of lead is very time dependent. At first pore volumes the concentration of EDTA is still less than 0.01 mole/L which was used in the input solution. As the concentration of the EDTA along the column soil extends to 0.01 the adsorption of lead into the kaolinite clay is diminished due to the formation of the complex form of lead with EDTA. The results of $K_d$ profiles, shown in Figure 7.2c, suggest that the $K_d$ values decrease with time due to lower adsorption and higher pore fluid concentration of lead, and it was reached to steady state condition at five pore volumes of effluent. As demonstrated, the presence of

EDTA affects the distribution coefficient results, $K_d$, which are time and space dependent. The distribution coefficient is also a function of EDTA concentrations which are not constant during the transient state in the column leaching test or actual landfill site. The computed distribution coefficient, $K_d$ can have an important effect on the uncertainty associated with the modelling results.



(a) Total Pb Profiles with EDTA in Kaolinite

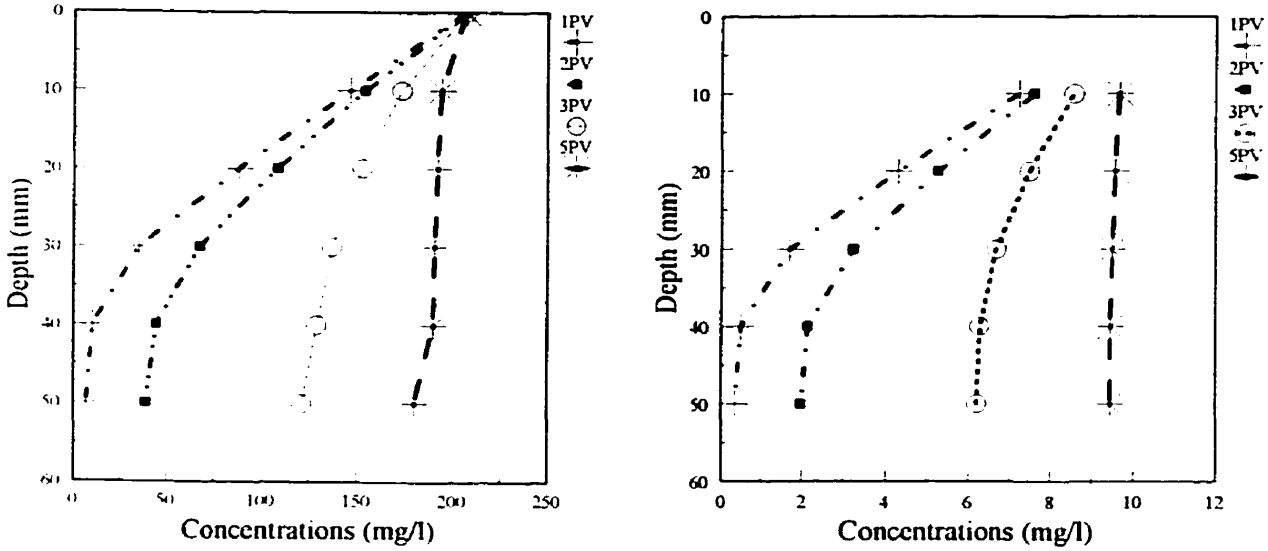
(b) Total EDTA Profiles in Kaolinite



(c) Pb Breakthrough Curve for Kaolinite

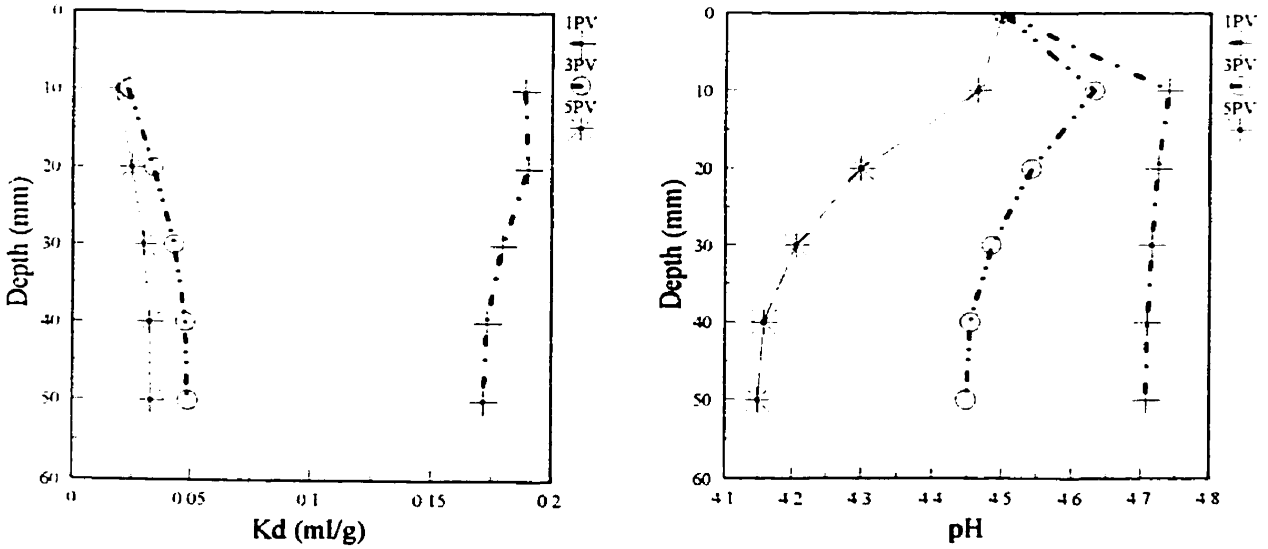
(d) EDTA Breakthrough Curve for Kaolinite

**Fig. 7.1 Pb Profiles with EDTA in K Soil.**



(a) Pb Dissolved Profiles with EDTA in Kaolinite

(b) Pb Adsorption Profiles with EDTA in Kaolinite



(c) Kd Profiles for lead with EDTA

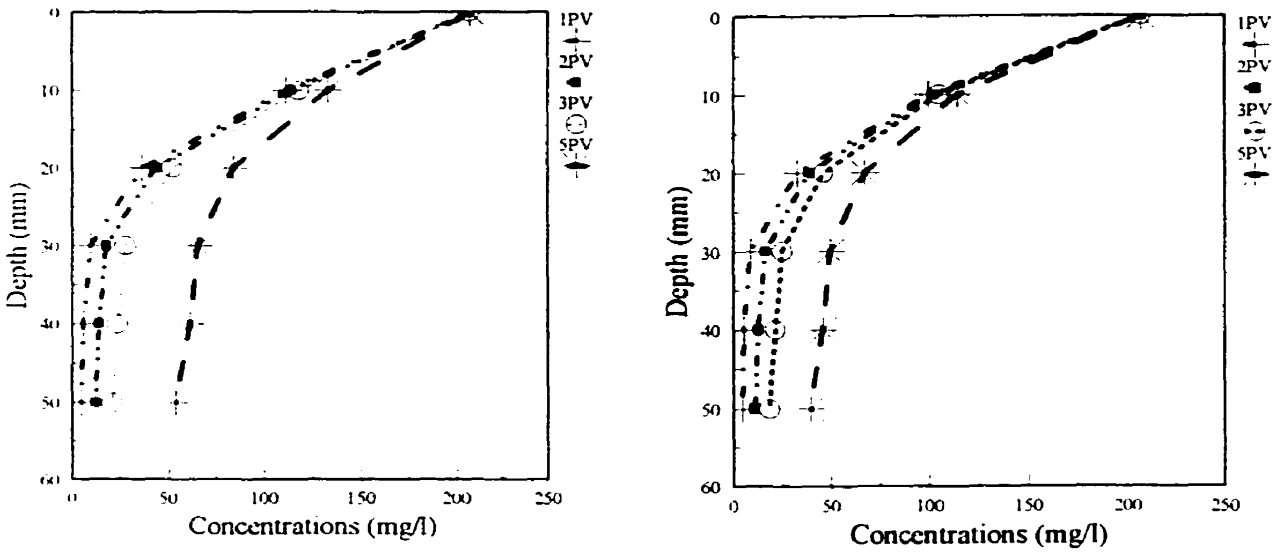
(d) pH Profiles for Pb with EDTA in Kaolinite

**Fig. 7.2** Pb (Dissolved, Adsorbed), pH, and Kd Profiles with EDTA in Kaolinite.

### 7.2.2 Kaolinite Mixtures

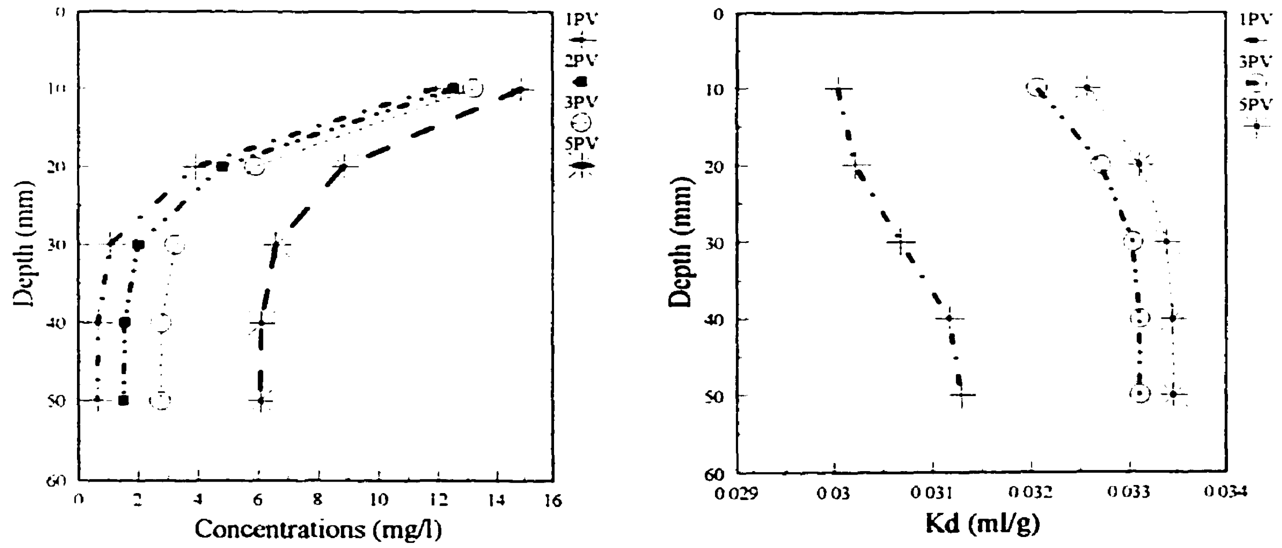
The experimental results of the total lead transported, migrated, adsorbed, and the computed $K_d$ profiles for KS, KC and KSC clay soils are shown in Figure 7.3a-d, 7.4a-d and 7.5a-d, respectively.

As shown in the previous chapters, in the kaolinite mixtures leached with lead, spiked with chloride, the appearance of the lead in the effluent took many days. It was 60 days for KS in the seventh pore volumes of effluent. In the case of the KC or KSC, lead spiked with chloride did not migrate to the effluent until up to 9 pore volumes of the effluent due to the precipitation of lead in the form of Pb $(OH)^2$ or $PbCO_3$ . Whereas, as shown in the Figure 7.3a, 7.4a and 7.5a, using EDTA with lead solution (with the kaolinite mixture, even for KSC for KC) speeded up the migration of the lead and it was observed that in both cases lead appeared in the effluent at the first pore volume. As shown, there is no evidence of lead which was precipitated due to the complexation of lead with EDTA, and little lead was adsorbed compared to the previous case using lead solution spiked with chloride as the permeant. This conclusion may also be drawn from the results of $K_d$ profiles, shown in Figure 7.3d, 7.4d and 7.5d due to low $K_d$ compared to the previous cases using chloride with lead solution.



(a) Total Pb Profiles with EDTA in KS Clay

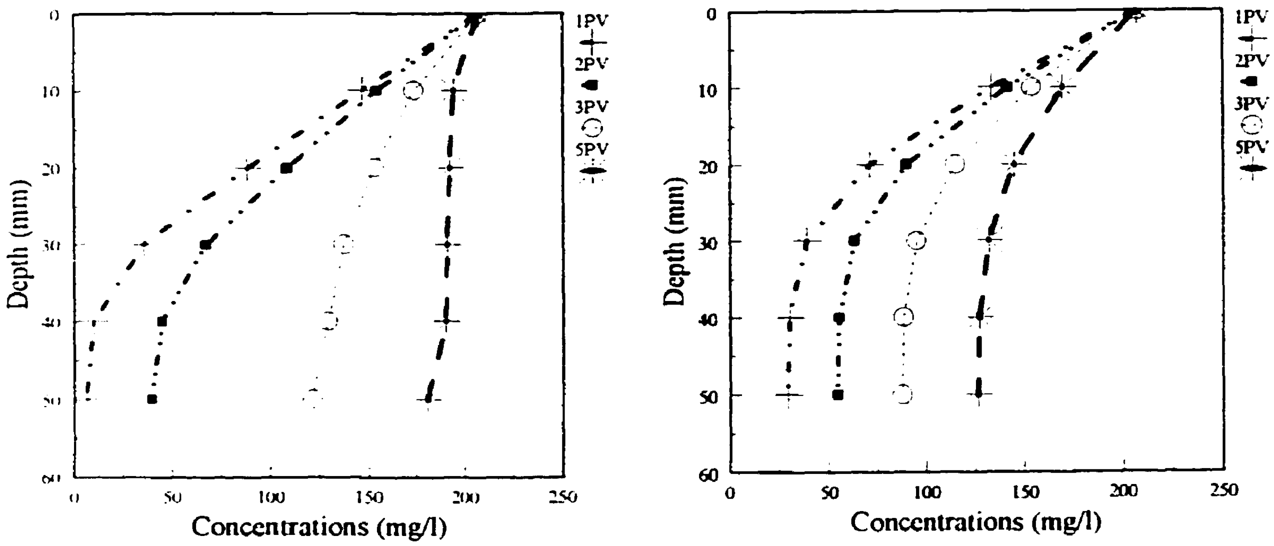
(b) Pb Pore Fluid Profiles with EDTA in KS Clay



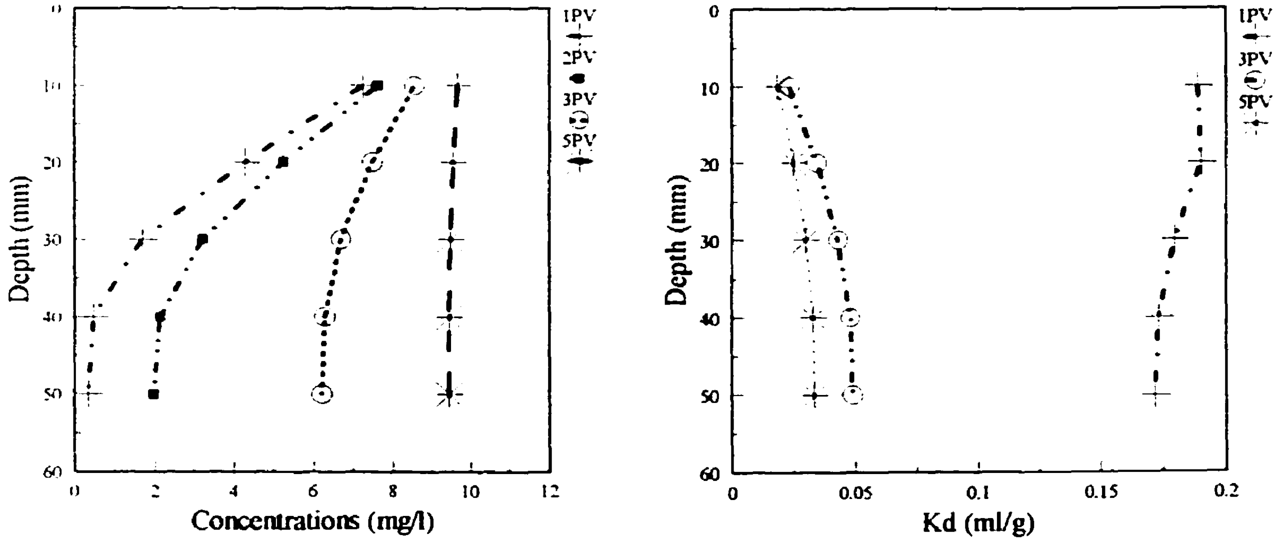
(c) Adsorbed Pb Profiles with EDTA in KS Clay

(d) Kd Profiles for Pb with EDTA in KS Clay

**Fig. 7.3** Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KS Clay.

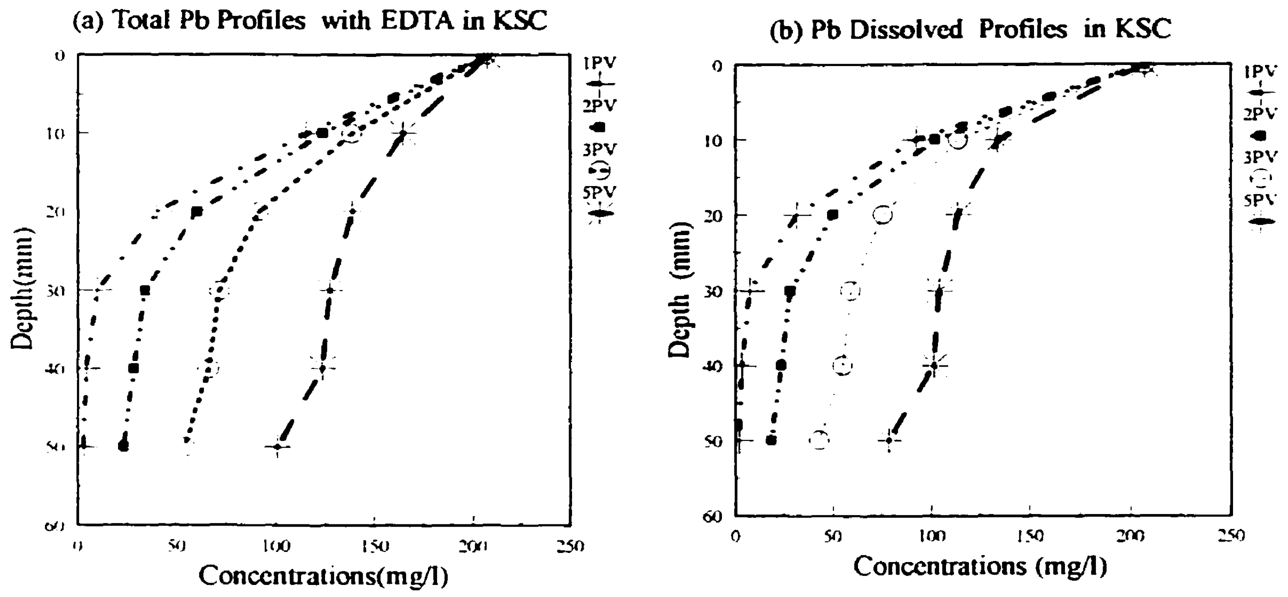

(a) Total Pb Profiles with EDTA in KC Clay

(b) Pore Fluid Pb Profiles with EDTA in KC Clay


(c) Pb Adsorption Profiles with EDTA in KC

(d) Computed Kd Profiles for Pb in KC

Fig. 7.4 Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KC Clay.



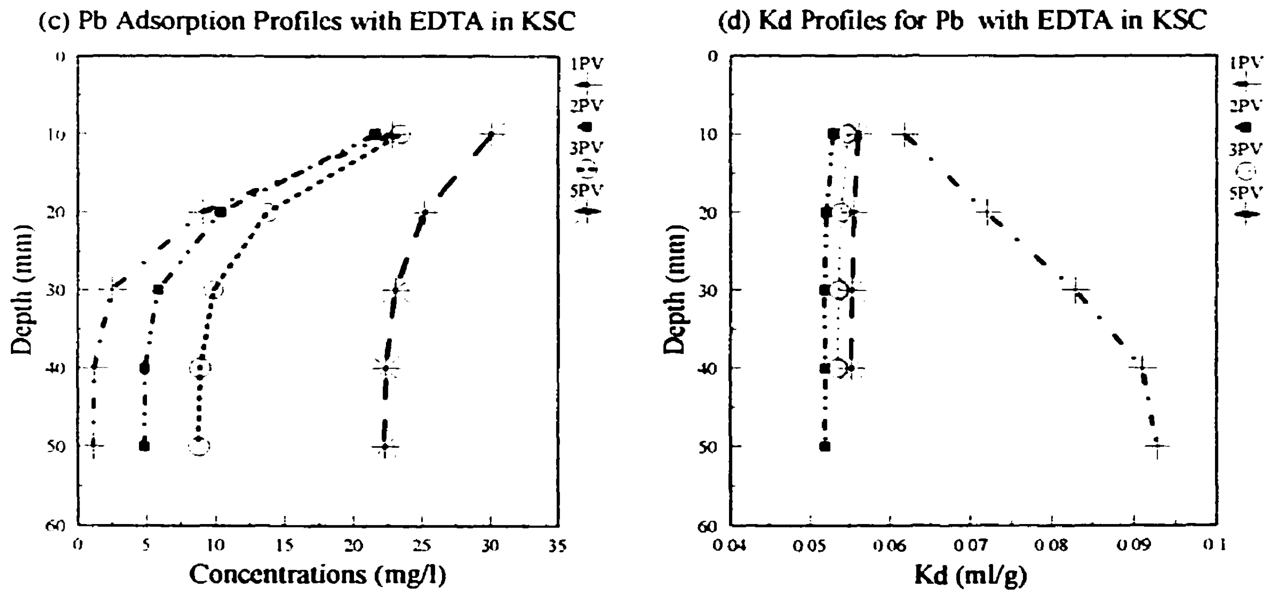


**Fig. 7.5** Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KSC Clay.

## 7.3 Heavy Metal Prediction

To simulate the above experiment by the proposed model (COSTCHESP), the concentration of all components in the leachate were specified in the CHESP model as the total aqueous concentration for each component. The concentration of the kaolinite, silica gel and calcium carbonate, depending of the clay mineral components (K, KS, KC, KSC), was specified as the solids in g/L. The concentration should match with the number of space step. In other words, the solids were specified for one space step. For all simulations, the physico-geochemical parameters were specified depending on the soil type with the exception of hydraulic head and total aqueous concentrations, which were held constant. The experimental results of total lead profiles for the first and third pore volumes were used for the calibrating of the model and to calculate the diffusion coefficient for lead into different clay soils. The resulting parameters are tabulated in Table 7.1 and the computed diffusion coefficients into kaolinite and kaolinite mixtures (KS, KC, KSC) are shown in Figures 7.6a-d, respectively. As shown, the diffusion coefficient is a function of time and space and is dependent on the soil constituent and its adsorption properties. The diffusion coefficient is maximum at the top of the column and minimum at the bottom. The diffusion coefficient is the highest in kaolinite due to the low adsorption and high coefficient of hydraulic conductivity of the kaolinite compared to the three other cases. The diffusion is lowest for KS due to the its high adsorption properties. It was also shown that the diffusion coefficient increases with time and it reaches to steady state. Another indication of the high mobility of lead spiked with EDTA is the results of diffusion coefficients as shown in Figure 7.6a-d. As these graphs show lead diffusion coefficients, in all cases, are much more than those of the previous case for the permeation of lead spiked with chloride. As shown, the diffusion coefficients vary with depth and time, lead migration from transient state to steady state is fast, and breakthrough curves of lead can be seen at low pore volumes of the effluent. This means that the diffusion coefficient may be assumed as a constant parameter for few pore volumes of the effluent at certain circumstances in which complexation ease the migration of cations. Using the above calculated transport parameters, long term total lead transported, migrated (dissolved), adsorbed, and partitioning coefficients into different clay soils (K, KS, KC, KSC) were predicted by the COSTCHESP program and are demonstrated in Figures 7.7a-d to 7.10a-d, respectively. As shown, there is no evidence of lead which was precipitated due to the complexation of lead with EDTA, and little lead was adsorbed compared to the previous case of leaching lead solution with chloride. A sample of the speciation results in the last node of the kaolinite soil column leached with lead spiked with EDTA for the species in solution and other species is shown in Table 7.2 and Table 7.3. The details of the complexation form of lead for the last node of kaolinite and kaolinite mixtures (KS, KC, KSC) can be found in Table E1-E4 in Appendix E.

**Table 7.1** Resulted Diffusion and Chemico-Osmotic Coefficients from PET Program.

| **Soil Type** | **Ion** | **A (cm$^2$/day)** | **B (L/mol)** | **$K_{ch}$ ( cm$^5$/g/day)** |
|---|---|---|---|---|
| Kaolinite | $Pb^{2+}$ | 0.325 | 1412.26 | -9.81 |
| KS | $Pb^{2+}$ | 0.1749 | 1217.16 | -8.89 |
| KC | $Pb^{2+}$ | 0.323 | 1154.11 | -8.82 |
| KSC | $Pb^{2+}$ | 0.1819 | 1271.18 | -8.78 |

**Table 7.2** All Species in Solution for the Last Node of a Kaolinite Soil Column Leached with Lead Solution Spiked with EDTA.

| **ID** | **Name** | **Calc Mol** | **Activity** | **Log Activity** | **Gamma** | **New logk** |
|---|---|---|---|---|---|---|
| 330 | H+1 | 2.050E-05 | 1.872E-05 | -4.72772 | .91295 | .040 |
| 30 | Al+3 | 1.103E-07 | 4.859E-08 | -7.31343 | .44056 | .356 |
| 70 | H4SiO4 | 9.833E-05 | 9.849E-05 | -4.00660 | 1.00171 | -.001 |
| 492 | NO3-1 | 2.000E-03 | 1.826E-03 | -2.73852 | .91295 | .040 |
| 600 | Pb+2 | 5.921E-08 | 4.113E-08 | -7.38581 | .69467 | .158 |
| 969 | EDTA-4 | 9.107E-14 | 2.121E-14 | -13.67351 | .23287 | .633 |
| 811 | ADS1TYP1 | 5.992E+00 | 5.992E+00 | .77759 | 1.00000 | .000 |

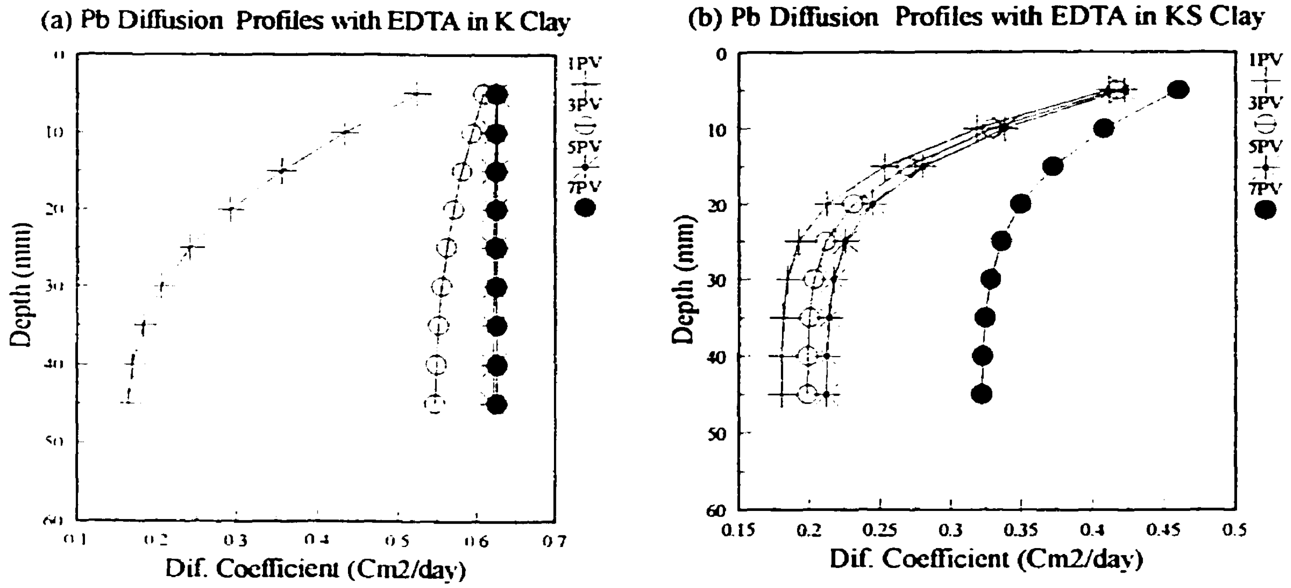
Table 7.3 Other Species in Solution or Adsorbed in the Last Node of Kaolinite Soil Column.

| ID | Name | Calc Mol | Activity | Log Activity | Gamma | New logk |
|---|---|---|---|---|---|---|
| 3307700 | H3SiO4 - | 6.790E-10 | 6.199E-10 | -9.20766 | .91295 | -9.889 |
| 3307701 | H2SiO4 -2 | 9.783E-17 | 6.796E-17 | -16.16776 | .69467 | -21.458 |
| 303300 | AlOH +2 | 3.821E-08 | 2.655E-08 | -7.57600 | .69467 | -4.832 |
| 303301 | Al(OH)2 + | 1.205E-08 | 1.100E-08 | -7.95858 | .91295 | -10.060 |
| 303302 | Al(OH)4 - | 4.323E-12 | 3.947E-12 | -11.40372 | .91295 | -22.960 |
| 303303 | Al(OH)3 AQ | 7.381E-10 | 7.394E-10 | -9.13115 | 1.00171 | -16.001 |
| 6003300 | PbOH + | 4.690E-11 | 4.282E-11 | -10.36838 | .91295 | -7.670 |
| 6003301 | Pb(OH)2 AQ | 8.878E-16 | 8.893E-16 | -15.05095 | 1.00171 | -17.121 |
| 6003302 | Pb(OH)3 - | 5.971E-22 | 5.451E-22 | -21.26353 | .91295 | -28.020 |
| 6003303 | Pb2OH +3 | 8.950E-17 | 3.943E-17 | -16.40419 | .44056 | -6.004 |
| 6004920 | PbNO3 + | 1.217E-09 | 1.111E-09 | -8.95433 | .91295 | 1.210 |
| 6003304 | Pb3(OH)4+2 | 1.073E-27 | 7.452E-28 | -27.12771 | .69467 | -23.722 |
| 6003305 | Pb(OH)4 -2 | 9.619E-29 | 6.682E-29 | -28.17510 | .69467 | -39.541 |
| 6009692 | PBHEDTA | 8.561E-17 | 7.816E-17 | -16.10704 | .91295 | 9.720 |
| 6009693 | PBH2EDTA | 5.064E-25 | 5.073E-25 | -24.29477 | 1.00171 | 6.219 |
| 6009691 | PBEDTA | 9.526E-04 | 6.617E-04 | -3.17932 | .69467 | 18.038 |
| 3309691 | EDTAH | 8.218E-09 | 3.620E-09 | -8.44123 | .44056 | 10.316 |
| 3309692 | EDTAH2 | 1.735E-07 | 1.205E-07 | -6.91896 | .69467 | 16.368 |
| 3309693 | EDTAH3 | 1.104E-09 | 1.008E-09 | -8.99668 | .91295 | 18.900 |
| 3309694 | EDTAH4 | 2.212E-12 | 2.216E-12 | -11.65441 | 1.00171 | 20.929 |
| 3309695 | EDTA H5 | 1.554E-14 | 1.419E-14 | -13.84813 | .91295 | 23.504 |
| 309690 | Al EDTA | 8.966E-03 | 8.186E-03 | -2.08694 | .91295 | 18.940 |
| 8116000 | SOPb | 4.778E-05 | 4.778E-05 | -4.32072 | 1.00000 | 4.959 |
| 8113300 | SO- | 7.483E-01 | 7.483E-01 | -.12593 | 1.00000 | -6.967 |

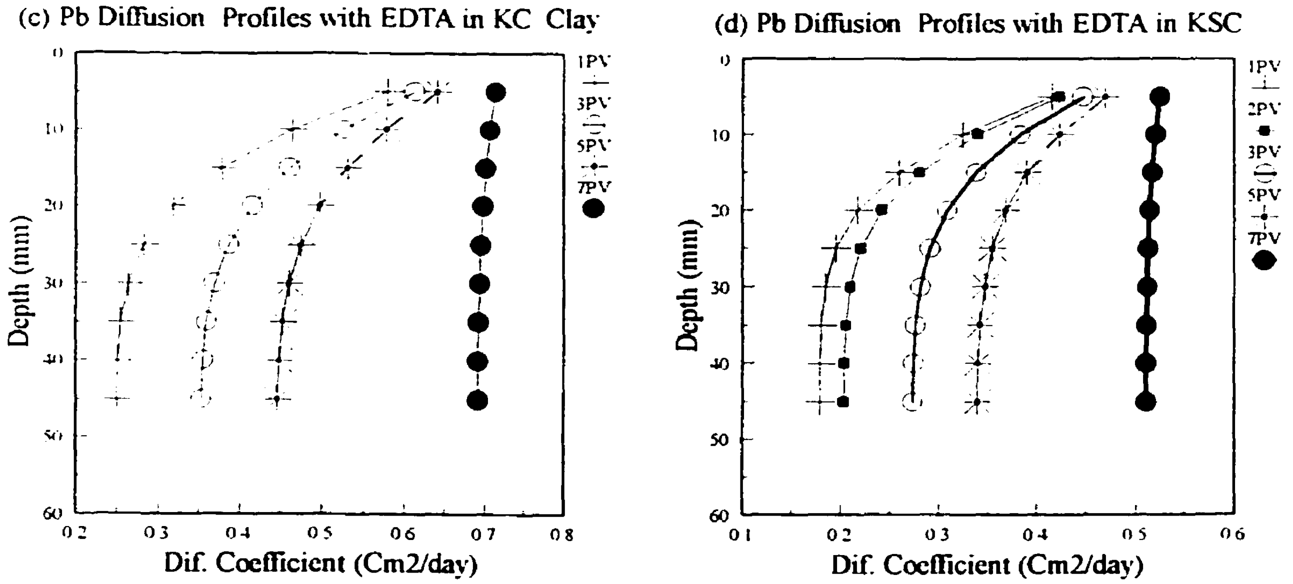
**Table 7.3** Continue

| ID | Name | Calc Mol | Activity | Log Activity | Gamma | New logk |
|---|---|---|---|---|---|---|
| 8113302 | SOH | 7.484E-01 | 7.484E-01 | -.12589 | 1.00000 | 5.160 |
| 309691 | AlHEDTA | 7.666E-05 | 7.680E-05 | -4.11466 | 1.00171 | 21.599 |
| 3300020 | OH- | 5.875E-10 | 5.363E-10 | -9.27057 | .91295 | -13.958 |

It is not possible to compute the adsorption profiles from the $K_d$ approach. As shown, lead appeared at the first pore volume of the passage of leachate in the effluent for kaolinite clay due to low affinity of kaolinite to heavy metals retention. The equivalent $K_d$ was calculated by the program and, as shown in Figures 7.7d, 7.8d, 7.9d and 7.10d, demonstrates the variation of $K_d$ with time and space. As can be seen from the $K_d$ profiles, it decreases with time as more leachate is passed through the column soil.

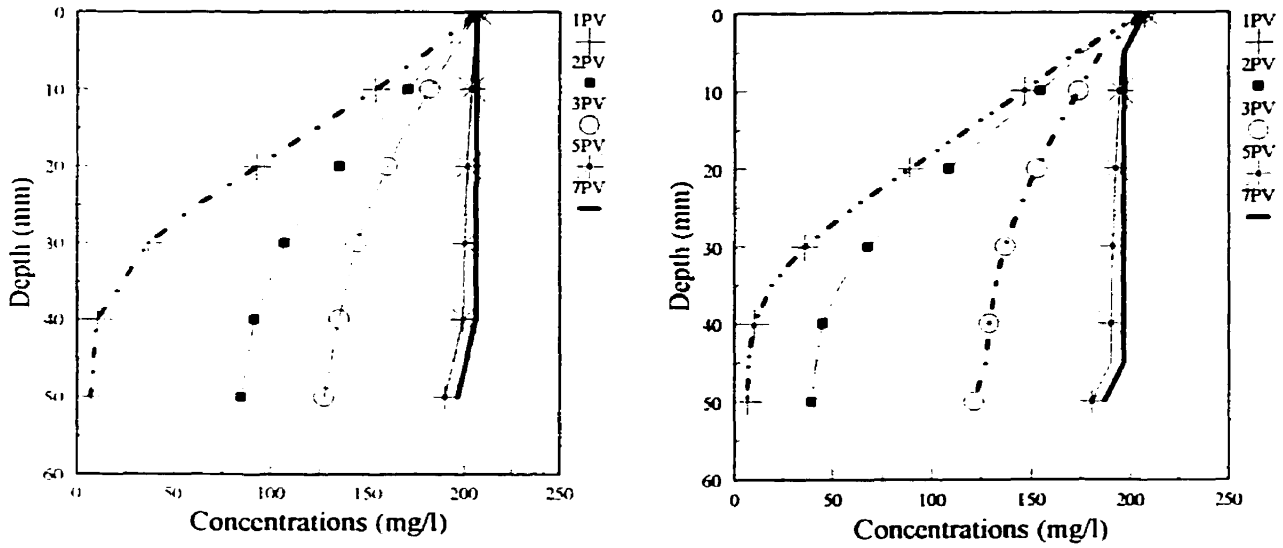

(a) Pb Diffusion Profiles with EDTA in K Clay

(b) Pb Diffusion Profiles with EDTA in KS Clay


(c) Pb Diffusion Profiles with EDTA in KC Clay

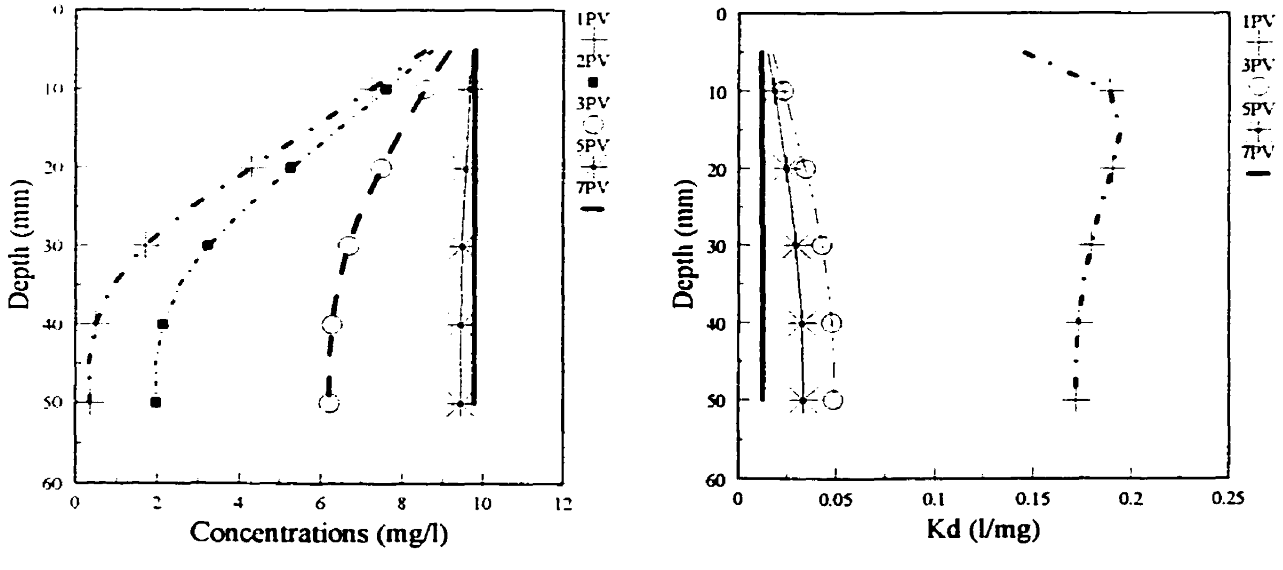
(d) Pb Diffusion Profiles with EDTA in KSC

**Fig. 7.6** Pb Diffusion Coefficient for Lead Spiked with EDTA in Different Clay Soils.



(a) Total Pb Profiles with EDTA in Kaolinite

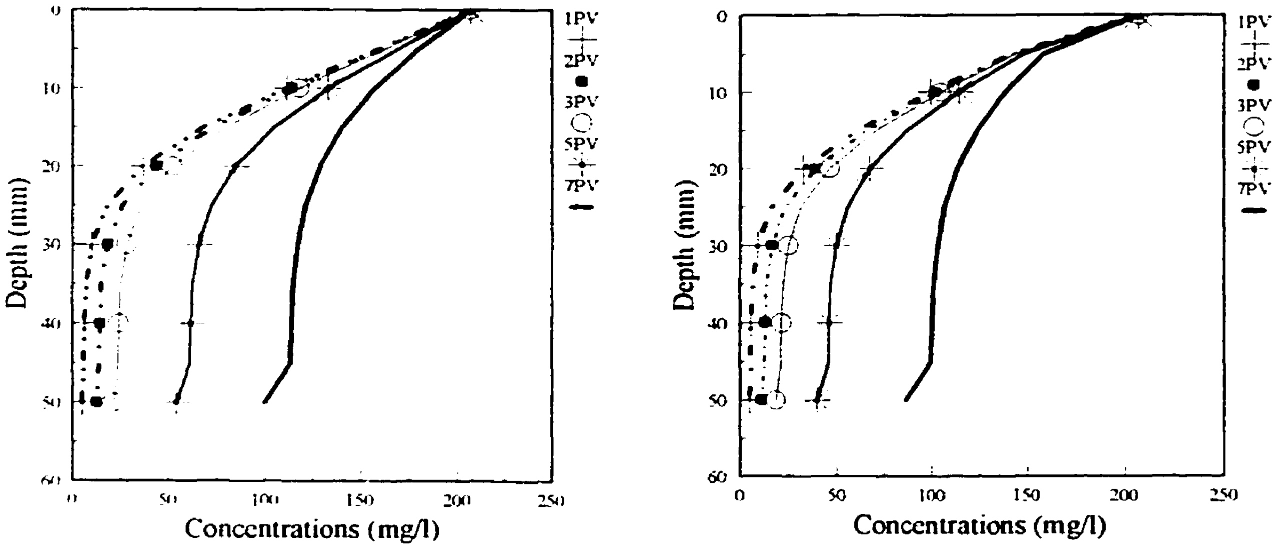
(b) Pb Dissolved Profiles in Kaolinite



(c) Pb Adsorption Profiles with EDTA in Kaolinite

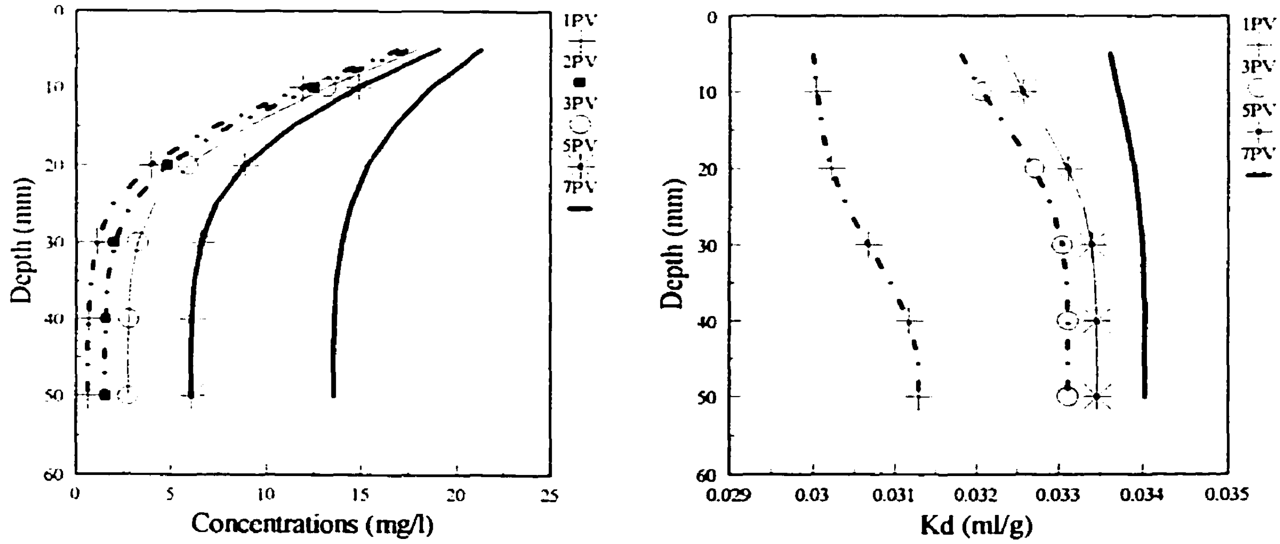
(d) Kd Profiles for Lead with EDTA in Kaolinite

**Fig. 7.7** Predicted Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in Kaolinite.



(a) Total Pb Profiles with EDTA in KS Clay

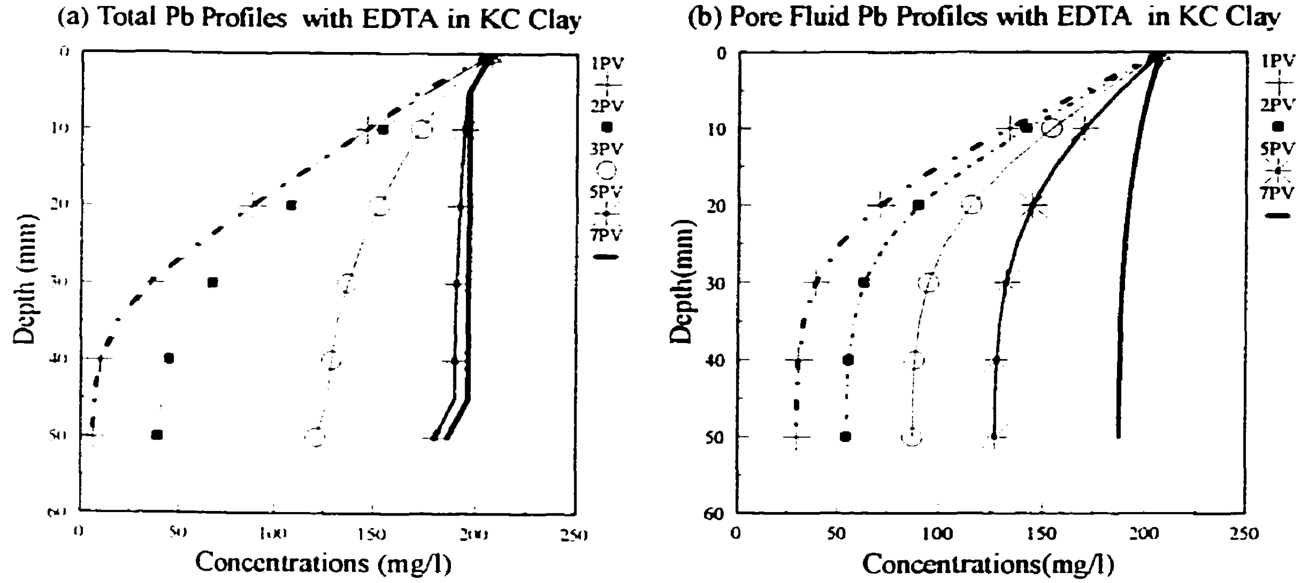
(b) Pb Pore Fluid Profiles with EDTA in KS Clay



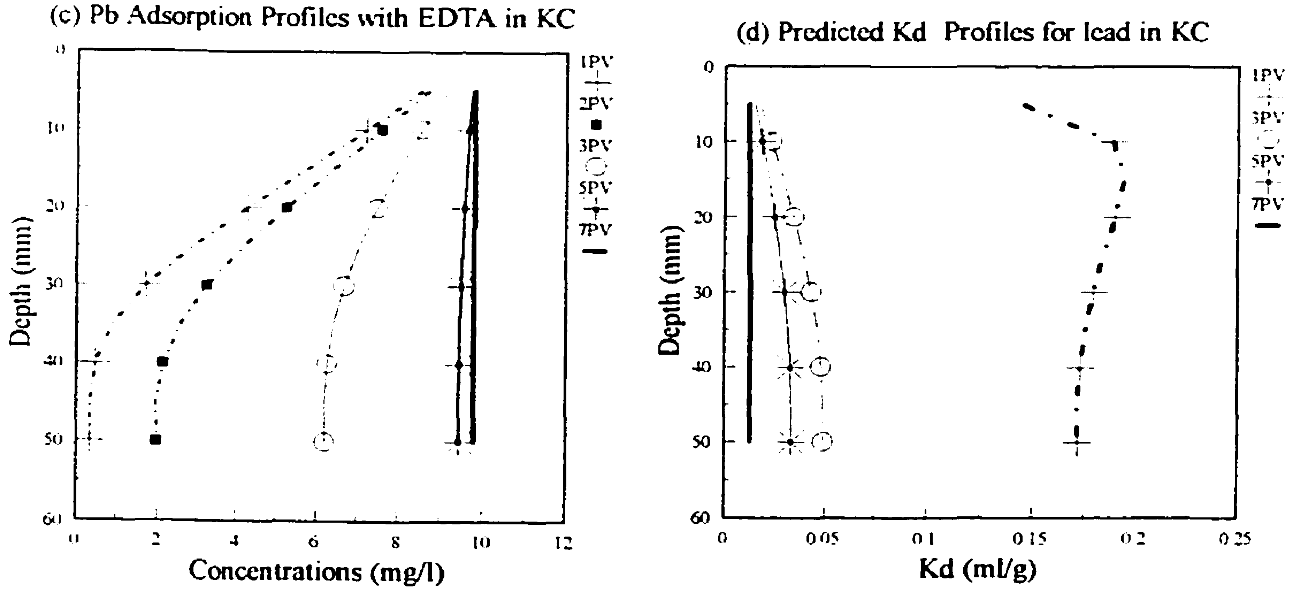
(c) Adsorbed Pb Profiles with EDTA in KS Clay

(d) Kd Profiles for Pb with EDTA in KS Clay

**Fig. 7.8** Predicted Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KS Clay.

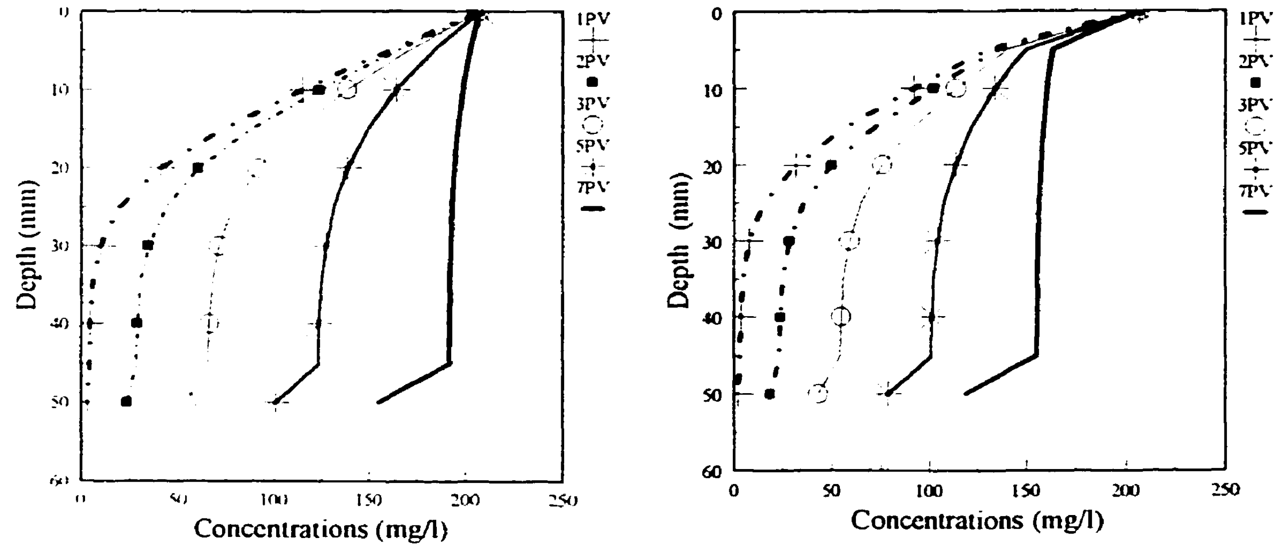

(a) Total Pb Profiles with EDTA in KC Clay

(b) Pore Fluid Pb Profiles with EDTA in KC Clay


(c) Pb Adsorption Profiles with EDTA in KC

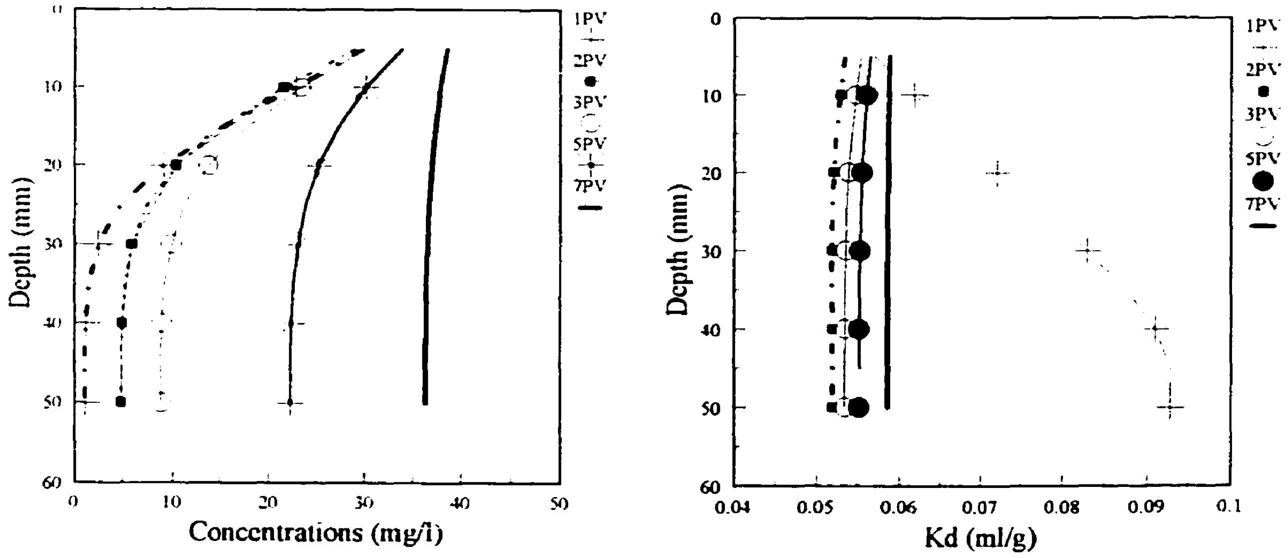
(d) Predicted Kd Profiles for lead in KC

**Fig. 7.9** Predicted Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KC Clay.



(a) Total Pb Profiles with EDTA in KSC

(b) Pb Dissolved Profiles in KSC



(c) Pb Adsorption Profiles with EDTA in KSC

(d) Kd Profiles for Pb with EDTA in KSC

**Fig. 7.10** Predicted Pb Concentration (Transported, Dissolved, Adsorbed), and Kd Profiles with EDTA in KSC Clay.

## 7.4 Summary

The effect of EDTA on the partitioning of lead and the distribution coefficient, $K_d$ for different clay soils at an acidic pH solution have been discussed in this chapter. It has been shown that the presence of other contaminants such as EDTA (as an strong organic complexing agent) significantly affects the migration, adsorption and precipitation profiles of the lead into clay soil.The partitioning coefficient was significantly reduced from the bottom to the top of the column and from low to high pore volumes when due to complextion of lead with EDTA. It is because the concentration of the complexing agent increases and the migration of lead is less to the bottom than the top part of the soil. In other words, the $K_d$ is time and space dependent. The model was able to simulate both solute transport and geochemical reaction of heavy metals with other contaminants and soil compositions in the clay barrier system. The prediction results show good accord between the values predicted and the values measured.

The results confirm that the distribution coefficient ($K_d$) is a function, not only of the contaminant and a given material, but also of a given leachate chemistry and the physicochemical-chemical properties of the soil liner material. Thus, the $K_d$ approach for the prediction of pollutants such as heavy metals is not a proper approach for the design of clay barrier systems. It was shown that attenuation of lead was governed by the adsorption. The results indicated that both $K_d$ and diffusion coefficient are space and time dependent and may not be assumed as a constant parameter. These results can also cast doubt on the validity of $K_d$ determined through batch equilibrium test since it often computed at constant pH. It was shown that the partitioning of the lead is time and space dependent and varies with EDTA concentration, soil constituents. CEC, SSA and pH of the soil solution.

**References:**

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Grand, P., and Norman, J.P., (1993), "Physical and Chemical Lead Decontamination of the Longue-Point Garrison Soils", Joint CSCE-ASCE National Conference on Environmental Engineering, Montreal, Quebec, Canada, pp. 1049-1056.

Mohamed, A.M.O., and Trasente, D., (1996), "Evaluation of EDTA Use for Metal Removal from Naturally Contaminated Geomaterial", 49th Canadian Geotechnical Conference, Frontier in Geotechnology, St. John's Newfoundland, Sep. 23-25, 1996.

Peters, R. B., and Shem, L., (1992), "Adsorption/Desorption Characteristics of Lead on Various Types of Soil", Environmental Progress, Vol. 11, No.3, pp 234-240.

Raghavan, R., Coles, E., Dietz, D., and Foster Wheeler Enviresponse Inc., (1989), "Cleaning Soil Using Extraction Agents. A State-of-the-Art Review", EPA/600/2-89/034/, U.S. EPA, Cincinnati, Ohio.

Trasente, D., (1995), "Evaluation of EDTA Use for Metal-ion Removal from Contaminated Soil, M. Eng. Project Report, Department of Civil Engineering and Applied Mechanics, McGill University.

# Chapter 8

# Desorption of Heavy Metals

## 8.1 General

In response to an increased demand, many treatment technologies for heavy metals contaminated waste in all soils have been developed. The standard remedial technique of evacuating and transporting contaminated soils to a secure landfill is quickly becoming a thing of the past since it is associated with high costs, liability insurance, and requires regulatory approval. One technology that is an alternative to land disposal is on-site treatment of excavated soil by soil washing. Soil washing involves soil excavation; above ground treatment to isolate, remove, or destroy contaminants; and reuse of the clean soil for fill or other purposes. (Raghavan *et al.* 1989). On-site soil washing has been successfully applied in Canada and the United States. Soil washing techniques can be performed by either in-site soil techniques or on-site extraction (Trasente, 1995). In the case of on-site extraction following excavation, the operation can be performed on a batch basis, or continuously.

An on-site extraction technique can be very expensive and result in a soil mass with an unacceptable long term stability. In the case of in-situ soil flooding, the aqueous extractive reagent is allowed to percolate through the soil to promote metals mobilization. One of the factors limiting the use of soil washing for heavy metals contaminated in different soils, however, is that a demonstrated performance record is not yet available; so uncertainty exists as to whether regulatory driven and risk-based contaminant levels can be achieved. Thus, there is a need to demonstrate that soil washing can successfully treat heavy metal-contaminated soils and to identify factors affecting washing performance.

The purpose of this chapter is to evaluate and compare the performance of EDTA and sodium acetate, in terms of their ability to extract heavy metals from different contaminated soil columns. The precontaminated kaolinite clay or kaolinite mixtures (KS, KC, KSC) from the leaching experiment were used for the decontamination processes by leaching with EDTA or sodium acetate. A very limited number of column leaching tests, for the contaminated soil with heavy metals (lead), has been carried out. Then, using the experimental data, long term soil remediation has been predicted through the COSTCHESP proposed model.

## 8.2 Remobilization of Heavy Metals by EDTA

A variety of chemical technologies may be of value in the extraction of heavy metals from soils, including washing with water salts, or complexing agents such as ethylene diamine-tetra acetic acid (EDTA), and sodium acetate (Van Benschoten, *et al.*, 1997; Mohamed and Trasente, 1996). Soil washing removes contaminants, resulting in a permanent solution to the contamination problem, the recycling of clean soil, and improved future land-use options.

On-site soil washing using a chelating resin has been used to remove lead from the Longue Pointe military base in Montreal, Quebec (Garand and Normand, 1993). The process used at this site exhibited Pb extraction efficiencies of 86.6% to 95.3%. Concentrations of 13-16% EDTA have been used to remove 94-97% of total lead from the Church of God contaminated site in Leeds, Alabama using a 4-5 ton/hour capacity pilot process (Raghaven *et al.*, 1989). Peters and Shem (1992) studies indicated that lead recovery equilibrium between 0.2M EDTA and 100 mg/kg lead-contaminated soil was reached within 30 minutes of contact time, while lead recovery equilibrium between 0.2 nitrilo-triacetic acid ( NTA) and 100 mg/kg lead-contaminated soil was reached only after 3 hours. Van Benschoten *et al.*, (1997) studies indicate that the average cost for soil washing ranges from $120 to $200 per ton of soil treated compared to less than $100 per ton for solidification/stabilization (S/S) technologies. However, the additional costs for S/S may include transportation and landfill disposal, which may make soil washing a cost-competitive remediation.

The mobilization of contaminated illite soil with heavy metals through soil washing by EDTA has been successfully performed by Castellan (1996). His test indicated that the best EDTA performance was achieved using EDTA with a concentration of 0.01 mole/L and with a pH level of 4-5. Sodium acetate has often been used to remobilize the heavy metals from the carbonated soil (Cabral and Yong, 1991; Yong *et al.*, 1995) using a concentration of 0.2 mole of sodium acetate at a pH of 5.0. Their tests were accomplished through the batch equilibrium test which is quite different from the actual field for a clay liner in the landfill. Thus the effectiveness of EDTA and sodium acetate to remove heavy metals in different clay soils in column tests will be investigated in the following section.

## 8.3 Experimental Results and COSTCHESP Application

The column soils which were used for remediation by EDTA were the precontaminated soils in the first part of the column leaching test in which soils were permeated up to seven pore volumes of effluent, with a solution of lead at a concentration of 1 mmol/L and sodium chloride at a concentration of 0.05 mol/L. Thus, the total lead profile along the column was known from the previous experiments. The above contaminated soil was permeated with EDTA at a concentration of 0.01 mol/L and with a pH of 4.5 and KC soil was leached with sodium acetate at a concentration of 0.2 mole with a pH of 5.0. EDTA is available in two forms: $H_4Y$ $Na_2H_2Y \times 2H_2O$, or $Na_4H_4Y \times 2H_2O$. The notation Y refers to the fully deprotonated form of EDTA. Since the tetra sodium form is most soluble in water, this form of EDTA was chosen for this study.

### 8.3.1 Kaolinite Results

#### 8.3.1.1 Total Aqueous Lead Profiles

The experimental results of the total aqueous lead concentration using EDTA for kaolinite contaminated soil, is shown in the Figure 8.1. The total aqueous lead results are plotted using equilibrium pore fluid concentration versus depth for various leachate PVs.

As shown in Figure 8.1, the concentrations of $Pb^{2+}$ in the pore fluid have decreased with PV through the soil column as a function of leachate PV. This is because, lead transported from the solid phase to the soluble phase due to complex formation with EDTA and then migrated to the effluent. The lead in the effluent will increase with time as a function of leachate PVs. The total lead transported to the effluent can be calculated through the mass balance using total introduced lead minus the mass of the total lead in the effluent. The total mass introduced after 5 pore volumes will be equal to 51.075 mg and the total lead in the effluent after 5 pore volumes is 4.5 mg , thus, the total mass which was transported to the effluent is equal to 46.575 mg. As shown, EDTA could mobilize almost all of the leads, which were retained in the soil column, to the aqueous phase due to the complex formation with lead. The EDTA removed the retained lead along the column which was adsorbed rather than the precipitated. This is because the pH of the soil solution and leachate was in an acidic condition.

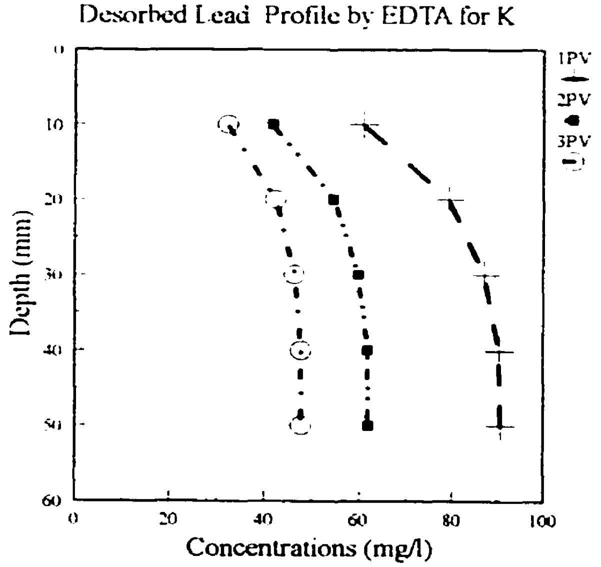


**Figure 8.1** Dissolved Lead Profiles into Kaolinite Soil.

### 8.3.1.2 Partitioning Coefficient Profiles

The experimental results of the partitioning coefficient, $K_d$ of the soil column for the first, second and third pore volume of the effluent are shown in the Figures 8.2. The $K_d$ profiles are computed, using the remaining retained lead for each slice of soil divided by lead pore fluid concentrations, to evaluate how fast the retained lead transported to the aqueous phase with time and space. The results of $K_d$ profiles shown in Figure 8.2 suggest that they have decreased with time and increased with space which is the reverse of the adsorption column test, described in the previous chapter. As shown, the computed $K_d$ is least at the top and maximum at the bottom of the column and decreases with time. The partition coefficient is at maximum for the first pore volume. The computed $K_d$ is very small compared to the previous cases in the adsorption test, using EDTA and lead solution as the permeant which shows that almost all of the adsorbed lead was transported to the aqueous phase.

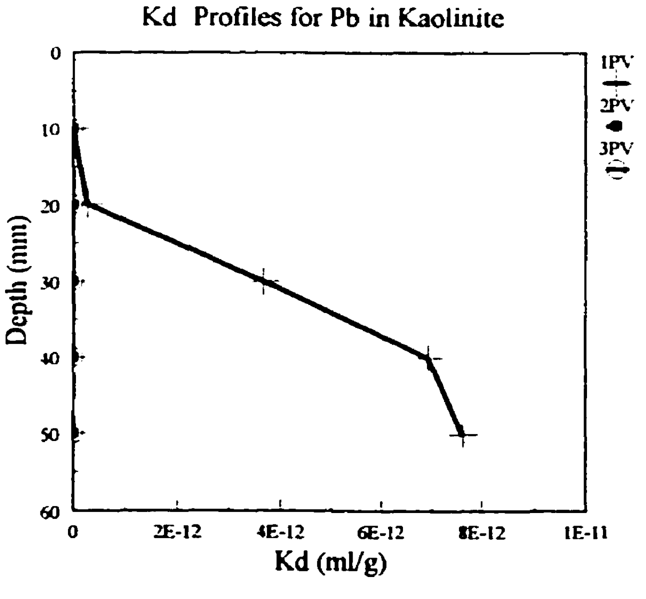


Figure 8.2 Computed Kd Profiles for Lead into Kaolinite Soil.

### 8.3.1.3 pH Profiles

The experimental results of pH profiles of the soil column for the first, second and third pore volume of the efflunet are shown in the Figures 8.3. As illustrated, the pH was not affected by the leachate solution and remained unchanged within the range of the experiment due to the closeness of the pH of the leachate solution (4.5) to the pH of the kaolinite soil (4.7). The pH, after an initial increase due to the buffer capacity of the soil, decreased with time along the depth of the column soil.

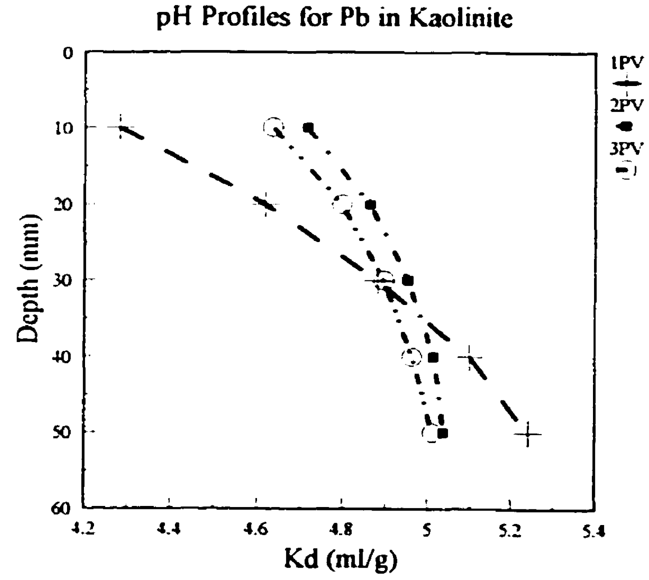


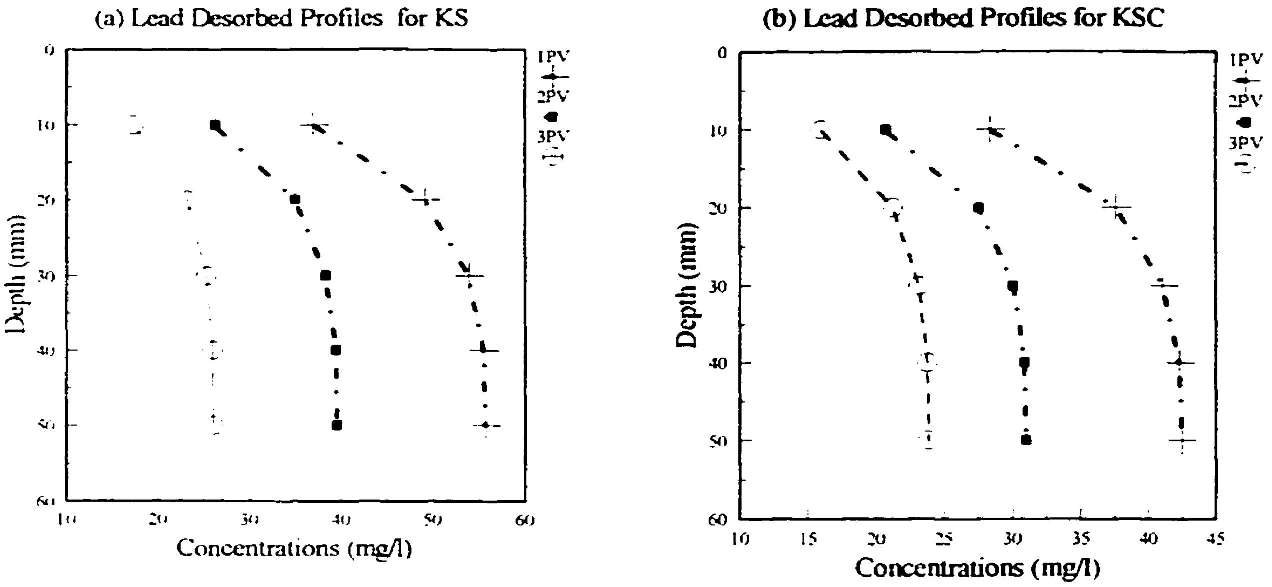
Figure 8.3 pH Profiles for Lead mobili zation with EDTA into Kaolinite Soil.

### 8.3.2 Kaolinite Mixtures

Since sodium acetate was recommended by (Yanful *et al.*, 1988; Yong *et al.*, 1995) for desorption of heavy metals from the carbonated soil, thus, sodium acetate was used only for lead contaminated in KC soil and the results were compared with using EDTA in the same soil and condition.

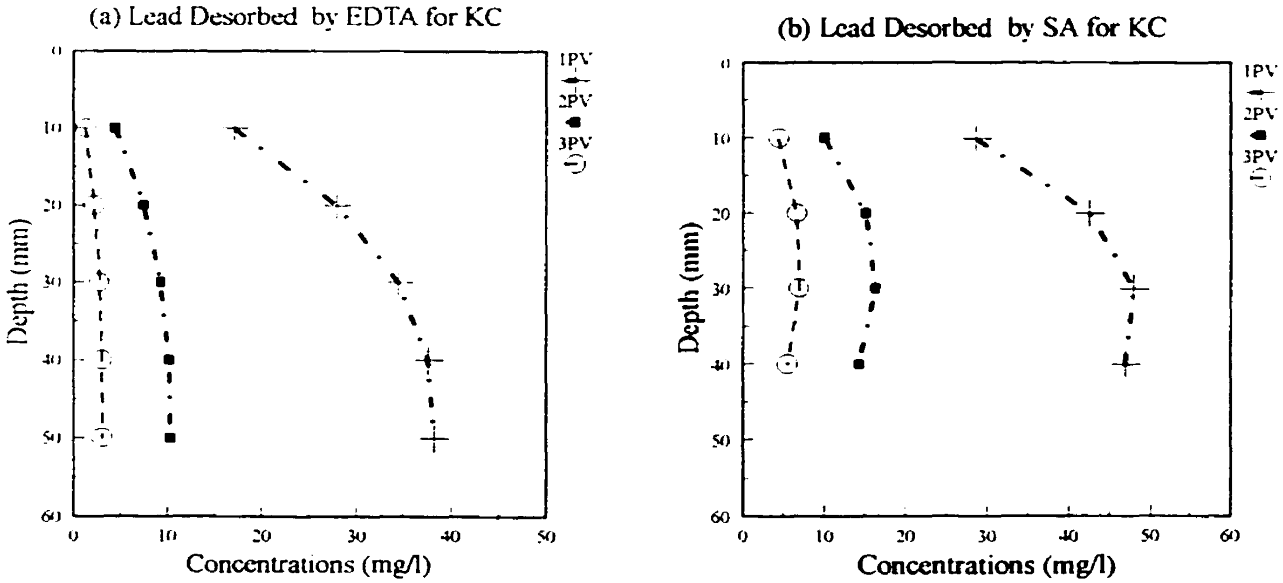
#### 8.3.2.1 Total Aqueous Lead Profiles

The experimental results of the total aqueous lead profiles for kaolinite mixtures (KS, KSC) using EDTA are shown in Figures 8.4a and 8.4b. The experimental results of the total aqueous lead profiles for KC soil, using EDTA and sodium acetate, are also shown in Figures 8.5a and 8.5b, respectively. As shown, EDTA could remove lead from different clay soils retained along the soil column and transport it to the aqueous phase. The EDTA removed the retained lead along the column which was adsorbed and precipitated. Sodium acetate is less effective for the remobilisation of the lead into the aqueous phase. As shown, the appearance of the lead in the effluent occurred at the first pore volume of the effluent. The total mass of lead which was transported into effluent will be equal to the total introduced mass. This is because no lead was transported to the effluent up to seven pore volumes of the effluent due to the retention of the lead at the top part of the column soil. Or in other words, kaolinite mixture soils are more contaminated than the kaolinite soil. Lead was detected for all types of the kaolinite mixtures at the first pore volumes of the effluent which occurred after 8 days due to the complex formation of lead with EDTA.


(a) Lead Desorbed Profiles for KS

(b) Lead Desorbed Profiles for KSC

Figure 8.4 Lead Desorbed Profiles for KS and KSC Soil Using EDTA.


(a) Lead Desorbed by EDTA for KC

(b) Lead Desorbed by SA for KC

**Figure 8.5** Lead Desorbed Profiles for KC Soil Using EDTA and Sodium Acetate.

### 8.3.2.2 Partitioning Coefficient Profiles

The experimental results of the lead partitioning coefficient profiles, $K_d$ along the soil column at the the first, second and third pore volume of the effluent for KS and KSC are shown in the Figures 8.6a and 8.6b. The experimental results of the lead partitioning coefficient profiles for KC soil, using EDTA and sodium acetate, are also shown in Figures 8.7a and 8.7b, respectively. As shown, EDTA could remove lead from different clay soils retained along the soil column and transport it to the aqueous phase. Sodium acetate is less effective for the remobilisation of the lead into the aqueous phase as shown by the higher $K_d$ profile results. The results of $K_d$ profiles indicate that they have decreased with time and increased $K_d$ with space that was inverse in case of an adsorption column test. The $K_d$ is maximum at the first pore volume. The computed $K_d$ is very small compared to the previous cases in adsorption test which shows that almost all of the retained lead was mobilized. The computed $K_d$ is larger in kaolinite mixtures than the kaolinite soil which shows that not all of the adsorbed lead was transported to the aqueous phase.

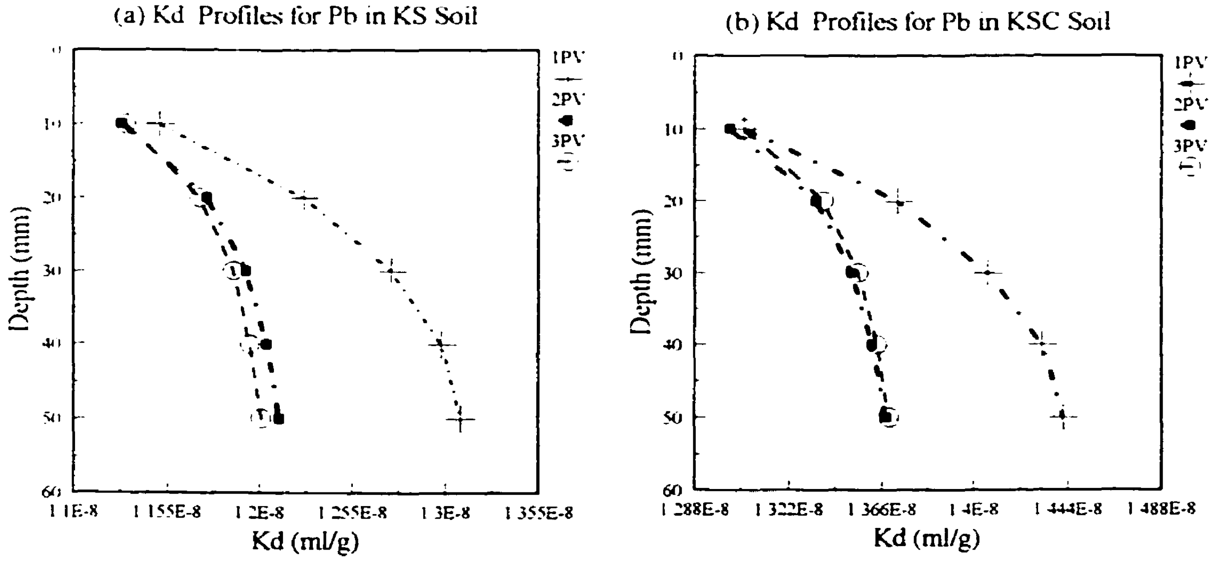


**Figure 8.6** Kd Profiles for KS and KSC Soil Using EDTA.

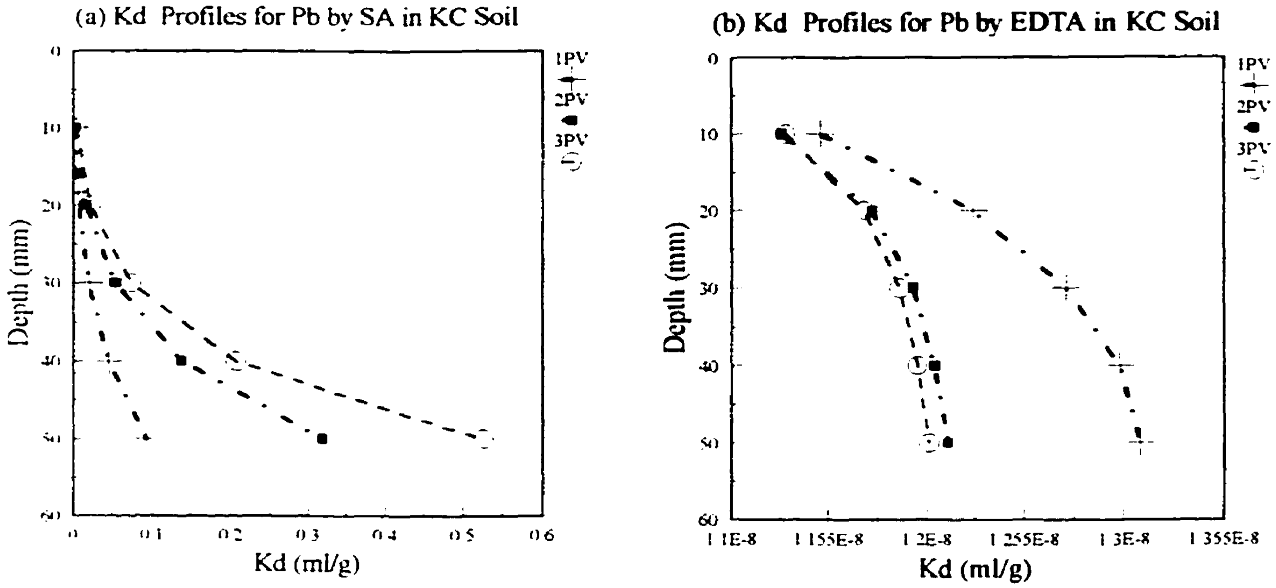
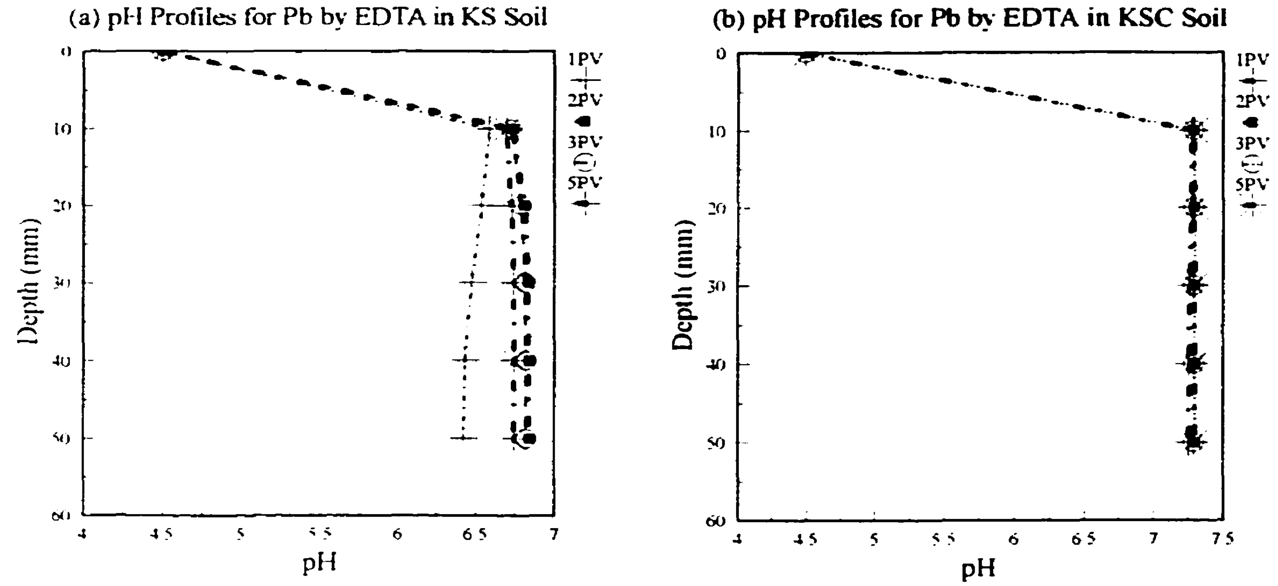


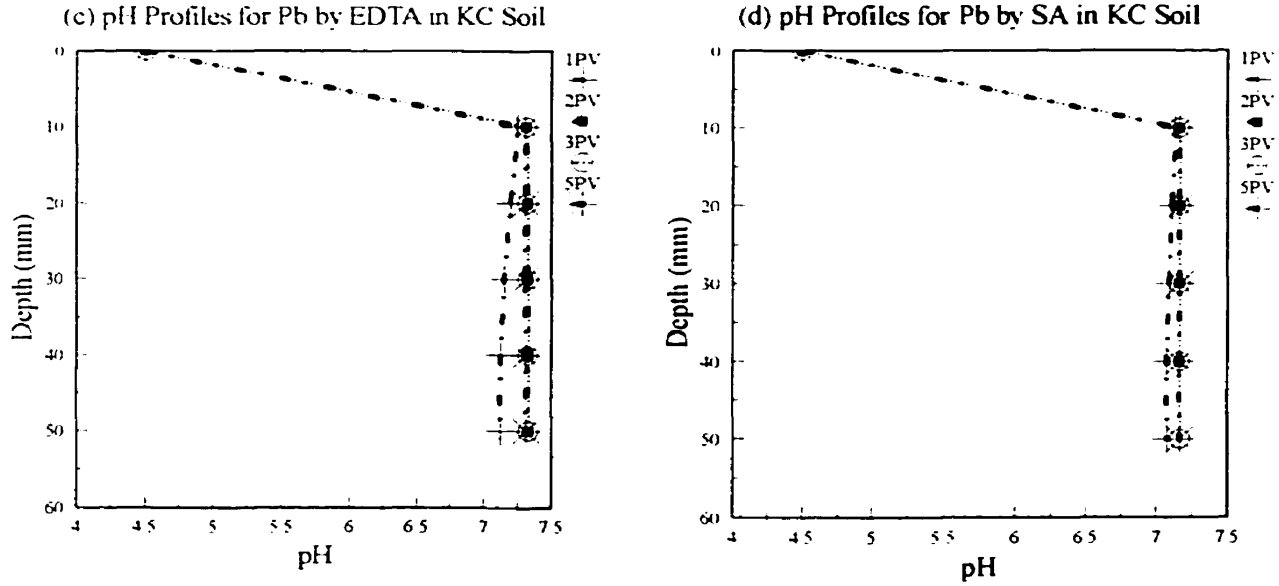
**Figure 8.7** Kd Profiles for KC Soil Using EDTA and Sodium Acetate.

### 8.3.2.3 pH Profiles

The experimental results of the pH profiles of the soil column at the the first, second and third pore volume of the effluent for KS, KSC and KC soils using EDTA and for KC soil using sodium acetate are shown in the Figures 8.8a-8.8c and 8.8d, respectively. As illustrated, the pH remained above 6.0 for KS soil and above 7.0 for KSC and KC soil along the column due to the high buffer capacity of the kaolinite mixtures soils. The pH of the premeant solution was 4.5.


(a) pH Profiles for Pb by EDTA in KS Soil

(b) pH Profiles for Pb by EDTA in KSC Soil


(c) pH Profiles for Pb by EDTA in KC Soil

(d) pH Profiles for Pb by SA in KC Soil

**Figure 8.8** pH Profiles for KC Soil Using EDTA and Sodium Acetate.

## 8.4 Prediction

The above experimental results were used for the calibration of the COSTCHESP.The experimental results of total lead profiles for first and third pore volumes were used for the calibration of the model and to calculate the diffusion coefficient for lead into different clay soils. In order to simulate the decontamination experiment by the COSTCHESP, the concentration of lead was specified as the background concentration along the soil column. The input concentrations for all components at the upper boundary condition, except the EDTA, were initiated to zero, other geochemical parameters were kept as in the previous cases.

The computed diffusion coefficient for lead into kaolinite and kaolinite mixtures (KS, KC, KSC) using EDTA are shown in Figures 8.9a-d, respectively. The computed diffusion coefficient into KC using sodium acetate as the permeant is shown in Figures 8.9e. As shown, the diffusion coefficient is a function of time and space and is dependent on soil constituent and its desorption properties. The diffusion coefficient is least at the top of the column and maximum at the bottom, contrary to the adsorption cases shown in previous chapter. The diffusion coefficient is maximum for the kaolinite due to the highest desorption of lead from the kaolinite. The diffusion is lowest for KSC due to its low desorption properties. It was also shown that the diffusion coefficient increases with time and it reaches a steady state. Using the above calculated transport parameters, long term remediation of the different clay soils are predicted by the COSTCHESP program and are demonstrated in Figures 8.10a-d and 8.10e for K, KS, KC and KSC soil, using EDTA and sodium acetate, respectively. The results of the predicted $K_d$ profiles for the above cases are also shown in Figure 8.11a-e.

A sample of the speciation results in the last node of the contaminated kaolinite soil column leached with EDTA and sodium acetate for the species in solution and other species is shown in Table 8.1 to Table 8.4., respectively. The details of the complexation form of lead in the last node for kaolinite and kaolinite mixtures (KS, KC, KSC) can be found in Table E1-E4 in Appendix E.

Table 8.1 - Components as Species in Solution at the Last Node for KC Soil Using EDTA

| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 330 | H+1 | 6.212E-08 | 4.531E-08 | -7.34376 | .72946 | .137 |
| 30 | Al+3 | 7.665E-14 | 4.483E-15 | -14.34847 | .05848 | 1.233 |
| 770 | H4SiO4 | 1.440E-05 | 1.517E-05 | -4.81901 | 1.05362 | -.023 |
| 150 | Ca+2 | 3.856E-05 | 1.092E-05 | -4.96187 | .28315 | .548 |
| 492 | NO3-1 | 2.000E-03 | 1.459E-03 | -2.83597 | .72946 | .137 |
| 140 | CO3-2 | 1.084E-03 | 3.069E-04 | -3.51306 | .28315 | .548 |
| 600 | Pb+2 | 1.419E-11 | 4.019E-12 | -11.39587 | .28315 | .548 |
| 969 | EDTA-4 | 1.445E-08 | 9.286E-11 | -10.03215 | .00643 | 2.192 |

Table 8.2 - Components as Species in Solution at the Last Node for KC Soil Using SA.

| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 330 | H+1 | 5.794E-07 | 5.292E-07 | -6.27640 | .91324 | .039 |
| 492 | NO3-1 | 2.000E-03 | 1.826E-03 | -2.73839 | .91324 | .039 |
| 600 | Pb+2 | 1.688E-07 | 1.174E-07 | -6.93032 | .69557 | .158 |
| 500 | Na+1 | 9.808E-04 | 8.957E-04 | -3.04785 | .91324 | .039 |
| 150 | Ca+2 | 4.689E-04 | 3.261E-04 | -3.48662 | .69557 | .158 |
| 770 | H4SiO4 | 9.752E-05 | 9.769E-05 | -4.01016 | 1.00169 | -.001 |
| 140 | CO3-2 | 1.136E-08 | 7.901E-09 | -8.10230 | .69557 | .158 |
| 30 | Al+3 | 2.505E-12 | 1.107E-12 | -11.95599 | .44185 | .355 |
| 992 | Acetate | 9.677E-03 | 8.837E-03 | -2.05368 | .91324 | .039 |

Table 8.3 Other Species in Solution or Adsorbed at the Last Node for KC Soil Using EDTA.

| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 8111500 | =1SOca | 3.884E-04 | 3.884E-04 | -3.41075 | 1.00000 | -5.310 |
| 1509691 | CaHEDTA | 6.298E-07 | 4.594E-07 | -6.33777 | .72946 | 16.137 |
| 309690 | Al EDTA | 4.533E-06 | 3.307E-06 | -5.48062 | .72946 | 19.037 |
| 309691 | AlHEDTA | 7.128E-11 | 7.510E-11 | -10.12438 | 1.05362 | 21.577 |
| 3300020 | OH- | 3.028E-07 | 2.209E-07 | -6.65582 | .72946 | -13.861 |
| 3307700 | H3SiO4 - | 5.407E-08 | 3.944E-08 | -7.40404 | .72946 | -9.792 |
| 3307701 | H2SiO4 -2 | 6.308E-12 | 1.786E-12 | -11.74811 | .28315 | -21.069 |
| 1503300 | CaOH + | 8.304E-11 | 6.058E-11 | -10.21769 | .72946 | -12.461 |
| 1501400 | CaHCO3 + | 4.607E-05 | 3.361E-05 | -4.47359 | .72946 | 11.482 |
| 1501401 | CaCO3 AQ | 4.519E-06 | 4.761E-06 | -5.32232 | 1.05362 | 3.130 |
| 303300 | AlOH +2 | 3.562E-12 | 1.009E-12 | -11.99629 | .28315 | -4.442 |
| 303301 | Al(OH)2 + | 2.360E-10 | 1.721E-10 | -9.76411 | .72946 | -9.963 |
| 303302 | Al(OH)4 - | 1.436E-08 | 1.048E-08 | -7.97975 | .72946 | -22.863 |
| 303303 | Al(OH)3 AQ | 4.523E-09 | 4.765E-09 | -8.32193 | 1.05362 | -16.023 |
| 6001400 | Pb(CO3)2-2 | 5.834E-08 | 1.652E-08 | -7.78199 | .28315 | 11.188 |
| 6003300 | PbOH + | 2.362E-12 | 1.723E-12 | -11.76368 | .72946 | -7.573 |
| 6003301 | Pb(OH)2 AQ | 1.399E-14 | 1.474E-14 | -13.83150 | 1.05362 | -17.143 |
| 6003302 | Pb(OH)3 - | 5.101E-18 | 3.721E-18 | -17.42932 | .72946 | -27.923 |
| 6003303 | Pb2OH +3 | 2.651E-21 | 1.550E-22 | -21.80955 | .05848 | -5.127 |
| 6004920 | PbNO3 + | 1.189E-13 | 8.673E-14 | -13.06183 | .72946 | 1.307 |
| 6003304 | Pb3(OH)4+2 | 7.065E-29 | 2.000E-29 | -28.69887 | .28315 | -23.332 |

Table 8.3 Continue

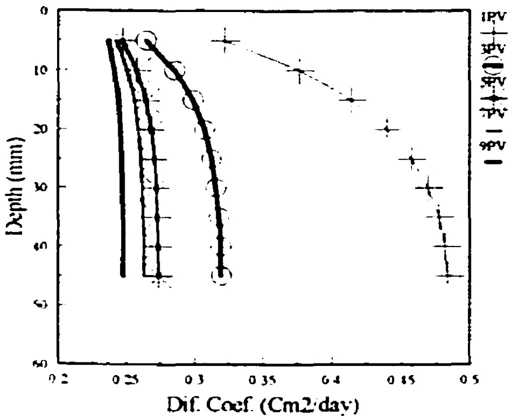
| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 6001401 | PbCO3 AQ | 2.034E-08 | 2.143E-08 | -7.66893 | 1.05362 | 7.217 |
| 6003305 | Pb(OH)4 -2 | 6.635E-22 | 1.879E-22 | -21.72614 | .28315 | -39.151 |
| 6001402 | PbHCO3 + | 1.214E-09 | 8.858E-10 | -9.05268 | .72946 | 13.337 |
| 3301400 | HCO3 - | 4.071E-01 | 2.970E-01 | -.52725 | .72946 | 10.467 |
| 3301401 | H2CO3 AQ | 2.869E-02 | 3.023E-02 | -1.51958 | 1.05362 | 16.658 |
| 6009692 | PBHEDTA | 1.110E-19 | 8.095E-20 | -19.09177 | .72946 | 9.817 |
| 6009693 | PBH2EDTA | 1.207E-30 | 1.272E-30 | -29.89553 | 1.05362 | 6.197 |
| 6009691 | PBEDTA | 9.999E-04 | 2.831E-04 | -3.54801 | .28315 | 8.428 |
| 3309691 | EDTAH | 6.562E-07 | 3.838E-08 | -7.41591 | .05848 | 11.193 |
| 3309692 | EDTAH2 | 1.092E-08 | 3.093E-09 | -8.50967 | .28315 | 16.758 |
| 3309693 | EDTAH3 | 8.582E-14 | 6.260E-14 | -13.20342 | .72946 | 18.997 |
| 3309694 | EDTAH4 | 3.163E-19 | 3.333E-19 | -18.47718 | 1.05362 | 20.907 |
| 3309695 | EDTA H5 | 7.080E-24 | 5.165E-24 | -23.28694 | .72946 | 23.601 |
| 1509690 | Ca EDTA | 8.994E-03 | 2.547E-03 | -2.59402 | .28315 | 12.948 |
| 8113300 | =1SO- | 2.675E+00 | 2.675E+00 | .42735 | 1.00000 | -5.910 |
| 8113301 | =1SOH+ | 2.675E+00 | 2.675E+00 | .42735 | 1.00000 | 6.150 |
| 8116000 | =1SOHPb | 3.870E-09 | 3.870E-09 | -8.41228 | 1.00000 | 9.230 |

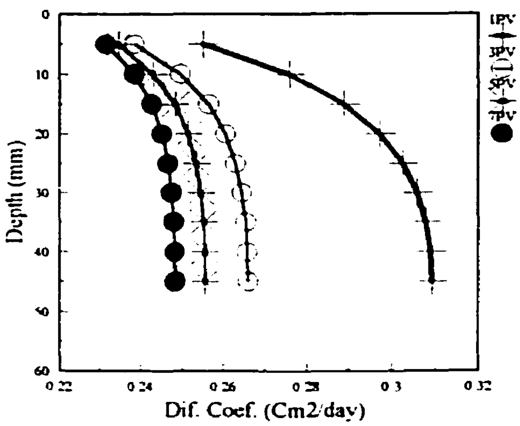
**Table 8.4** Other Species in Solution or Adsorbed at the Last Node for KC Soil Using SA.

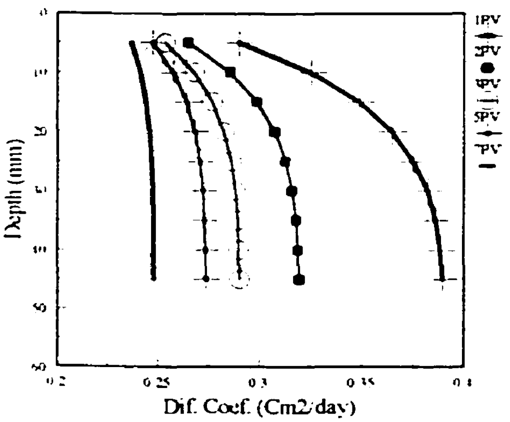
| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 8216002 | 2SOPbOH | 4.943E-07 | 4.943E-07 | -6.30599 | 1.00000 | -9.970 |
| 5009920 | NaACETATE | 5.221E-06 | 5.230E-06 | -5.28152 | 1.00169 | -.181 |
| 1509920 | CaACETATE | 4.777E-05 | 4.362E-05 | -4.36029 | .91324 | 1.219 |
| 3300020 | OH- | 2.078E-08 | 1.898E-08 | -7.72170 | .91324 | -13.959 |
| 3307700 | H3SiO4 - | 2.382E-08 | 2.175E-08 | -7.66254 | .91324 | -9.889 |
| 3307701 | H2SiO4 -2 | 1.213E-13 | 8.434E-14 | -13.07397 | .69557 | -21.459 |
| 1503300 | CaOH + | 1.703E-10 | 1.555E-10 | -9.80832 | .91324 | -12.559 |
| 1501400 | CaHCO3 + | 3.305E-07 | 3.018E-07 | -6.52023 | .91324 | 11.385 |
| 1501401 | CaCO3 AQ | 3.656E-09 | 3.662E-09 | -8.43631 | 1.00169 | 3.152 |
| 5001400 | NaCO3 - | 1.436E-10 | 1.312E-10 | -9.88215 | .91324 | 1.307 |
| 5001401 | NaHCO3 AQ | 4.495E-08 | 4.502E-08 | -7.34655 | 1.00169 | 10.079 |
| 303300 | AlOH +2 | 3.076E-11 | 2.139E-11 | -10.66970 | .69557 | -4.832 |
| 303301 | Al(OH)2 + | 3.436E-10 | 3.138E-10 | -9.50340 | .91324 | -10.061 |
| 303302 | Al(OH)4 - | 1.544E-10 | 1.410E-10 | -9.85081 | .91324 | -22.961 |
| 303303 | Al(OH)3 AQ | 7.450E-10 | 7.463E-10 | -9.12711 | 1.00169 | -16.001 |
| 6001400 | Pb(CO3)2-2 | 4.600E-13 | 3.199E-13 | -12.49492 | .69557 | 10.798 |
| 6003300 | PbOH + | 4.736E-09 | 4.325E-09 | -8.36402 | .91324 | -7.671 |
| 6003301 | Pb(OH)2 AQ | 3.174E-12 | 3.179E-12 | -11.49773 | 1.00169 | -17.121 |
| 6003302 | Pb(OH)3 - | 7.551E-17 | 6.896E-17 | -16.16143 | .91324 | -28.021 |
| 6003303 | Pb2OH +3 | 2.573E-14 | 1.137E-14 | -13.94434 | .44185 | -6.005 |
| 6004920 | PbNO3 + | 3.473E-09 | 3.172E-09 | -8.49871 | .91324 | 1.209 |

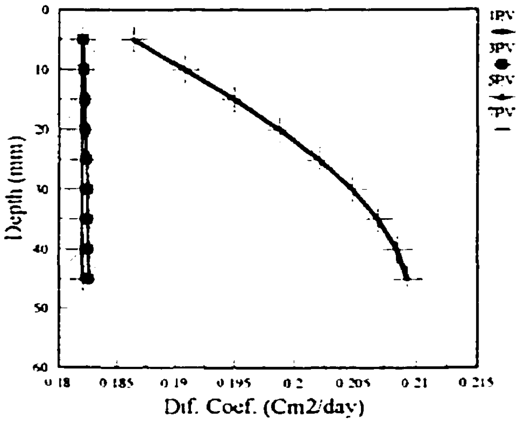
**Table 8.4** Continue

| Id | Name | Calc Mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 6003304 | Pb3(OH)4+2 | 3.907E-20 | 2.718E-20 | -19.56577 | .69557 | -23.722 |
| 6001401 | PbCO3 AQ | 1.609E-08 | 1.612E-08 | -7.79262 | 1.00169 | 7.239 |
| 6003305 | Pb(OH)4 -2 | 4.301E-22 | 2.991E-22 | -21.52413 | .69557 | -39.541 |
| 6001402 | PbHCO3 + | 8.519E-09 | 7.780E-09 | -8.10902 | .91324 | 13.239 |
| 3301400 | HCO3 - | 9.779E-05 | 8.930E-05 | -4.04914 | .91324 | 10.369 |
| 3301401 | H2CO3 AQ | 1.060E-04 | 1.061E-04 | -3.97411 | 1.00169 | 16.680 |
| 3309921 | H ACETATE | 2.687E-04 | 2.691E-04 | -3.57008 | 1.00169 | 4.759 |
| 6009921 | PBACETATE | 8.422E-07 | 7.691E-07 | -6.11399 | .91324 | 2.909 |
| 6009922 | PBACETATE2 | 1.101E-07 | 1.102E-07 | -6.95767 | 1.00169 | 4.079 |
| 6009923 | PBACETATE3 | 3.452E-10 | 3.152E-10 | -9.50135 | .91324 | 3.629 |
| 6009924 | PBACETATE4 | 2.586E-12 | 1.799E-12 | -11.74502 | .69557 | 3.558 |
| 8113300 | =1SO- | 3.280E-02 | 3.280E-02 | -1.48410 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 3.290E-02 | 3.290E-02 | -1.48285 | 1.00000 | 7.860 |
| 8116000 | =1SOPb+ | 2.868E-12 | 2.868E-12 | -11.54239 | 1.00000 | -8.930 |
| 8115000 | =1SONa | 1.381E-07 | 1.381E-07 | -6.85992 | 1.00000 | -8.130 |
| 8116002 | =SOPbOH | 4.943E-07 | 4.943E-07 | -6.30599 | 1.00000 | -9.970 |
| 8213300 | =2SO- | 1.228E-02 | 1.228E-02 | -1.91073 | 1.00000 | -6.910 |
| 8213302 | =2SOH | 1.229E-02 | 1.229E-02 | -1.91055 | 1.00000 | 6.160 |
| 8215000 | =2SONa | 1.381E-05 | 1.381E-05 | -4.85992 | 1.00000 | -6.130 |
| 8216000 | =2SOPb+ | 5.420E-06 | 5.420E-06 | -5.26599 | 1.00000 | -8.930 |


(a) Diffusion Profiles Using EDTA in Kaolinite


(b) Diffusion Profiles Using EDTA in KS Soil


(c) Pb Diffusion Profiles using EDTA KC Clay


(d) Diffusion Profiles Using EDTA in KSC Soil

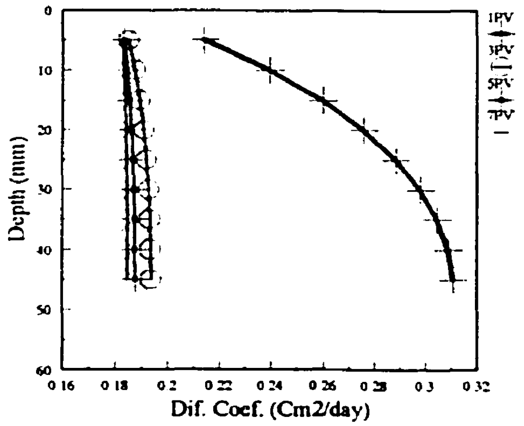
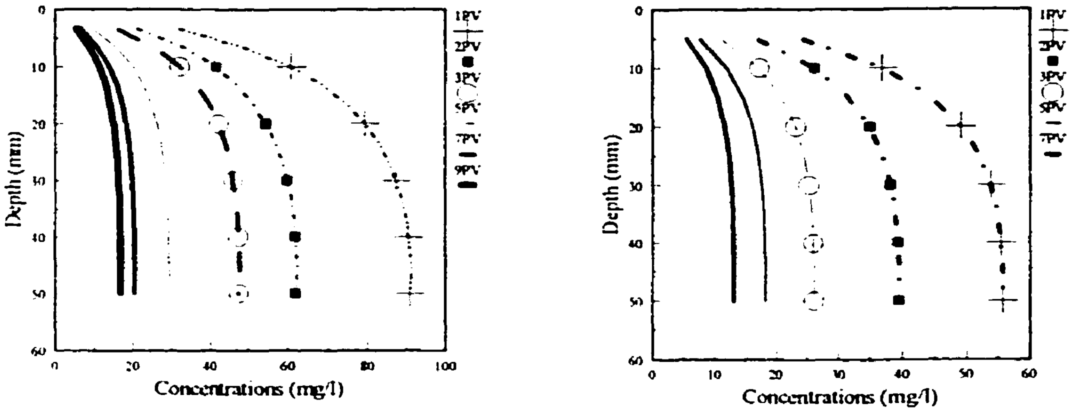

(e) Diffusion Profiles for Pb by SA in KSC Soil

**Figure 8.9** Pb Diffusion Profiles for all Soils Using EDTA and Sodium Acetate.

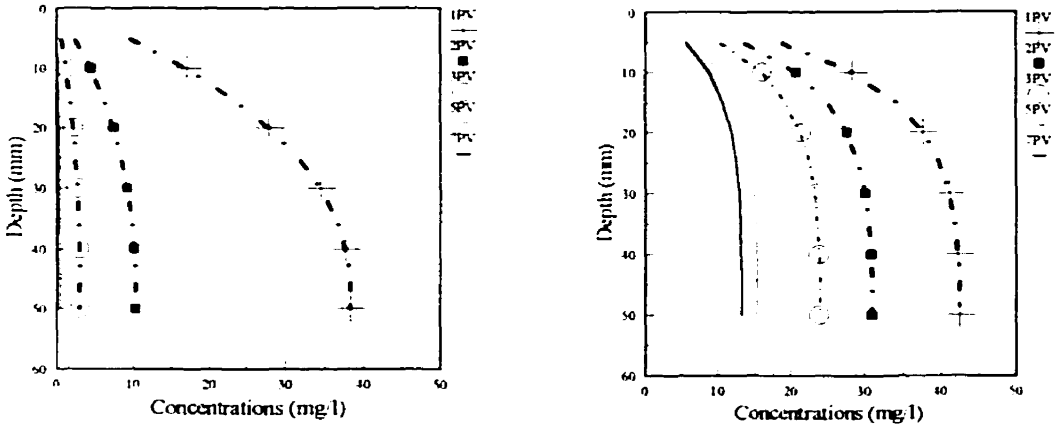
(a) Lead Desorption Profiles by EDTA for K

(b) Lead Desorption Profiles by EDTA for KS



(c) Lead Desorption Profiles by EDTA for KC

(d) Lead Desorption Profiles by EDTA for KSC



(e) Lead Desorption Profiles by SA for KC

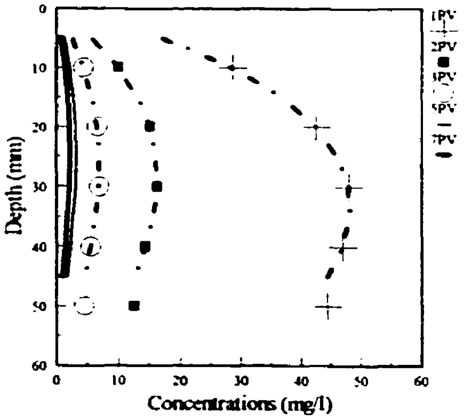
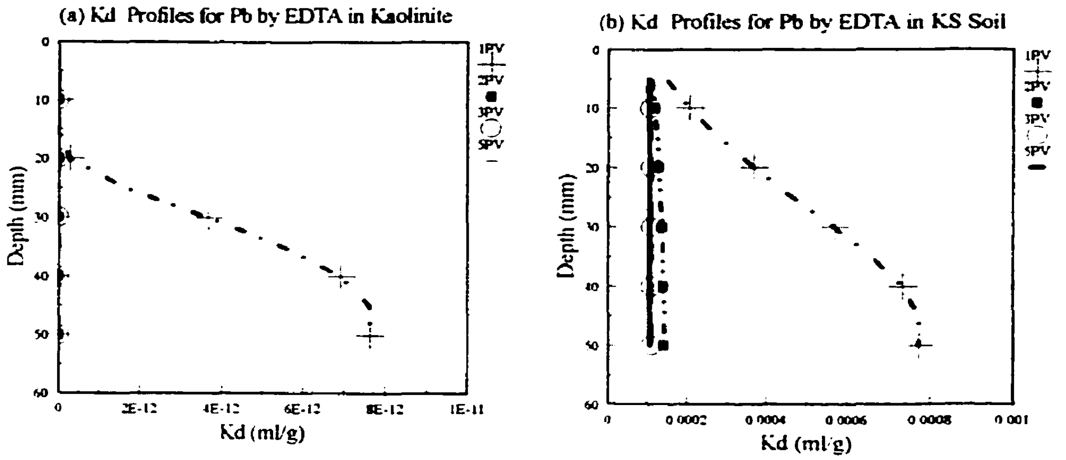
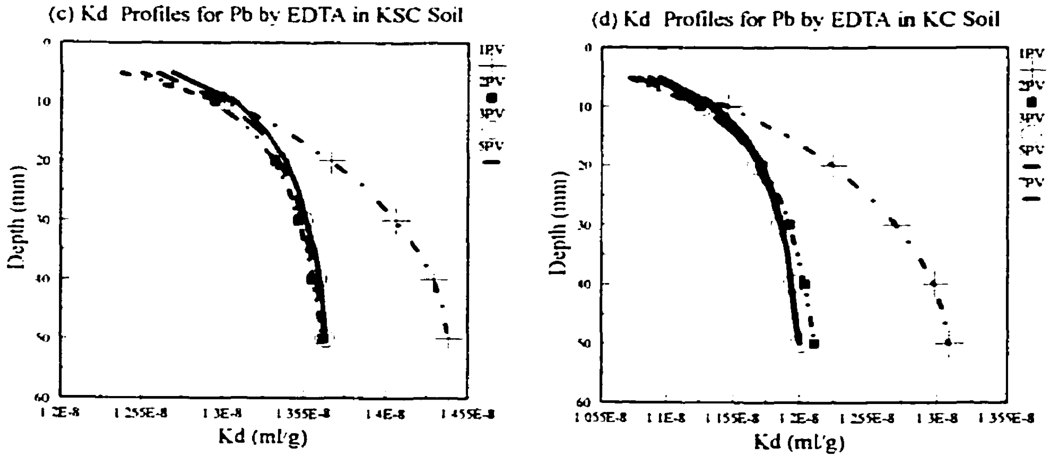


**Figure 8.10** Predicted Desorbed Pb Profiles for all Soils Using EDTA and Sodium Acetate.



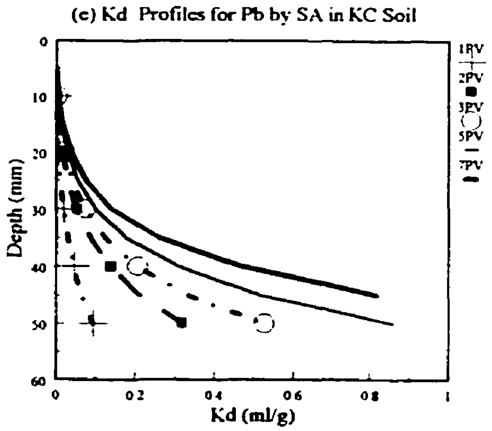
(a) Kd Profiles for Pb by EDTA in Kaolinite

(b) Kd Profiles for Pb by EDTA in KS Soil



(c) Kd Profiles for Pb by EDTA in KSC Soil

(d) Kd Profiles for Pb by EDTA in KC Soil



(e) Kd Profiles for Pb by SA in KC Soil

**Figure 8.11** Predicted Kd Profiles for Pb in all Soils Using EDTA and Sodium Acetate.

## 8.5 Summary

The effectiveness of EDTA to remove lead from the contaminated column in different clay soils and the COSTCHESP simulation for the prediction of mobilization of lead were discussed in this chapter. It was shown that EDTA could remove 50% of lead from the contaminated clay at the first pore volumes and subsequently it could remove 80% of lead at three pore volumes. EDTA could transfer the adsorbed heavy metals even from the carbonated soil (KC, KSC) to the aqueous phase at low pore volumes. Sodium acetate (SA) is less effective for the remobilization of the lead into the aqueous phase as shown by the higher $K_d$ profile results. It was shown that the COSTCHESP could reasonably predict the migration and distribution profiles of lead.

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# Chapter 9

# Parametric Sensitivity

## 9.1 General

One of the distinctive features of the prediction model, based on laboratory experiments, is the spatial heterogeneity of the soil properties in the field or, in other words, the uncertainty of the parameters measured in the lab and the problem of scale. This spatial heterogeneity is, generally, of an irregular nature, occurring on a scale that is not captured by laboratory samples. Our interest lies in transport occurring in the field scale, to a much larger extent than the laboratory scale. Even the parameter estimation of this study is based on column study and pore volume of leach out from the samples which, offer a good tool for the validation of a multi-component transport system in the field. There is still some doubt about the soil properties and chemical reaction occurring in nature. In addition, it is not possible to study the effect of all parameters including soil porosity, coefficient of permeability, diffusion coefficient, hydraulic gradient and adsorption parameters such as specific surface area (SSA), cation exchange capacity (CEC) and pH of the soil solution , on the transport of heavy metals into a clay barrier system.

To overcome the problem of the uncertainty, a parametric study is undertaken to examine the effect of the transport and chemical parameters on the transport of multi-component of heavy metals into clay using the COSTCHESP model. This requirement is basic for sensitivity analysis. The sensitivity analysis should answer the question of how parameter variations affects the transport of multi-component heavy metals into a clay barrier system. In other words, the response of the proposed mathematical model to parameter variation should be clearly understood. The sensitivity of the proposed model with respect to chemical and transport parameters will be evaluated in this chapter.

## 9.2 Evaluation of Transport and Partitioning Coefficient Parameters

As shown in various studies by Yong *et al.* (1992), the diffusion coefficient could not be assumed as a constant parameter. It varies with time and space. From the experimental and predicted results of this investigation (in the previous chapters), it was also concluded that $K_d$ varies with type of heavy metal and soil and is also time and space dependent. Thus, each component in a multi-contaminant system has its own diffusion and distribution coefficient, depending on the soil adsorption characteristics (SSA, CEC), geometry of the problem, pH of the solution, and other contaminants in the solution. Or in other words , the diffusion and partitioning coefficients are functions of the hydro-physico-chemical interaction of contaminants with soil which can be evaluated through the COupled Solute Transport and Equilibrium Speciation (COSTCHESP) model. The importance of various parameters including; heavy metals concentrations, chloride concentrations, pH of the solution, CEC, SSA, hydraulic gradient, temperature, $CO_2$ pressure, coefficient of the hydraulic conductivity to the partitioning coefficient , diffusion coefficient, depth of clay liner and the migration of the heavy metals into different clay barriers are presented in the following sections.

### 9.2.1 The Effect of Heavy Metals Concentrations

COSTCHEM was simulated, using lead or zinc with a higher concentration (1cmol of lead or zinc) i.e. 10 times the concentration of the previous case. All other physico-chemical properties were kept constant except the adsorption parameter which was changed for the new concentration. The predicted results for the total heavy metals transported, retained (adsorbed+precipitated) profiles and the computed distribution coefficient and diffusion coefficient profiles for lead and zinc into kaolinite soil are shown in Fig. 9.1a-d and 9.5 a-d and Figs 9.2a-e to 9.4a-e for lead and 9.6a-e-9.8a-e for zinc into kaolinite mixtures (KS, KC, KSC), respectively.

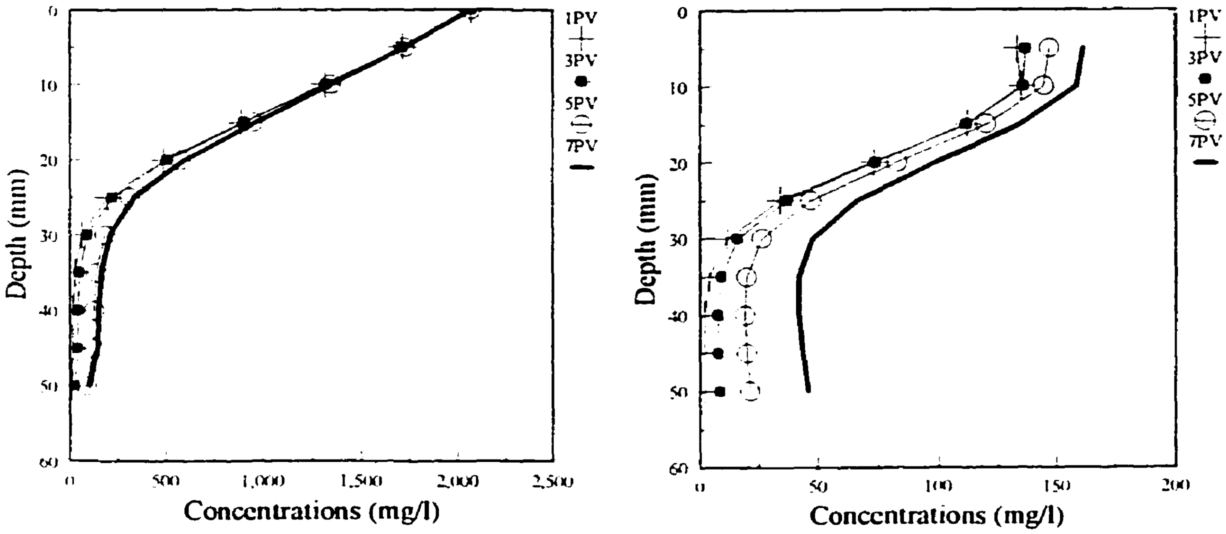
As shown, the mobilization of heavy metals along the depth of the column soil is accelerated when higher concentrations of heavy metals are applied. This is because, at high $Pb^{2+}$ or $Zn^{2+}$ concentrations, clay particles tend to conglomerate due to the disintegration of the diffuse double layer (Yong *et al.* 1992). Hence, a decrease in the net repulsive forces between clay particles within fabric unit is obtained (Mohamed *et al.* 1994). For this case, the clay particle surfaces in contact with the $Pb^{2+}$ or $Zn^{2+}$ solution tend to decrease and become coarser and form aggregates. The resultant surface areas exposed to $Pb^{2+}$ or $Zn^{2+}$ solution are less than those of low concentrations. Therefore, the $Pb^{2+}$ or $Zn^{2+}$ adsorption capacity of the newly formed structure, for high concentrations, is less than that of low concentrations. Also, the decrease in $Pb^{2+}$ or $Zn^{2+}$ adsorption at high concentrations could be attributed to the decrease in ion activity (Yong *et al.* 1992). The thickness of the diffuse double layer tends to decrease, which facilitates the mobility of the heavy metals or other cations in the solution.

On the other hand, the higher the concentration of Pb or Zn applied, the higher will be the $H^+$ remaining in the solution, which results in a reduction of the equilibrium soil solution pH. The lower the pH, the higher the mobility of heavy metals. The mobility of Zn in all cases is higher than Pb. The mobility of Pb or Zn increases as their concentration in the permeant solution increases, especially for kaolinite clay which has a low soil solution pH and the possible retention of Pb or Zn in form of precipitation is zero. For high soil pH >5 like KS, KC or KSC, most of the applied Pb is retained on the top part of the soil column in the form of precipitation. Whereas, when the soil solution pH is <5 the amounts of Pb retained decrease rapidly.

However, the higher the concentration of Pb or Zn applied, the higher will be the diffusion coefficient, a shown in Figure 9.1d and 9.5d for lead and zinc in kaolinite and Figures 9.2e-9.4e for lead and 9.5e-9.8e for zinc in kaolinite mixtures, which results in an increase of mobility of both heavy metals. This conclusion may also be drawn from $K_d$ results shown in Figures 9.1c and 9.2c for lead and zinc in kaolinite and 9.2d, 9.3d, 9.4d for lead and 9.6d, 9.7d, 9.8d for zinc in kaolinite mixtures (KS, KC, KSC), respectively.

(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite



(c) Kd Profiles for Pb in Kaolinite

(d) Pb Diffusion Profiles in Kaolinite

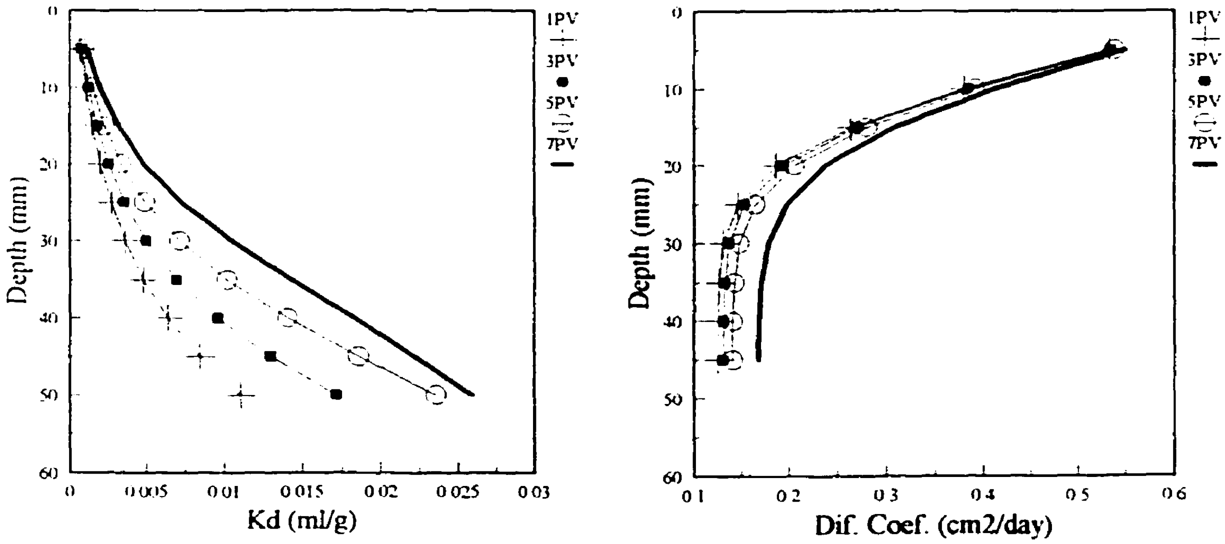
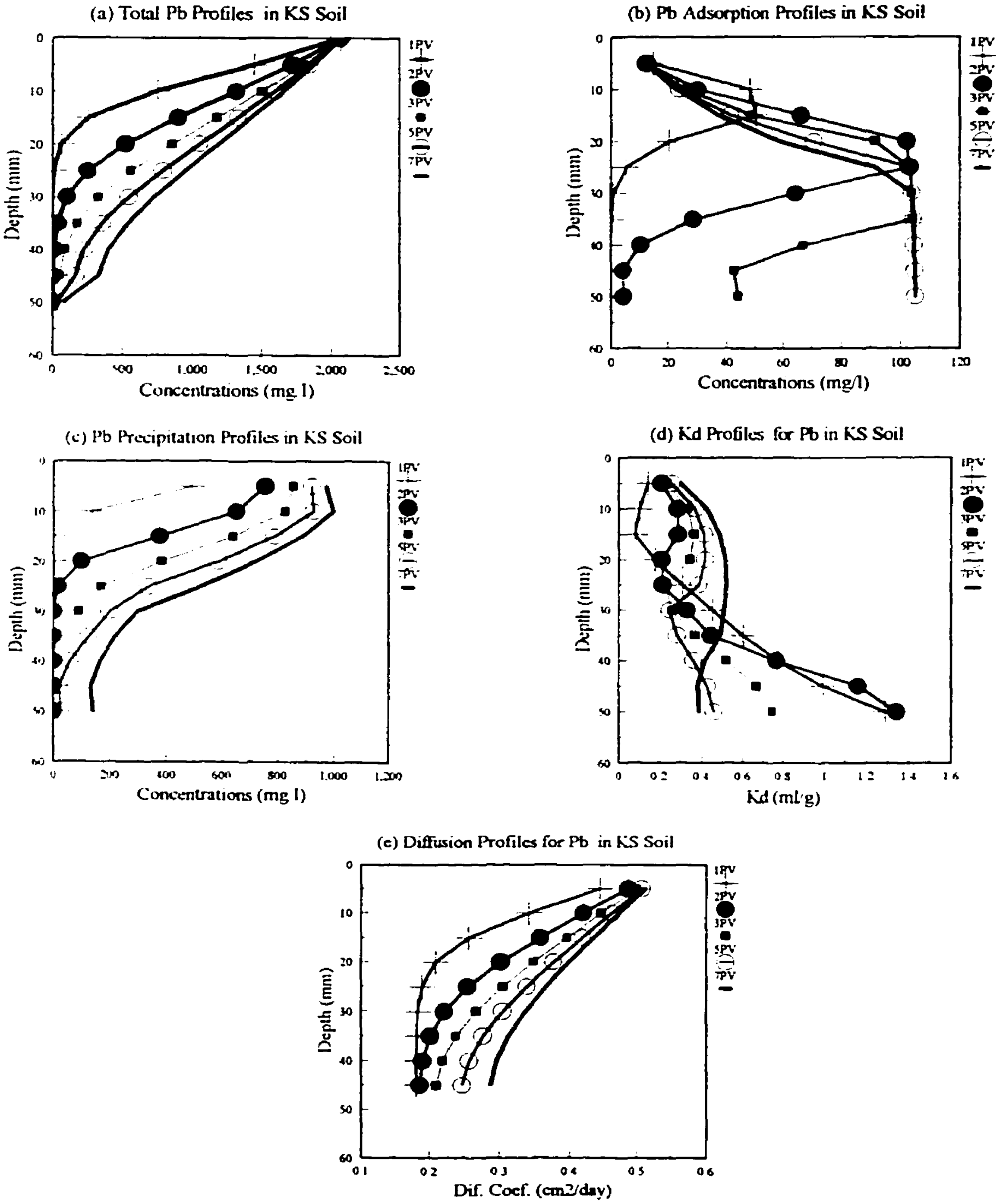


**Fig. 9.1** Predicted Pb Characteristics Profiles for Kaolinite Using 10 mmol/L Pb Solution.


(a) Total Pb Profiles in KS Soil

(b) Pb Adsorption Profiles in KS Soil

(c) Pb Precipitation Profiles in KS Soil

(d) Kd Profiles for Pb in KS Soil

(e) Diffusion Profiles for Pb in KS Soil

Fig. 9.2 Predicted Pb Characteristics Profiles for KS Using 10 mmol/L Pb Solution.

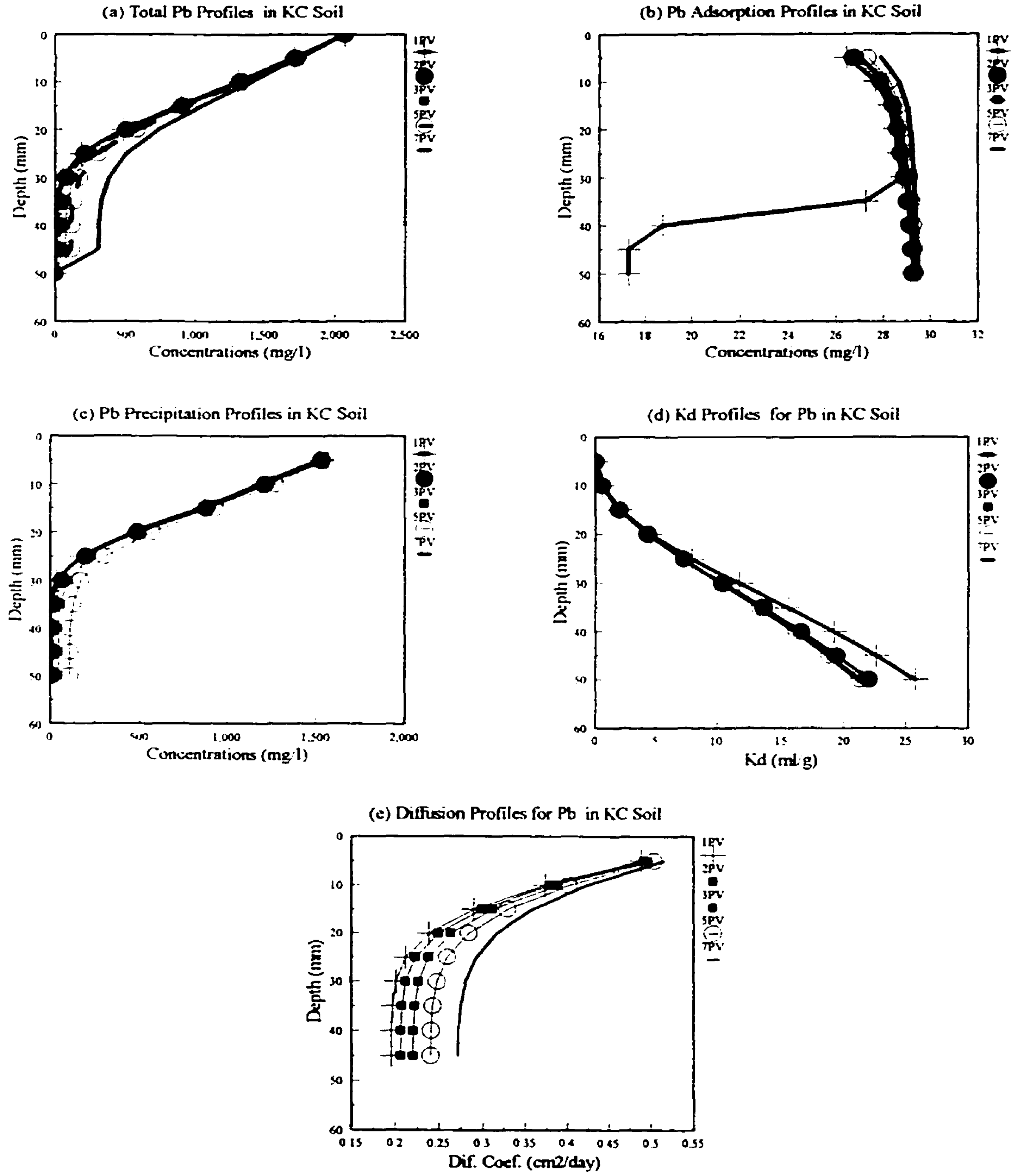
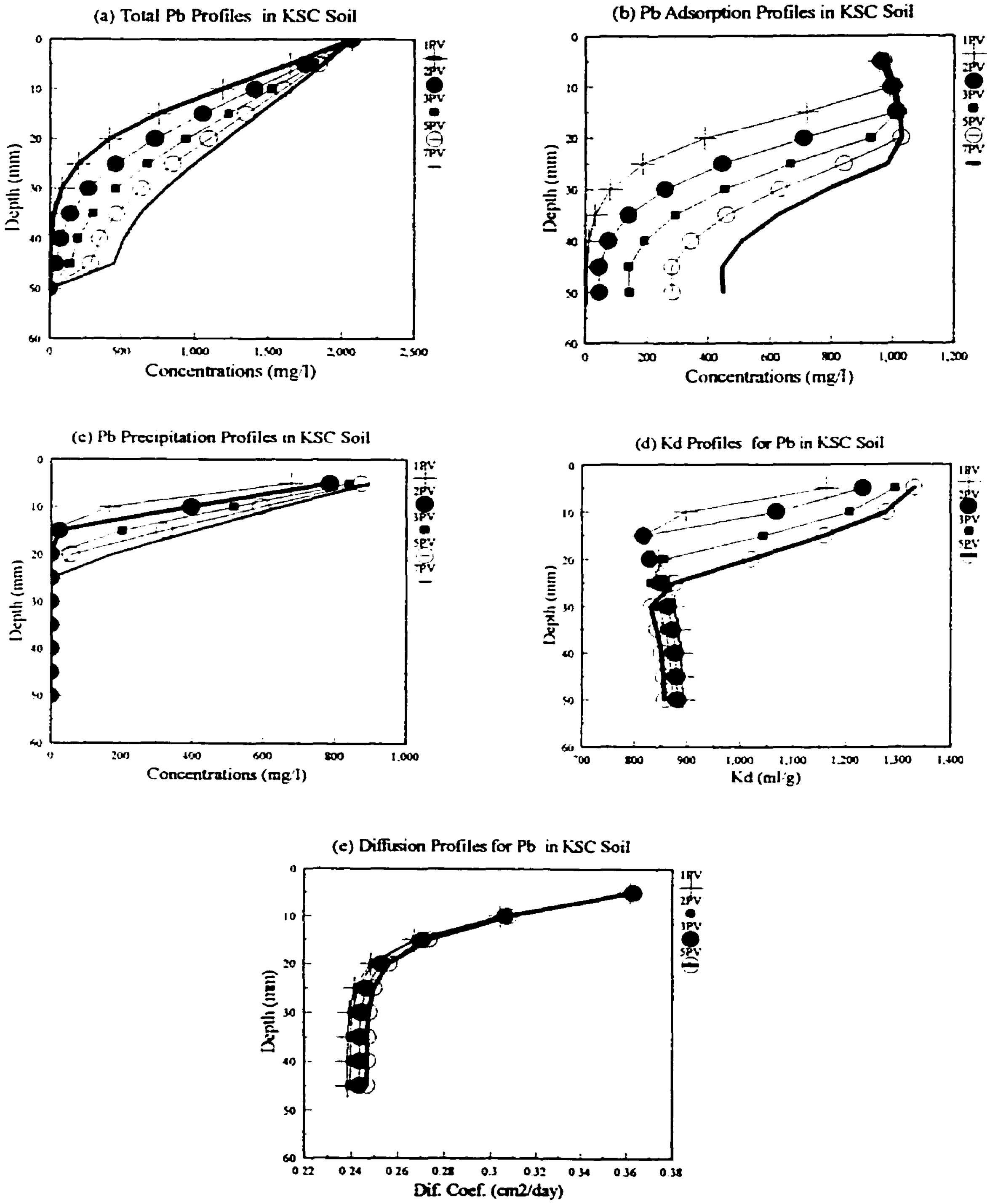


Fig. 9.3 Predicted Pb Characteristics Profiles for KC Uusing 10 mmol/l Pb Solution.



(a) Total Pb Profiles in KSC Soil

(b) Pb Adsorption Profiles in KSC Soil

(c) Pb Precipitation Profiles in KSC Soil

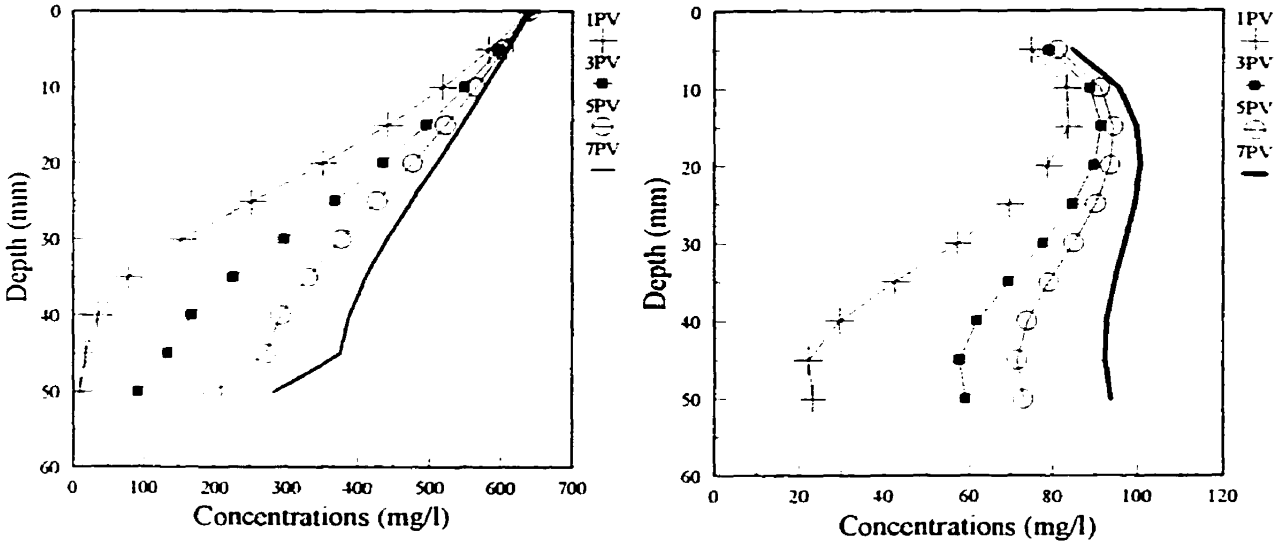
(d) Kd Profiles for Pb in KSC Soil

(e) Diffusion Profiles for Pb in KSC Soil

Fig. 9.4 Predicted Pb Characteristics Profiles for KSC Using 10 mmol/L Pb Solution.

(a) Total Zn Profiles in Kaolinite

(b) Zn Adsorption Profiles in Kaolinite



(c) Kd Profiles for Zn in Kaolinite

(d) Zn Diffusion Profiles in Kaolinite

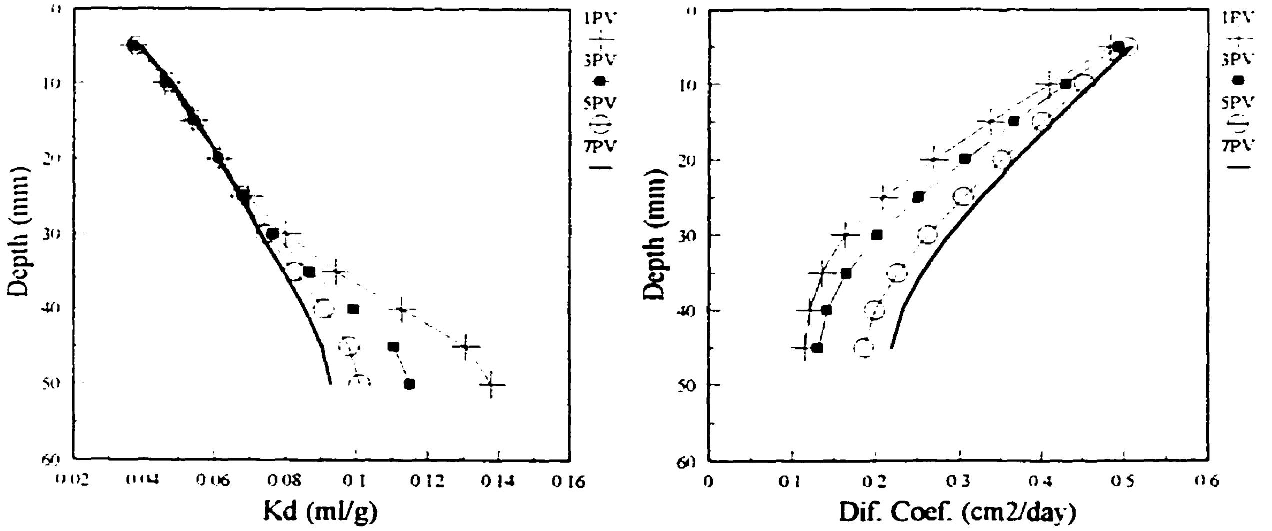
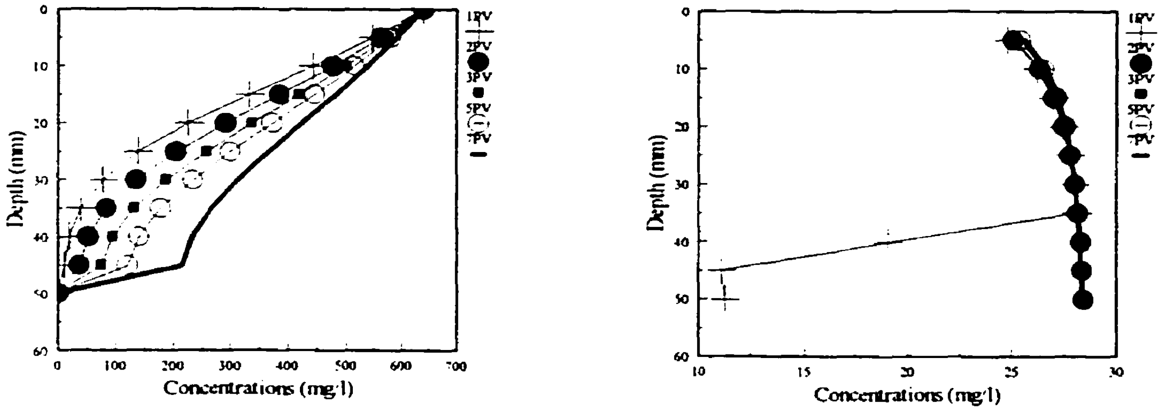
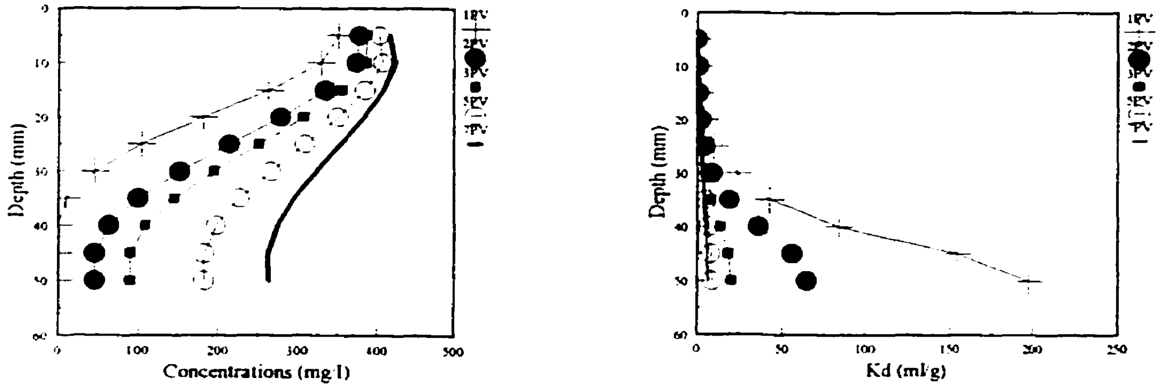


**Fig. 9.5** Predicted Zn Characteristics Profiles for Kaolinite Using 10 mmol/L Zn Solution.



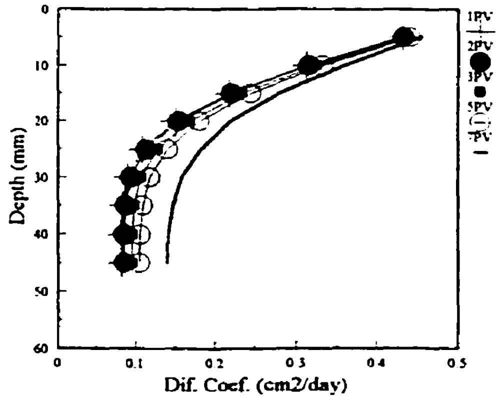
(a) Total Zn Profiles in KS Soil

(b) Zn Adsorption Profiles in KS Soil



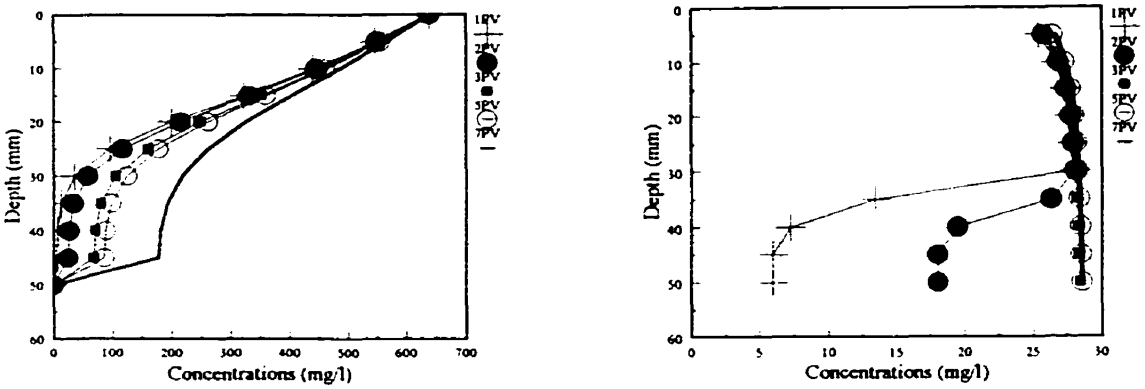
(c) Zn Precipitation Profiles in KS Soil

(d) Kd Profiles for Zn in KS Soil

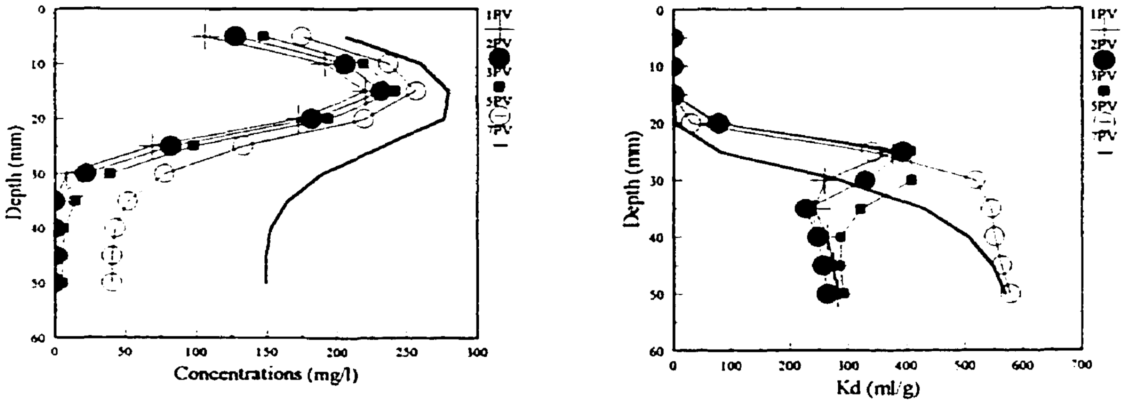


(e) Diffusion Profiles for Zn in KS Soil

**Fig. 9.6** Zn Characteristics Profiles for KS Using 1cmol/l Zn Solution.


(a) Total Zn Profiles in KC Soil

(b) Zn Adsorption Profiles in KC Soil


(c) Zn Precipitation Profiles in KC Soil

(d) Kd Profiles for Zn in KC Soil

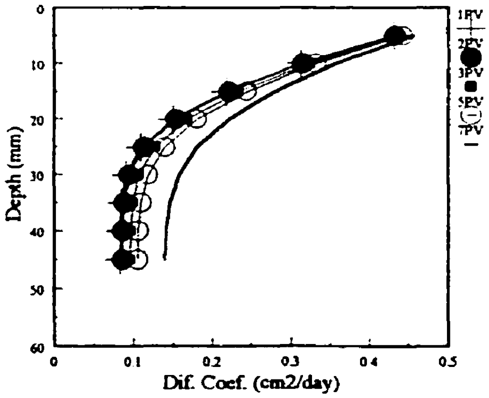
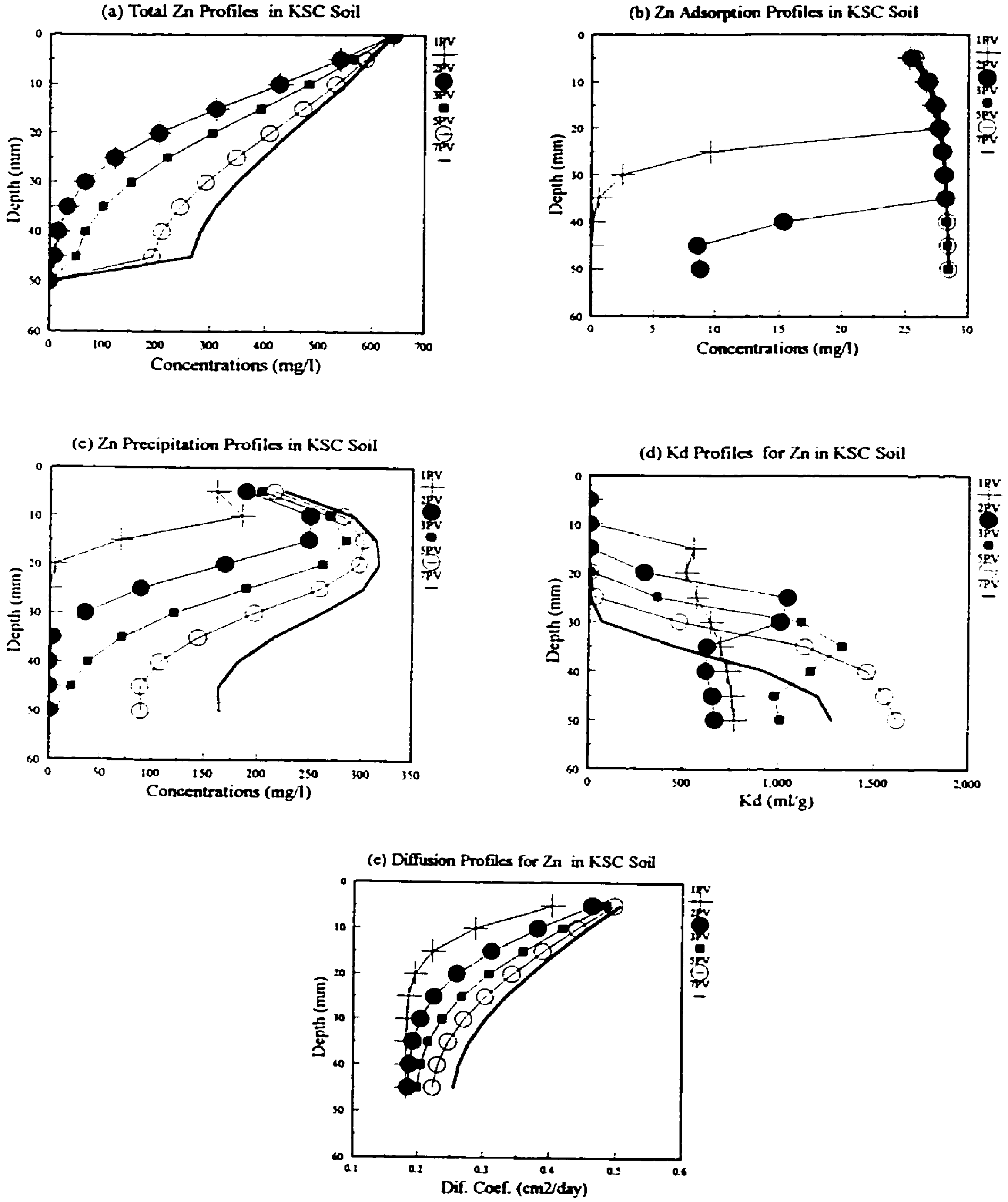

(e) Diffusion Profiles for Zn in KC Soil

**Fig. 9.7** Zn Characteristics Profiles for KC Using 1cmol/l Zn Solution.



(a) Total Zn Profiles in KSC Soil

(b) Zn Adsorption Profiles in KSC Soil

(c) Zn Precipitation Profiles in KSC Soil

(d) Kd Profiles for Zn in KSC Soil

(e) Diffusion Profiles for Zn in KSC Soil

**Fig. 9.8** Zn Characteristics Profiles for KSC Using 1cmol/l Zn Solution.

### 9.2.2 The Effect of Chloride Concentrations

Chloride, under certain circumstances, may also be of great significance in the mobilization of heavy metals when it is spiked in solution with heavy metals. To evaluate the effect of chloride concentration on the mobility of lead into kaolinite or kaolinite mixtures, COSTCHESP was simulated using chloride with a concentration of 0.5 mole in the input solution. All other physico-chemical properties were kept constant.

The predicted results for the total lead transported, retained (adsorbed + precipitated) profiles and the computed distribution coefficient and diffusion coefficient profiles for kaolinite soil are shown in Figs 9.9a-d and for kaolinite mixtures (KS, KC, KSC) are shown in Figs 9.10a-e to 9.12a-e. As expected, the figure shows the addition of chloride, as a complexing component, reduced the amounts of heavy metals retained in all types of soil. The chloride concentration varies with time and space. The higher the NaCl concentration, the lower the degree of heavy metals sorption, due to the complex formation of lead with chloride and the selectivity of $Na^+$ over $Pb^{2+}$.

Macroscopically, the tendency of an ion to be sorbed depends on its concentration in the aqueous phase relative to the concentration of other sorbable ions, the selectivity of the sorptive substrate for an ion relative to the other ions, and the number of sites on the sorptive substrate (Milller and Benson, 1983 ). Given similar concentrations of sorbable ions in the aqueous phase, the selectivity of $Pb^{2+}$ is higher than the selectivity of $Na^+$. However, as the concentration of $Na^+$ is increased, the enhanced selectivity for Pb is outweighed by the Na concentration effect, and the adsorption of $Pb^{2+}$ is reduced. The mobility of lead was enhanced as the pore volumes of the influent was passed through the column. Since the Cl moves very fast and may reach its breakthrough between 3-4 pore volumes of effluent, depending of the type of the soil, the mobility of heavy metals may be slow at first due to the low concentration of Cl, but it accelerates after the third pore volume of the influent was passed through the column soil because the mobility is increased with the increasing concentrations of Cl. The effect was found to be directly related to the degree of chloro-complex formation, as predicted from COSTCHESP. In the case of kaolinite, there is a relative drop in Pb retention with increasing chloride concentrations.

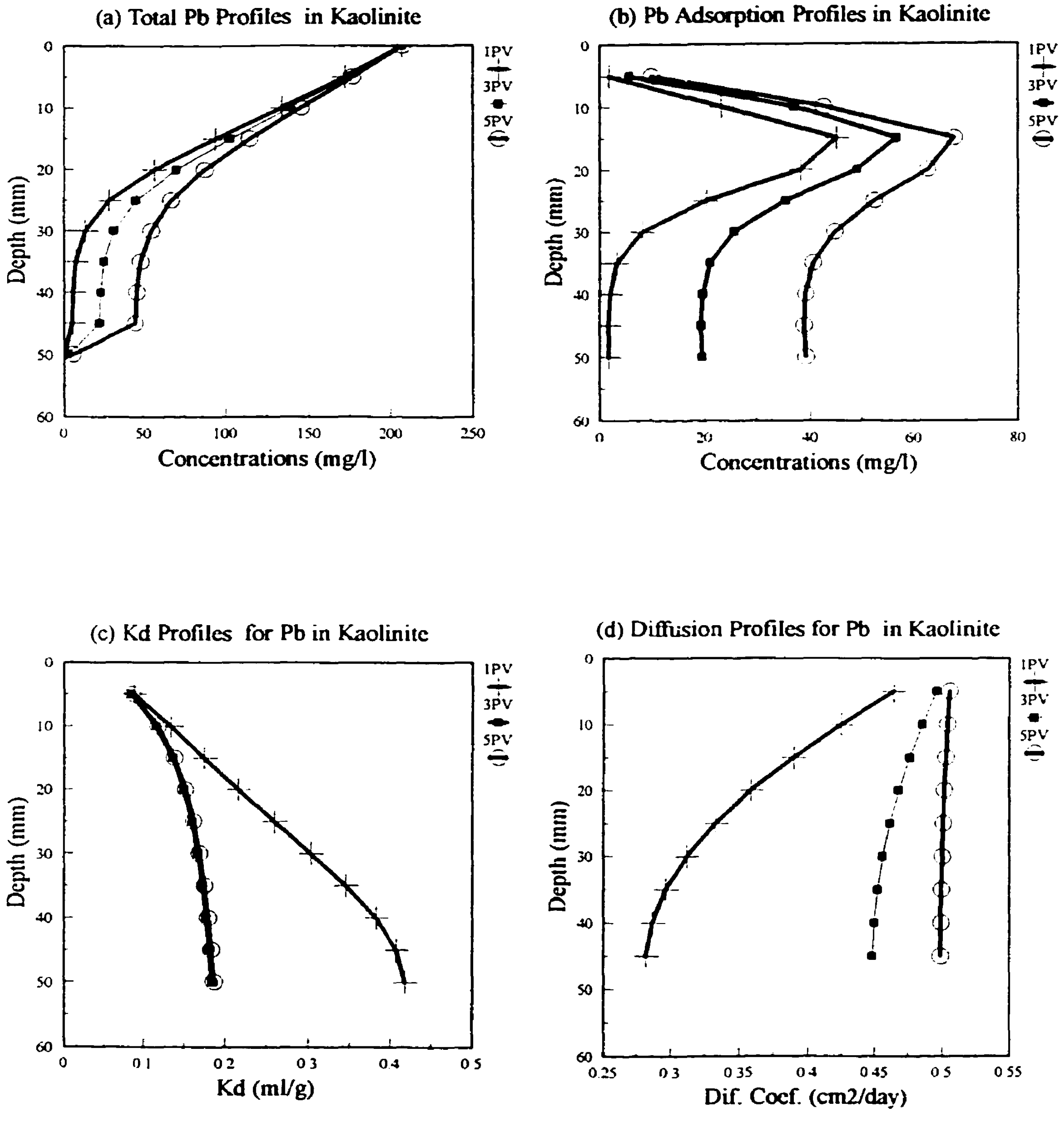


**Fig. 9.9** Chloride Concentration Effect on Pb Characteristics Profiles for Kaolinite

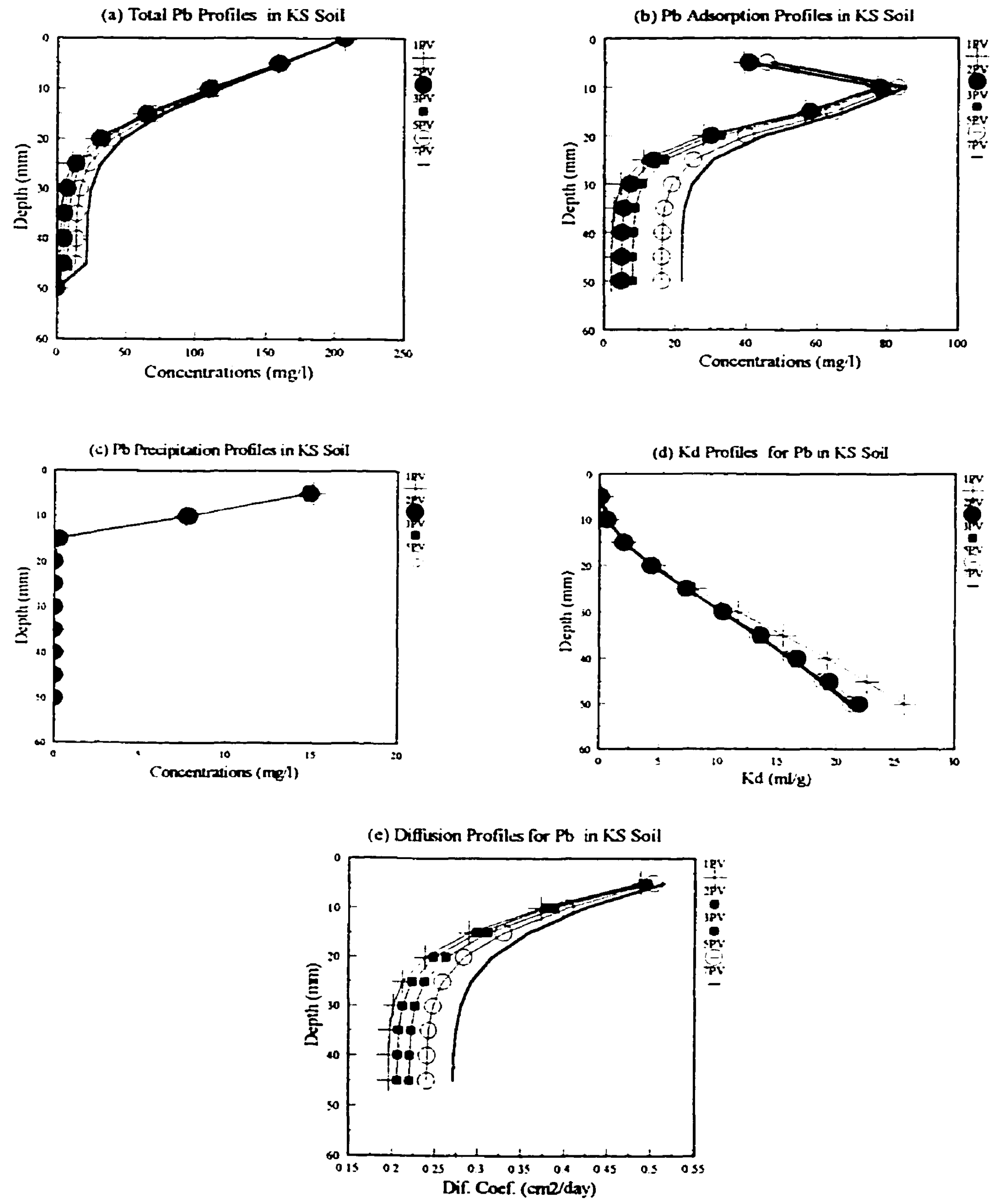
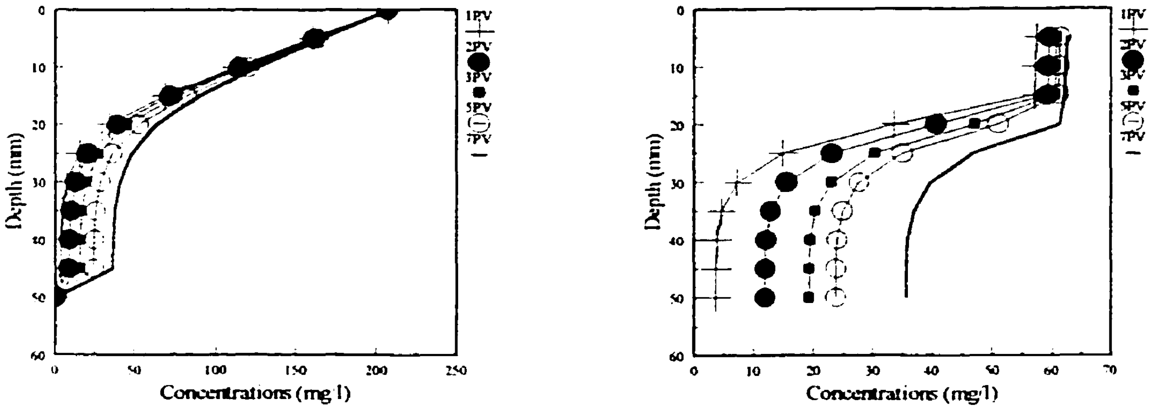
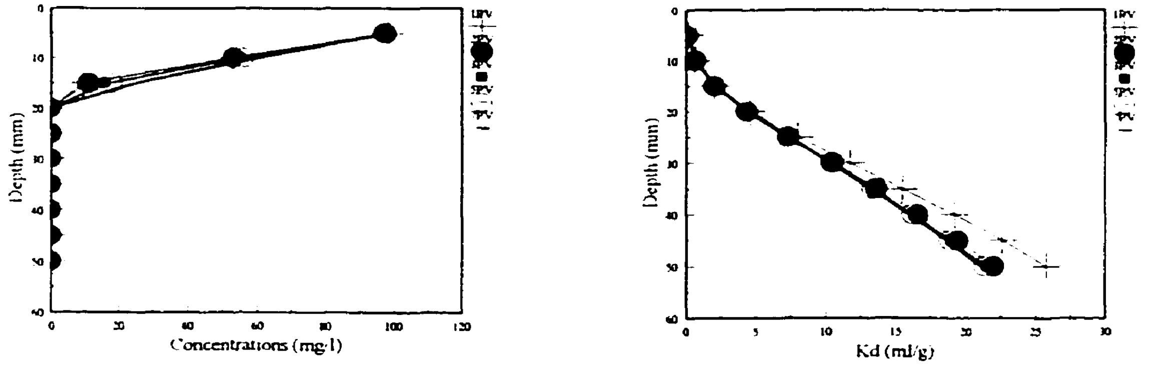


**Fig. 9.10** Predicted Chloride Concentration Effect on Pb Characteristics Profiles for KS.


(a) Total Pb Profiles in KC Soil

(b) Pb Adsorption Profiles in KC Soil


(c) Pb Precipitation Profiles in KC Soil

(d) Kd Profiles for Pb in KC Soil

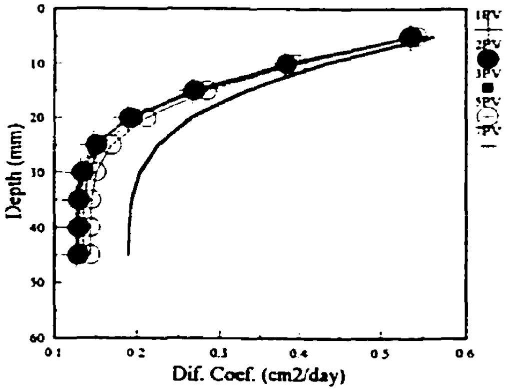
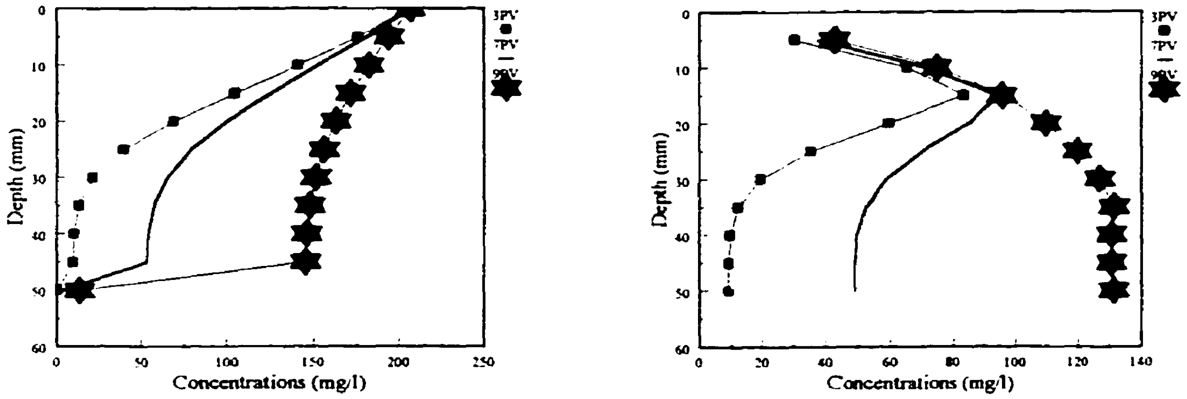

(e) Diffusion Profiles for Pb in KS Soil

Fig. 9.11 Predicted Chloride Concentration Effect on Pb Characteristics Profiles for KC.

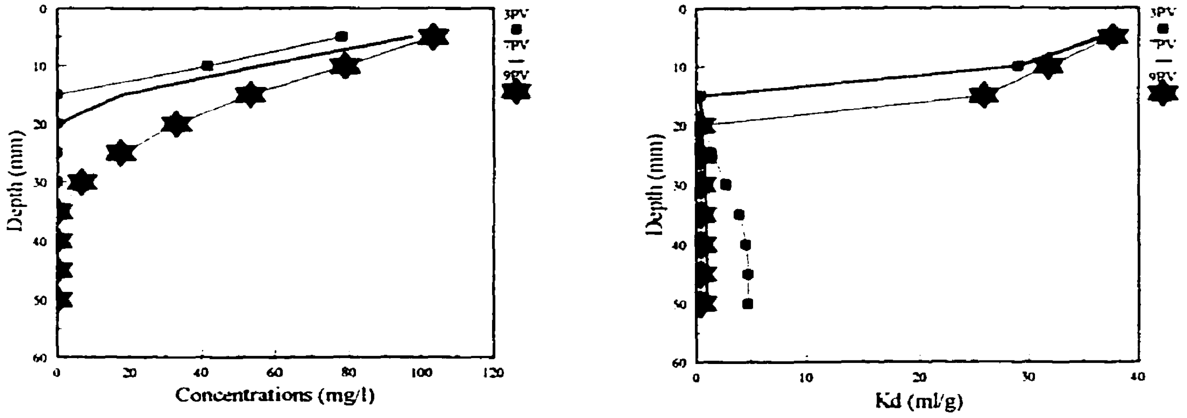
(a) Total Pb Profiles in KSC Soil

(b) Pb Adsorption Profiles in KSC Soil



(c) Pb Precipitation Profiles in KSC Soil

(d) Kd Profiles for Pb in KSC Soil



(e) Diffusion Profiles for Pb in KSC Soil

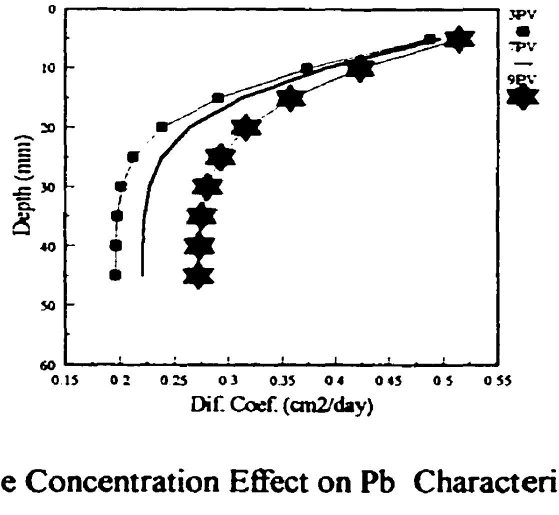
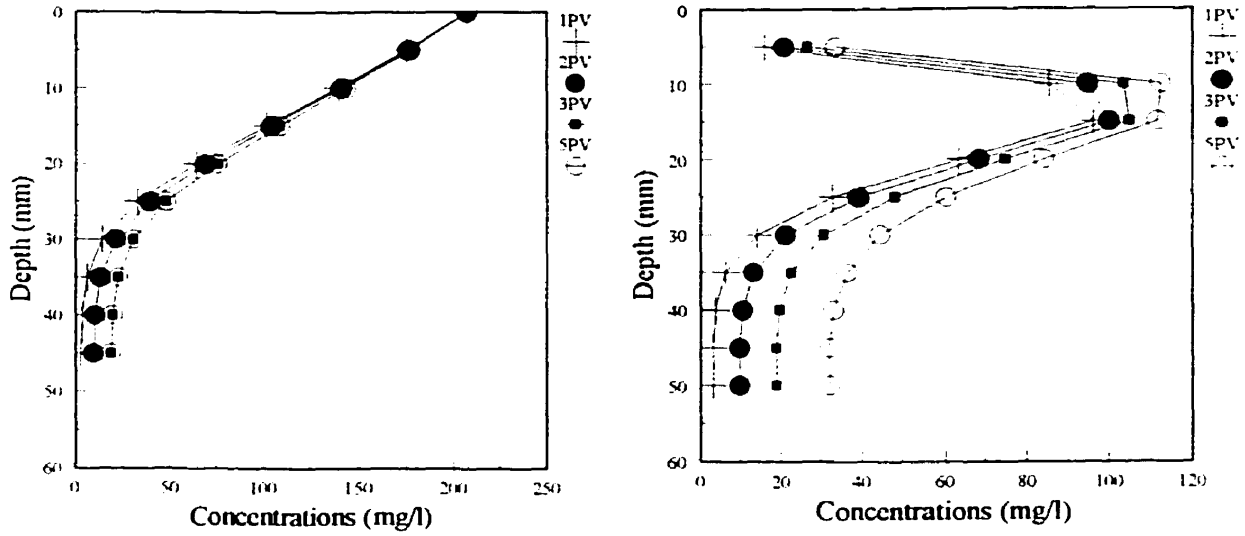


Fig. 9.12 Chloride Concentration Effect on Pb Characteristics Profiles for KSC.

### 9.2.3 The Effect of pH of the Leachate Solution

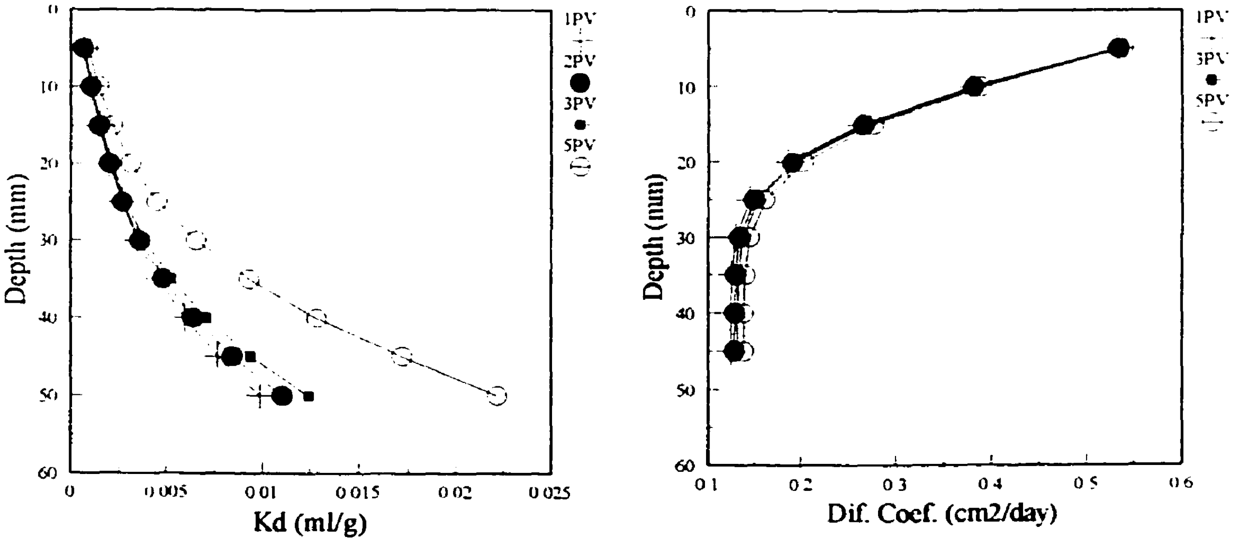
pH is known as the one of the most important factors which, under certain circumstances, may also be of great significance in the retention of heavy metals in a clay liner. This is due to competition between hydrogen ions and heavy metals for the adsorption on clay soil (Yong *et al.* 1995). To evaluate the effect of leachate solution pH on the mobility of lead into kaolinite or kaolinite mixture, COSTCHESP was simulated using leachate solution pH of 1.00, and all other physico-chemical properties were kept constant. The predicted results for the total lead transported, retention (adsorbed + precipitated) profiles and the computed distribution coefficient and diffusion coefficient profiles for kaolinite and kaolinite mixtures for all four types of soils (K, KS, KC, KSC) are shown in Figs 9.13a-d, 9.14a-d, 9.15a-d and 9.16a-d. As shown, the pH of the leachate solution may enhance the mobilization of the heavy metals into a clay barrier, especially, when the buffer capacity of clay is low, as shown in Fig 9.13 for kaolinite soil. This is because, at low pH the possible retention of heavy metals in the form of precipitation is low. On the other hand, at a low pH value for a variable charged clay like kaolinite, clay surfaces are positively charged. Electrostatic interaction is thus not in favour of the adsorption of heavy metals or other cations (Sposito, 1990). In addition, due to competition between the hydrogen ions and heavy metals the adsorption of the cations in the form of complextion or ion exchange is reduced.

The results of model simulation for three other soils (KS, KC, KSC), shown in Fig 9.14, 9.15 and 9.16 indicate, that when clay has a high buffer capacity it can still retain high amounts of heavy metals. Especially, in carbonate soil, ( KC, KSC), low pH permeant solution could dissolve the carbonate of the clay soil and increase the possibility of precipitation of heavy metals in the form of carbonate in the top part of the column. After passing some pore volumes of the leachate the retention in all forms is reduced. Overall, as shown in Fig 9.13c, 9.14d, 9.15d, 9.16d, the partitioning coefficient for all types of the soils is minimum at the top and maximum at the bottom of the column due to low pH of permeant solution.



(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite



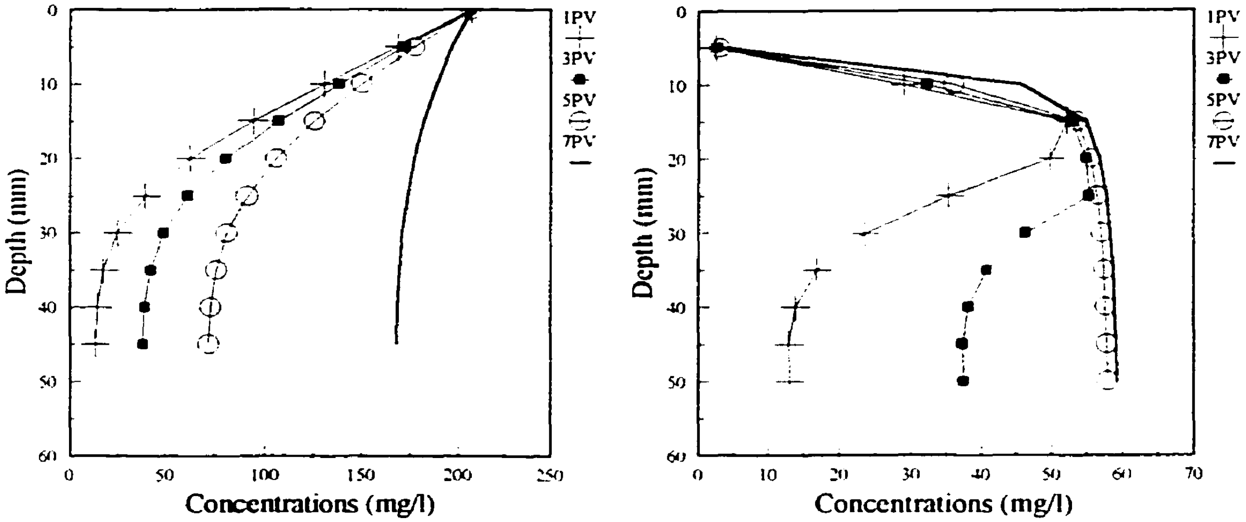
(c) Kd Profiles for Pb in Kaolinite

(d) Diffusion Profiles for Pb in Kaolinite

**Fig. 9.13** Predicted Solution pH Effect on Pb Characteristics Profiles for Kaolinite.

(a) Total Pb Profiles in KS Clay

(b) Pb Adsoption Profiles for KS Clay



(c) Calculated Kd Profiles

(d) Diffusion Profiles for KS

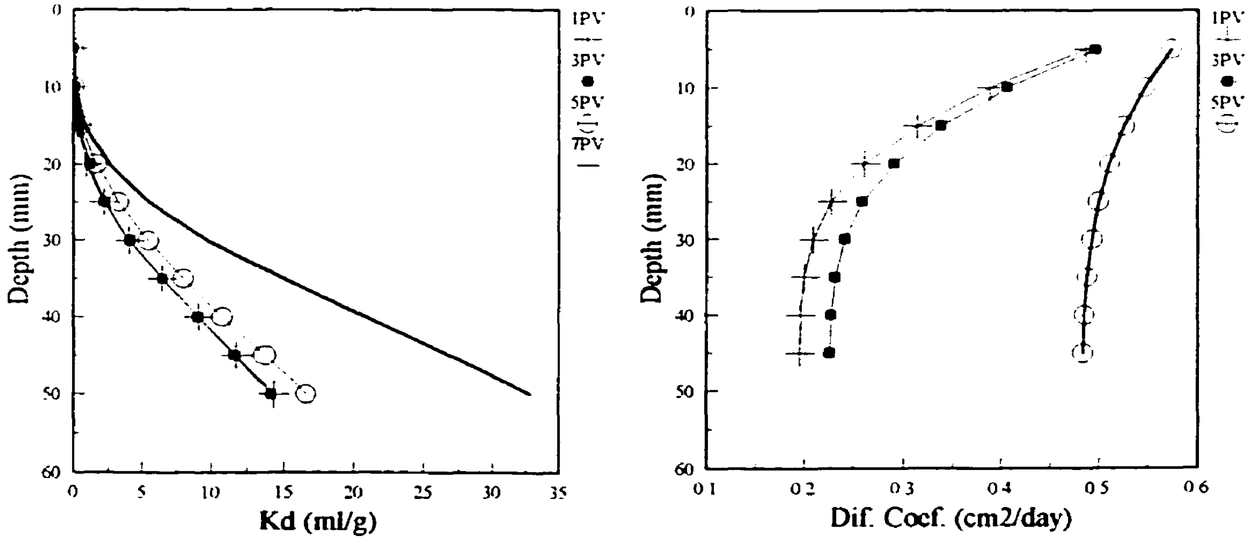
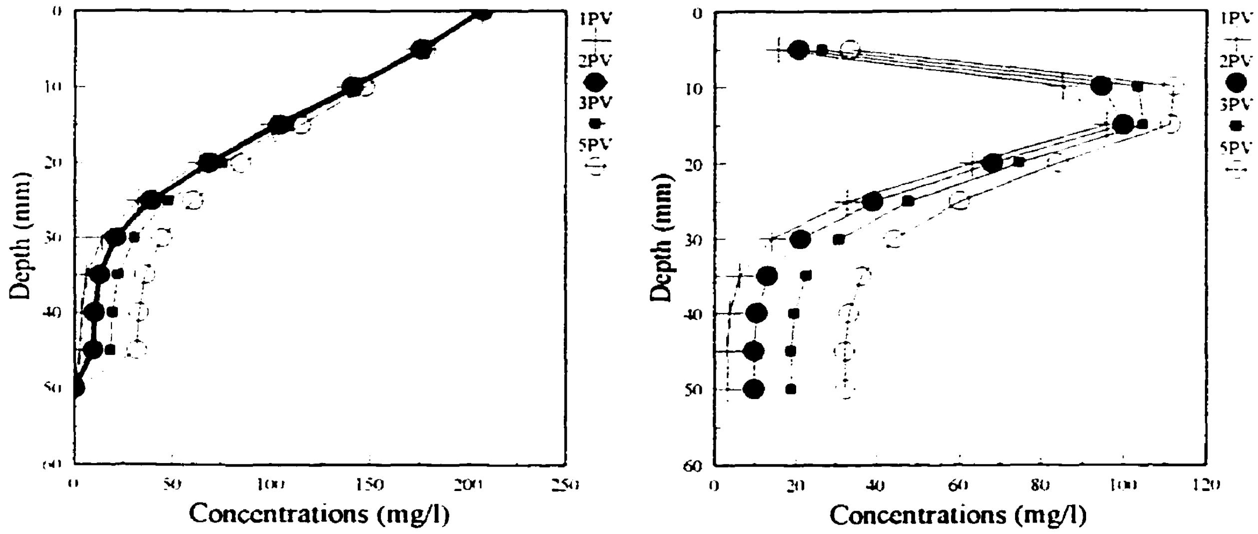


Fig. 9.14 Solution pH Effect on Pb Characteristics Profiles for KS.

(a) Total Pb Profiles in KC Soil (b) Pb Retention Profiles in KC



(d) Kd Profiles for Pb in KC Soil (c) Diffusion Profiles for Pb in KC Soil

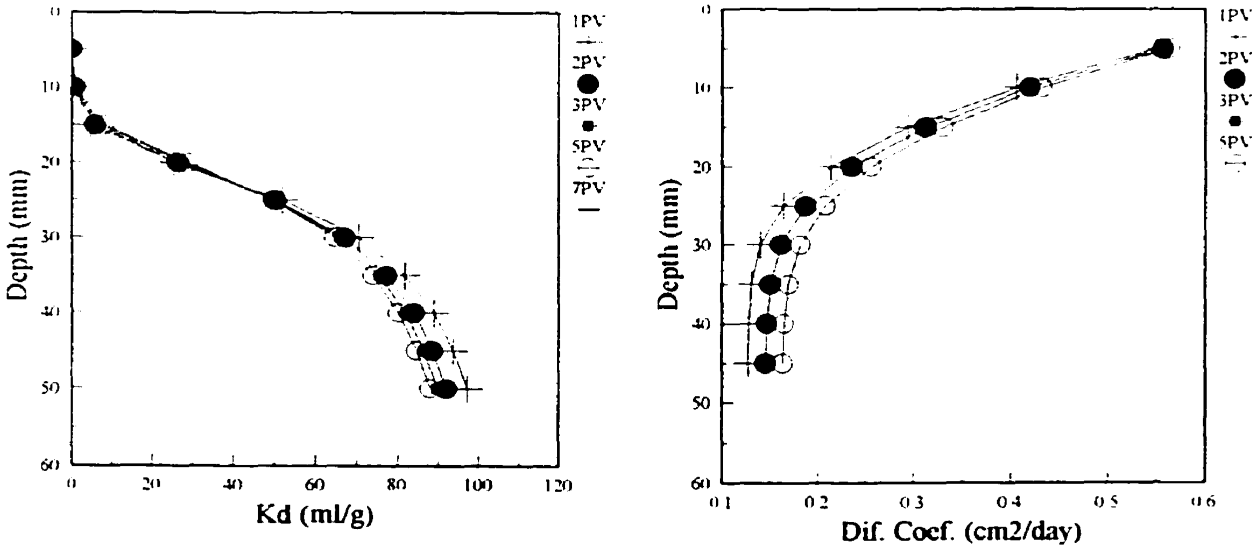
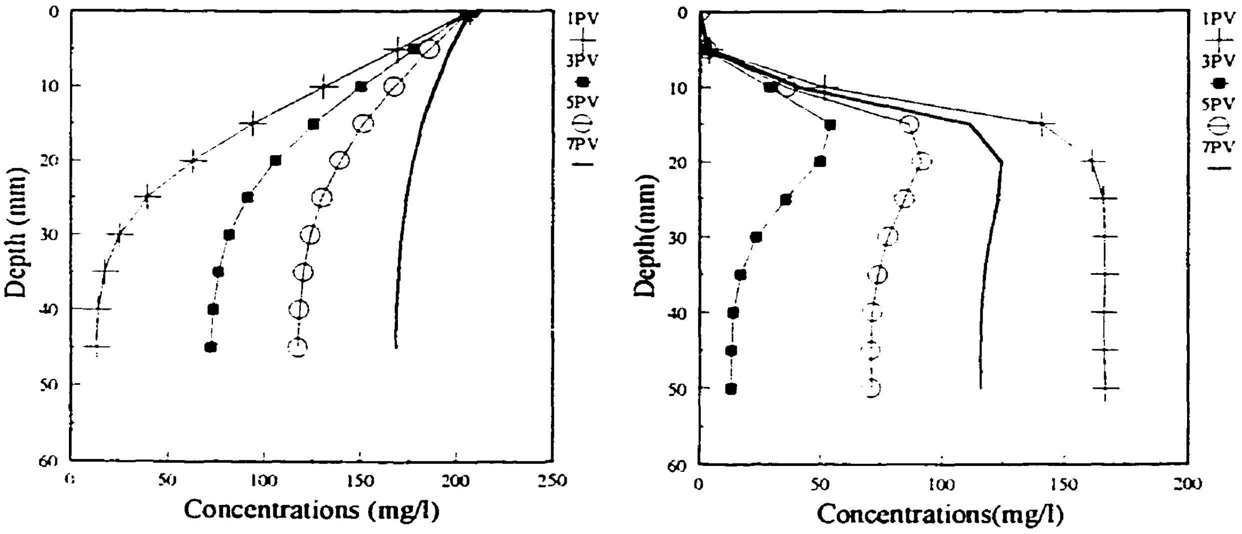
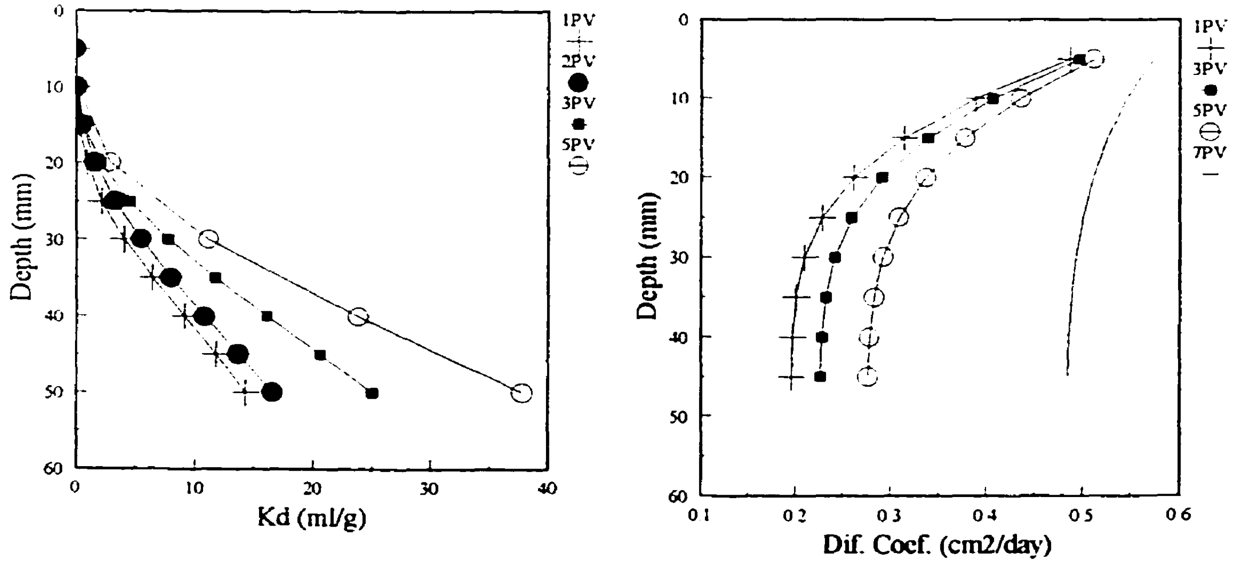


**Fig. 9.15 Predicted Solution pH Effect on Pb Characteristics Profiles for KC.**



(a) Total Pb Profiles in KSC Clay

(b) Pb Adsorption Profiles in KSC



(c) Calculated Kd Profiles

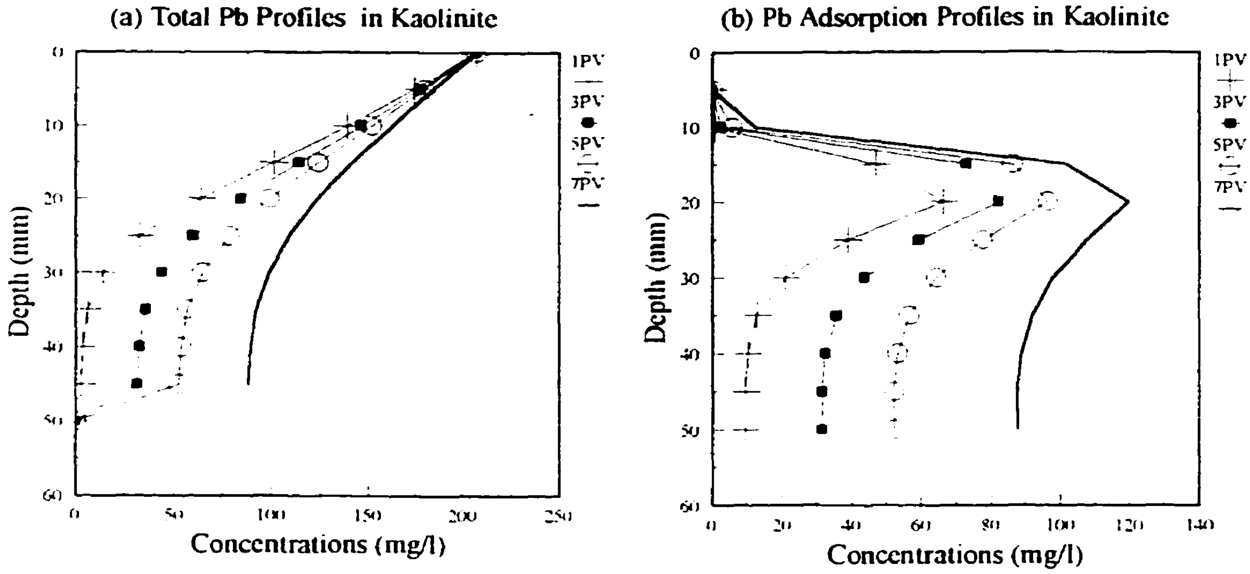
(d) Diffusion Profiles for KSC

**Fig. 9.16** Solution pH Effect on Pb Characteristics Profiles for KSC.

### 9.2.4 The Effect of SSA

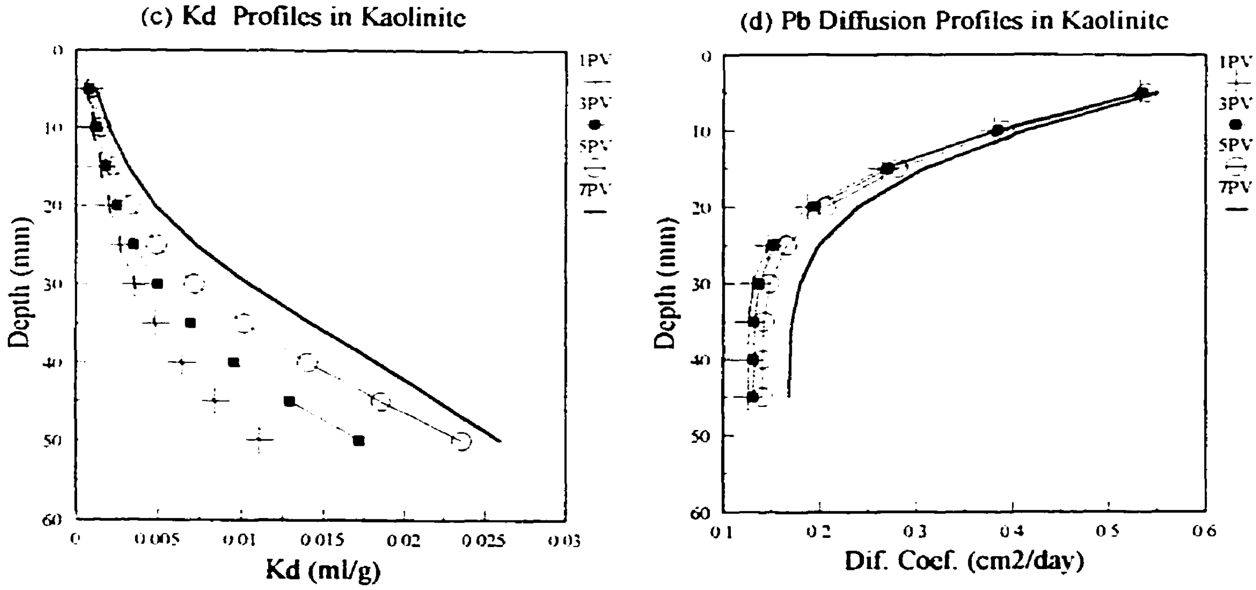
Theoretically, it is accepted that the surface area of the clay soil is one of the most important components which directly enhances the adsorption of the heavy metals or decreases the mobility of ions along the soil depth (Yong et al., 1992; Sposito, 1990, Warren and Zimmerman, 1994). As shown in previous chapters, the difference between the adsorption of a kaolinite mixture and pure kaolinite to heavy metals retention was due to SSA. However, in order to evaluate how the model is sensitive to the surface area, leaving all other parameters constant, the surface area of the kaolinite soil was enlarged five times and kaolinite mixtures (KS, KC, KSC) were reduced to 1/fifth of their actual surface, all other physico-chemical properties were kept constant and COSTCHESP was simulated. The SSA of the kaolinite mixtures were not enlarged because kaolinite mixtures already have enough capacity to retain lead.

The predicted results for the total lead transported, retained (adsorbed+precipitated), distribution coefficient and diffusion coefficient profiles for kaolinite are shown in Figures 9.17a-d and for kaolinite mixtures (KS, KC, KSC) are shown in Figs 9.18a-e to 9.20a-e, respectively. As expected, the figures show the addition of surface area increased the amounts of heavy metals retained in kaolinite soil. The reduction of SSA for kaolinite mixtures increases the mobility of lead and decreases adsorption and the partitioning coefficients. As shown, all soils were sensitive to the increase or decrease of the SSA. The mobility of lead in kaolinite was reduced, due to the increase of the SSA with the same soil pH.



(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite



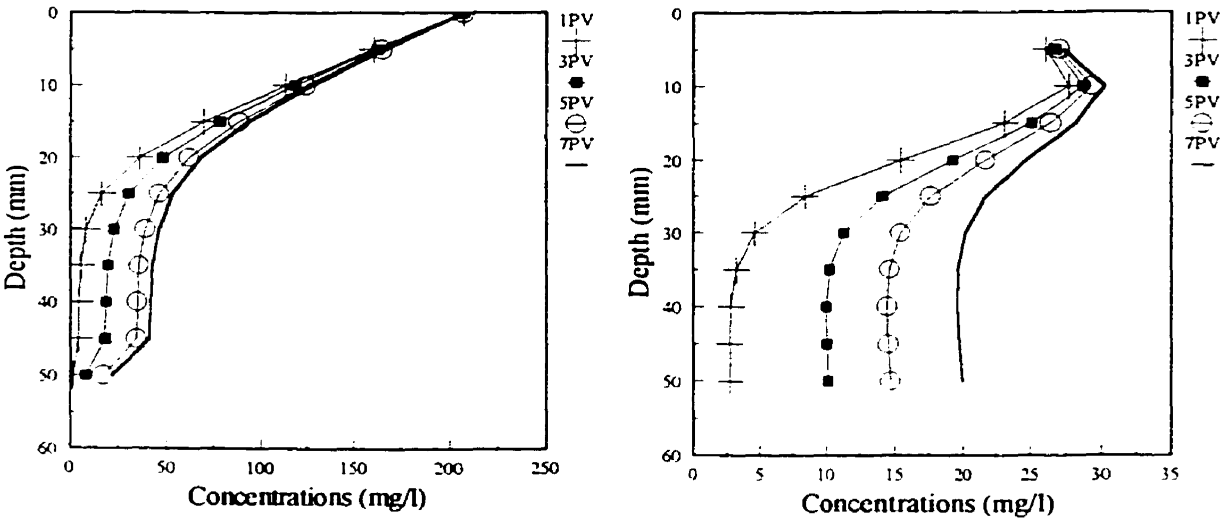
(c) Kd Profiles in Kaolinite

(d) Pb Diffusion Profiles in Kaolinite

**Fig. 9.17** Predicted SSA Effect on Pb Characteristics Profiles for Kaolinite Using 75 m2/g SSA.

(a) Total Pb Profiles in KS

(b) Pb Retention Profiles in KS



(c) Kd Profiles for Pb in KS

(d) Diffusion Profiles for Pb in KS

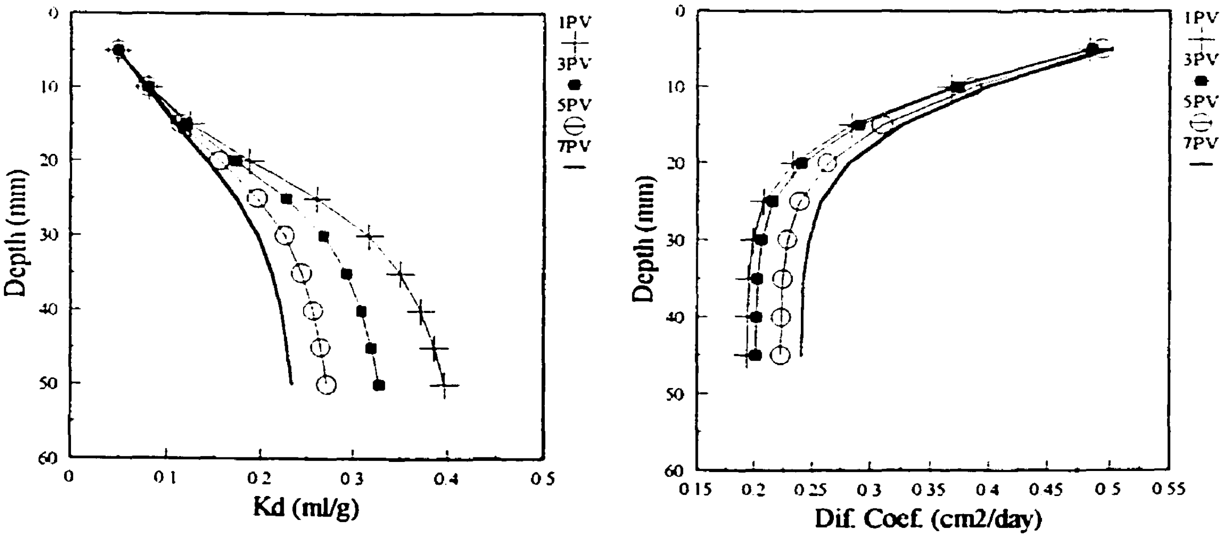
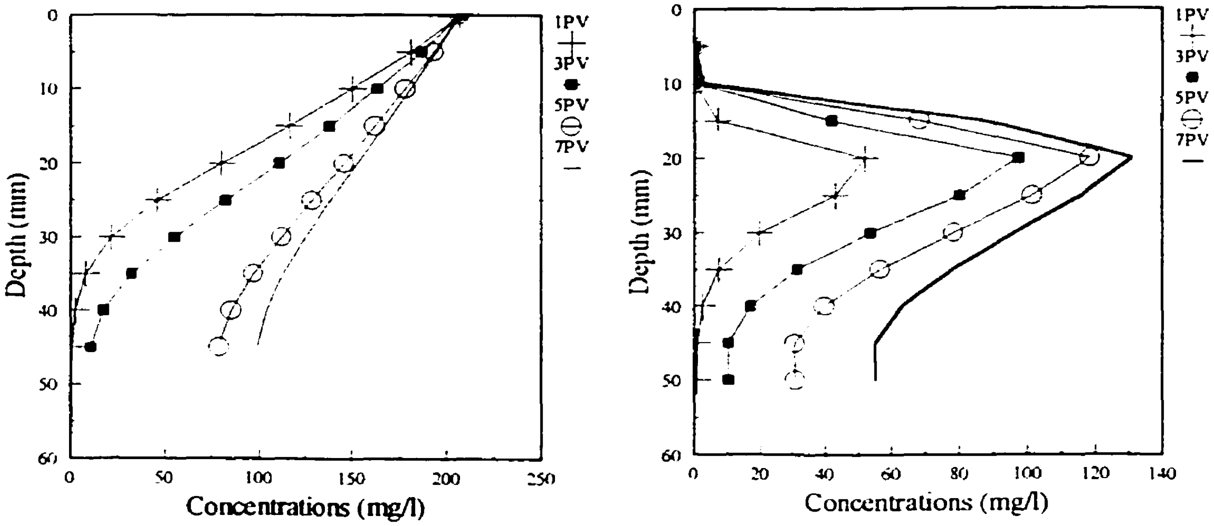
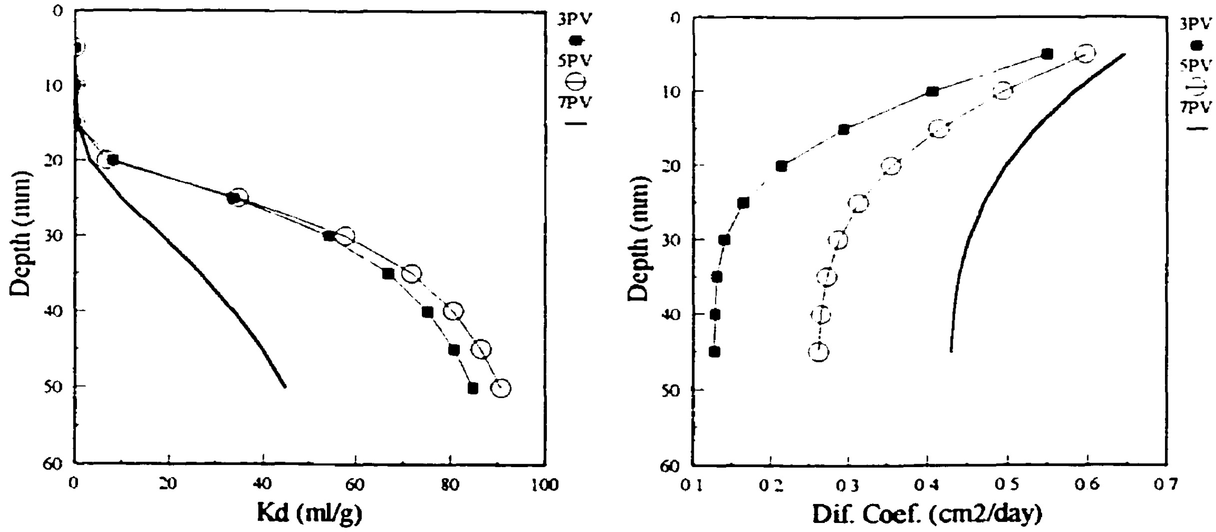


**Fig. 9.18** SSA Effect om Pb Characteristics Profiles for KS using 25 m2/g SSA.



(a) Total Pb Profiles in KC

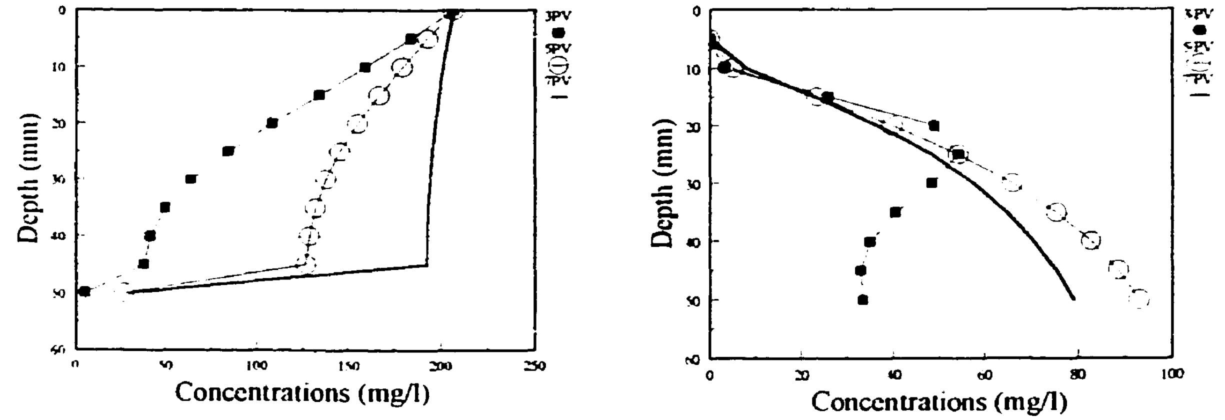
(b) Pb Retention Profiles in KC Soil



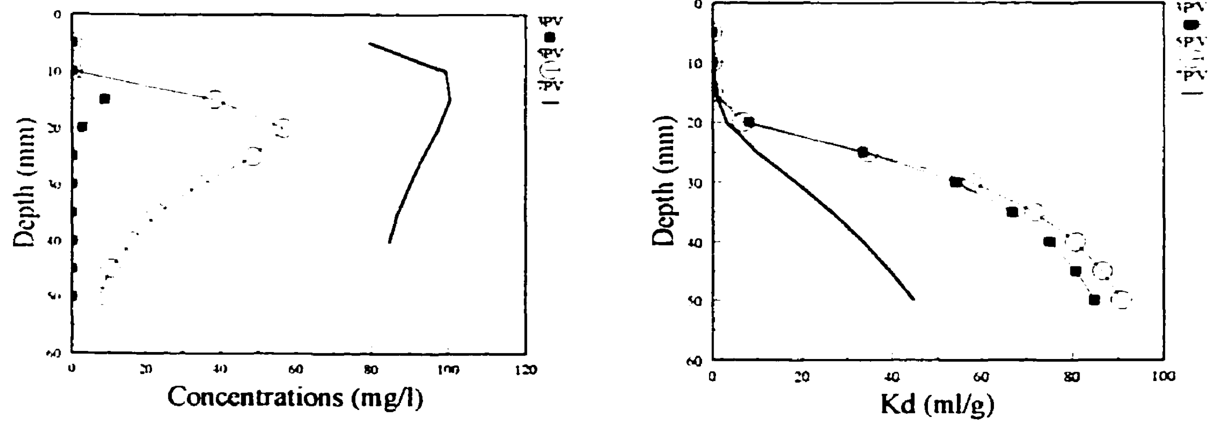
(c) Kd Profiles for Pb in KC

(d) Pb Diffusion Profiles in KC

**Fig. 9.19 SSA Effect on Pb Characteristics Profiles for KC using 11 m2/g SSA.**


(a) Total Pb Profiles in KSC

(b) Pb Adsorption Profiles in KSC


(c) Pb Precipitation Profiles in KSC

(d) Kd Profiles for Pb in KSC

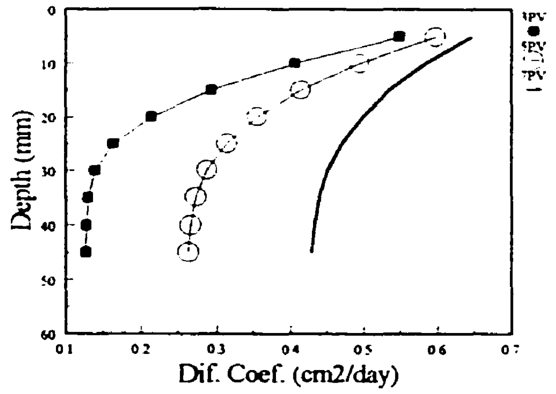
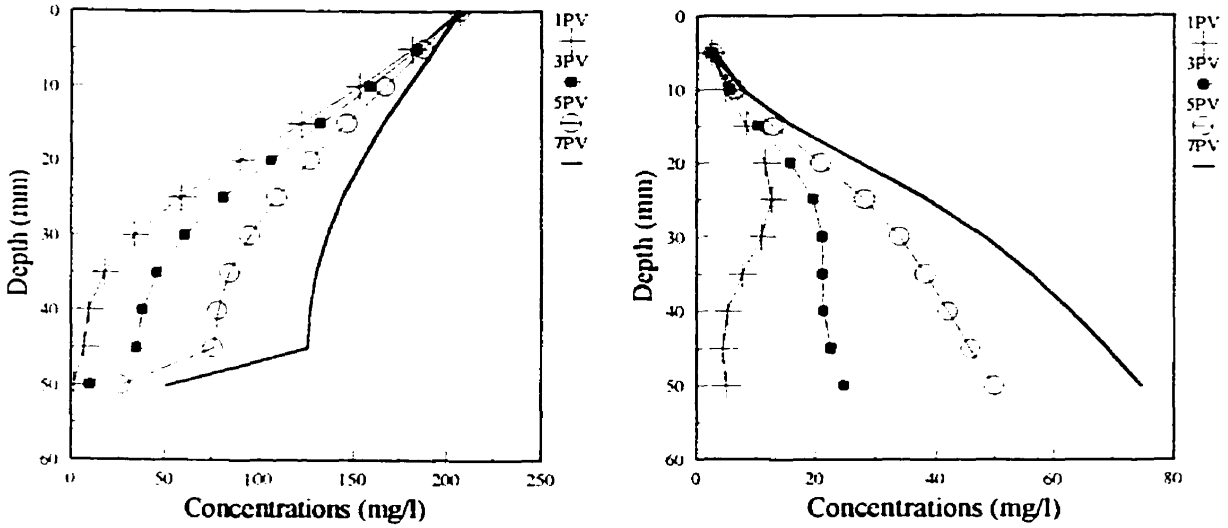

(e) Pb Diffusion Profiles in KSC

**Fig. 9.20** Predicted SSA Effect on Pb Characteristics Profiles for KSC Using 11 m2/g as the SSA.

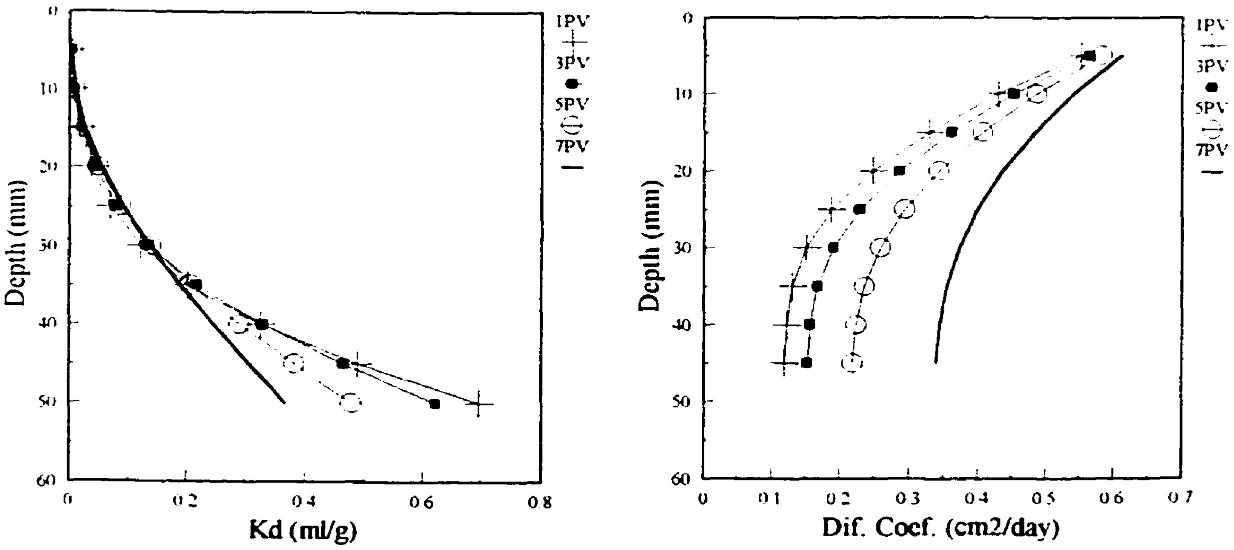
### 9.2.5 The Effect of CEC

It is generally accepted that the cation exchange capacity of clay soil is one of the most important factors which determines the adsorption of the heavy metals (Sposito, 1990; Yong and MacDonald, 1997). The higher the CEC, the more sites are available for adsorption. As discussed in the previous chapter, one of the reasons that a kaolinite mixture has a higher affinity for the adsorption of heavy metals is the higher CEC of kaolinite mixture compared to pure kaolinite. However, in order to evaluate how the model is sensitive to the CEC (using all other parameters constant) the CEC of the kaolinite was enlarged to five times and kaolinite mixtures were reduced to 1/fifth their actual CEC of each soil and COSTCHESP was simulated. The predicted results for the total lead transported, adsorbed/ precipitated and the computed distribution coefficient and diffusion coefficient profiles for kaolinite are shown in Figures 9.21a-d, respectively . As expected, the figures show the addition of CEC increased the amounts of heavy metals retained in kaolinite soil. As expected, the kaolinite soil is more sensitive to the addition of the CEC. It is also shown that the model is sensitive to the CEC.

The predicted results for the total lead transported, adsorbed/ precipitated and the computed distribution coefficient and diffusion coefficient profiles for kaolinite mixture, shown in Figures 9.22a-e to 9.24a-e, demonstrate the influence of the reduction of CEC on the mobility of lead which results in a decrease of adsorption and precipitation profiles and consequently, an increase of the diffusion coefficients and a decrease of partitioning coefficient profiles.


(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite

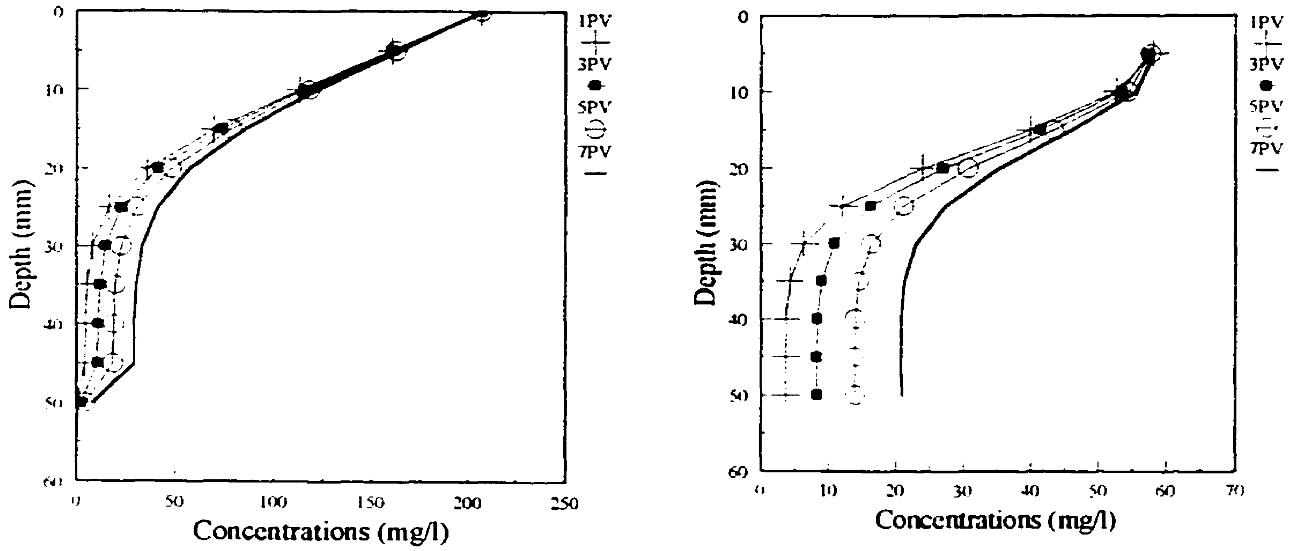

(c) Kd Profiles in Kaolinite

(d) Pb Diffusion Profiles in Kaolinite

**Fig. 9.21** Predicted CEC Effect on Pb Characteristics Profiles for Kaolinite Using 35 m2/g CEC.

(a) Total Pb Profiles in KS

(b) Pb Retention Profiles in KS



(c) Kd Profiles for Pb in KS

(d) Diffusion Profiles for Pb in KS

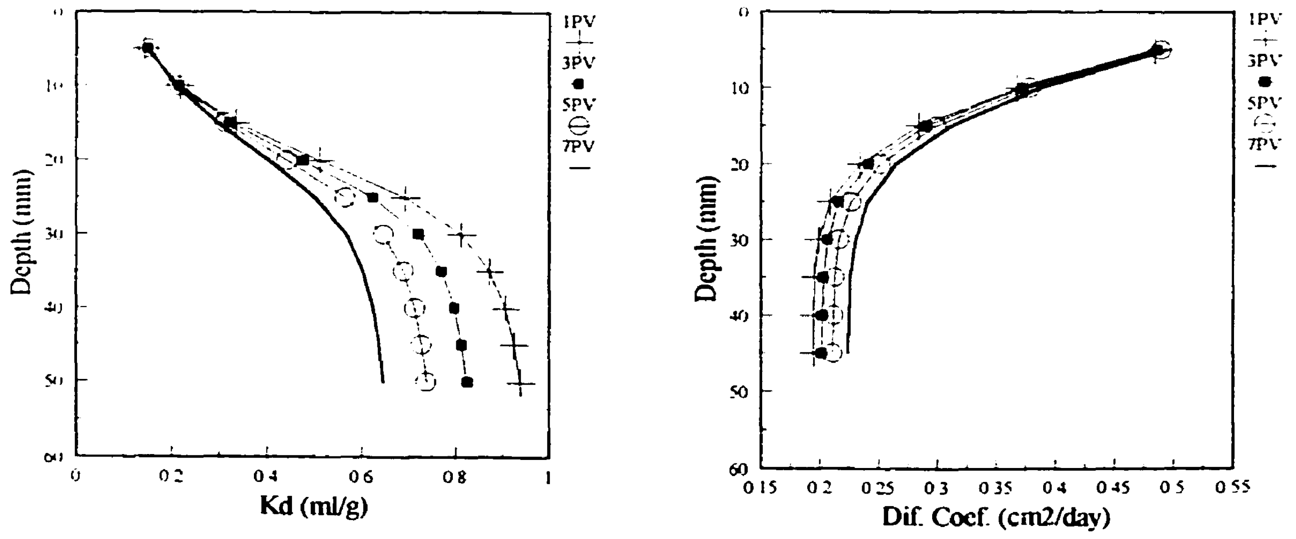


**Fig. 9.22** Predicted CEC Effect on Pb Characteristics Profiles for KS Uusing a CEC of 15 meq/100 .

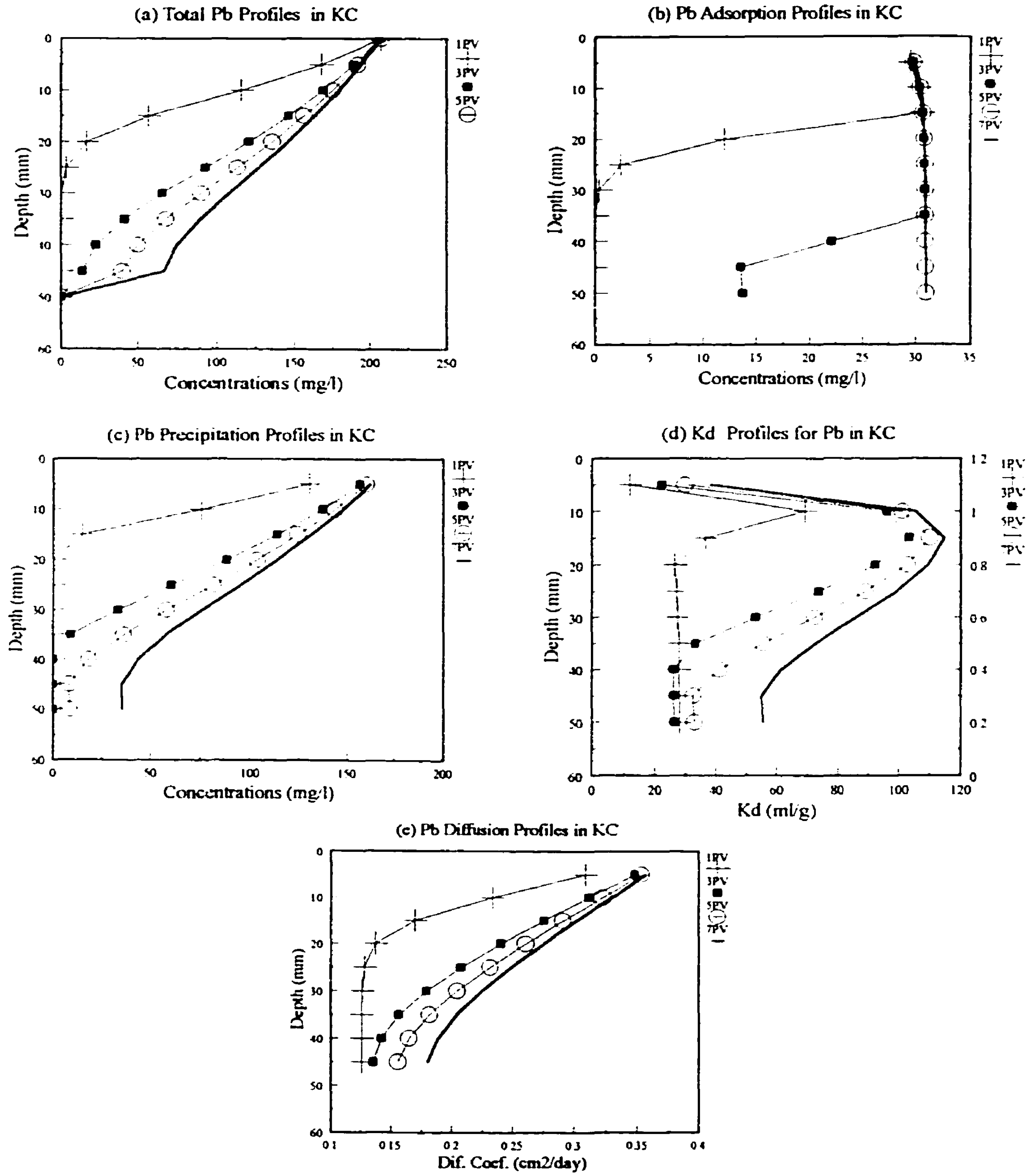
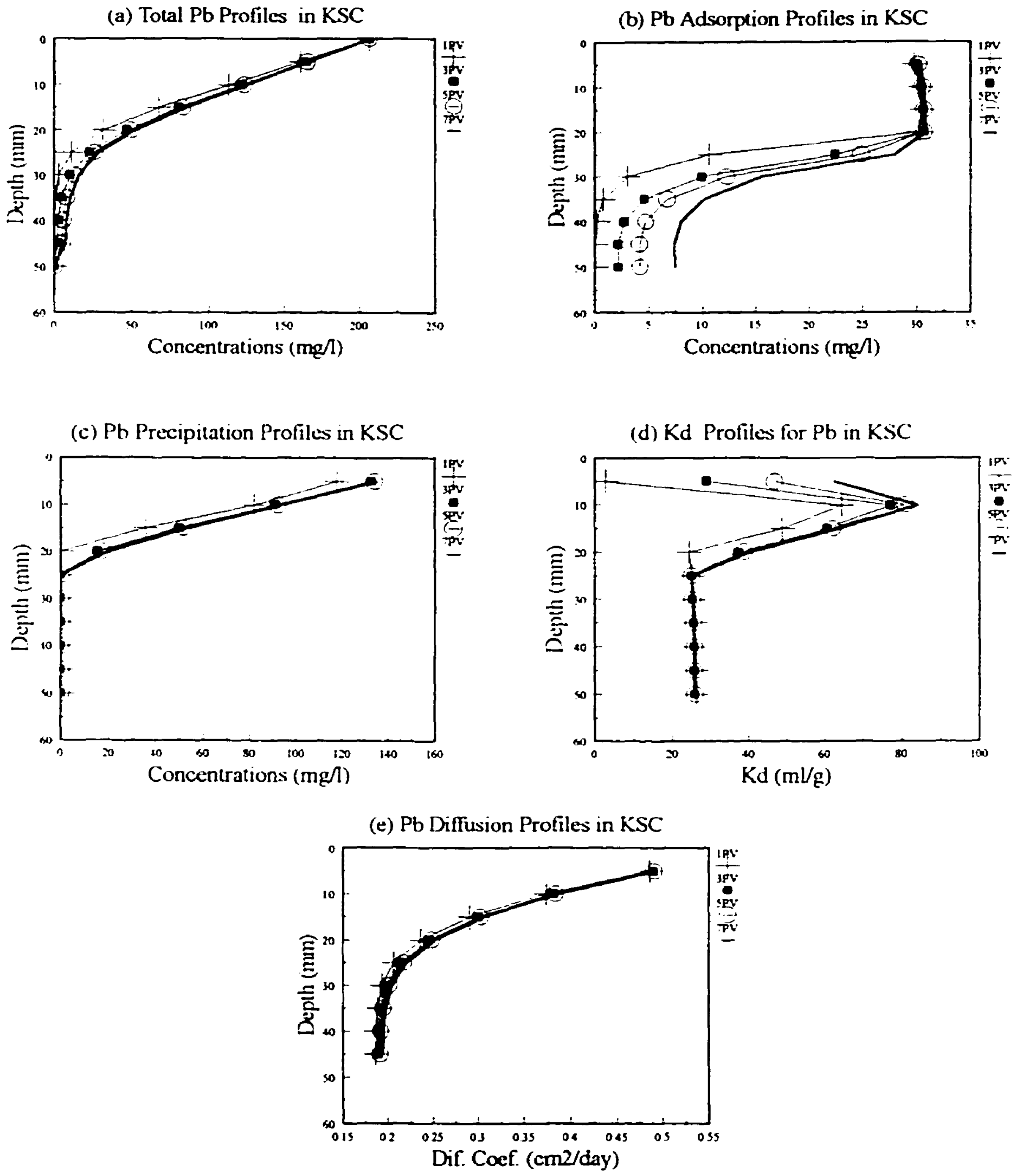


**Fig. 9.23** Predicted CEC Effect on Pb Characteristics Profiles for KC Uusing 5 meq/100 Soil.



(a) Total Pb Profiles in KSC

(b) Pb Adsorption Profiles in KSC

(c) Pb Precipitation Profiles in KSC

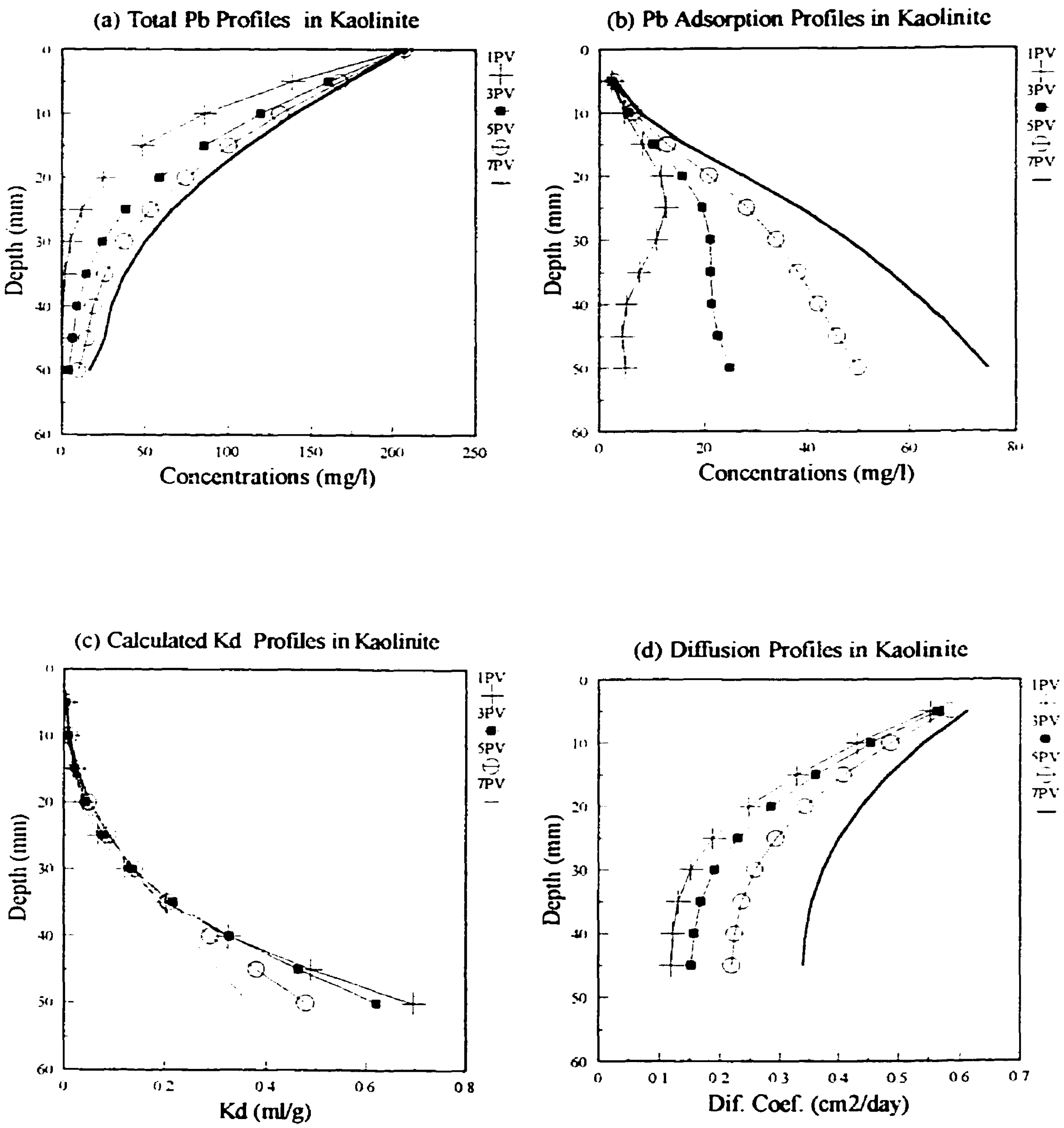
(d) Kd Profiles for Pb in KSC

(e) Pb Diffusion Profiles in KSC

**Fig. 9.24 Predicted CEC Effect on Pb Characteristics Profiles for KSC Using 35 meq/100 Soil.**

### 9.2.6 The Effect of Hydraulic Gradient

Cabaral and Yong (1993) studies indicate that the hydraulic gradient has a minor effect on the coefficient of the permeability. A higher gradient results in a faster mobility of the solution along the depth of the column. Since using a very low gradient was time consuming, a relatively medium gradient was chosen to carry out the column leaching test. In order to evaluate how the proposed model is sensitive to hydraulic gradient, the hydraulic gradient was reduced to 1/10 of the gradient in the experiments. The predicted results for the total lead transported, adsorbed/precipitated profiles and the computed distribution coefficient and diffusion coefficient profiles for kaolinite are shown in Figures 9.25a-d and for kaolinite mixtures are shown in Figs 9.26a-e to 9.28a-e, respectively. As shown, the higher the gradient, the higher the mobility, which results in more heavy metals transported to the subsurface. Using a lower gradient causes the permeant transport at very low rate. For example, in order to pass one pore volume of leachate into kaolinite soil it took 40 days and for KSC and KC 100 and 110 day. These results agree with previous research done by Bailey and Lynch (1996), which shows that at a very low flow rate the adsorption of heavy metals into clay soils increased.

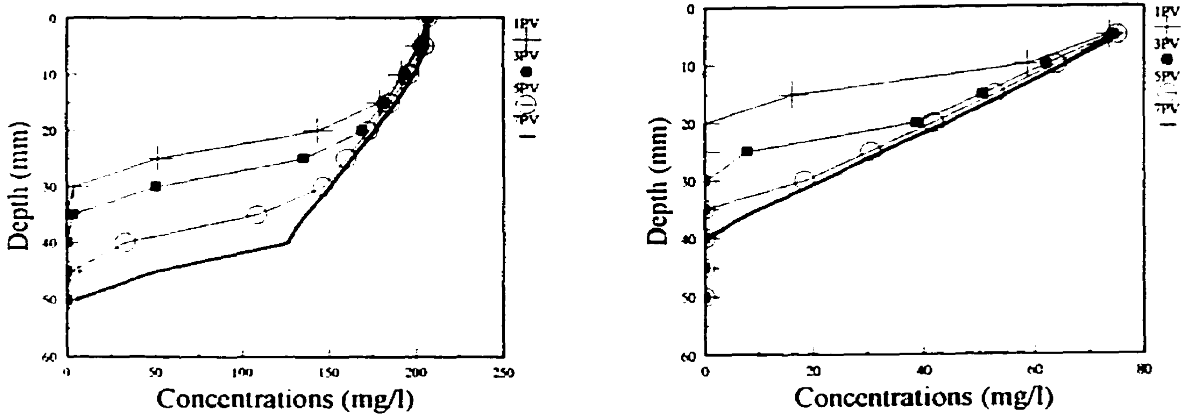

(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite

(c) Calculated Kd Profiles in Kaolinite

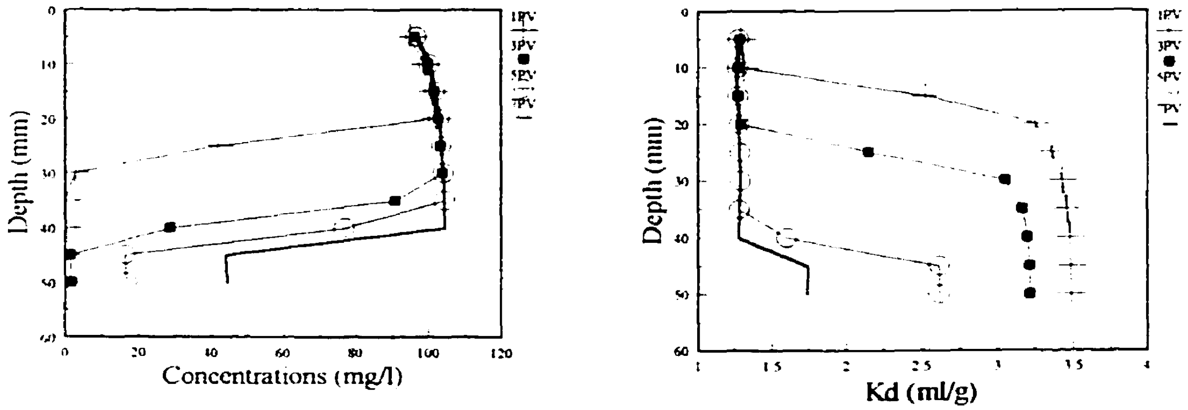
(d) Diffusion Profiles in Kaolinite

**Fig. 9.25** Predicted Gradient Effect on Pb Characteristics Profiles for Kaolinite Using Gradient of 4.00.



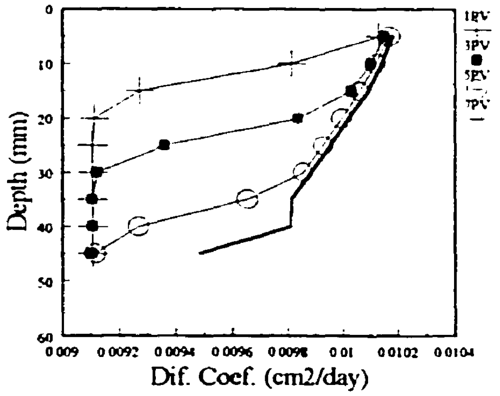
(a) Total Pb Profiles in KS

(b) Pb Adsorption Profiles in KS



(c) Pb Precipitation Profiles in KS

(d) Kd Profiles for Pb in KS



(e) Pb Diffusion Profiles in KS

**Fig. 9.26** Predicted Gradient Effect on Pb Characteristics Profiles for KS Using Gradient of 4.00.

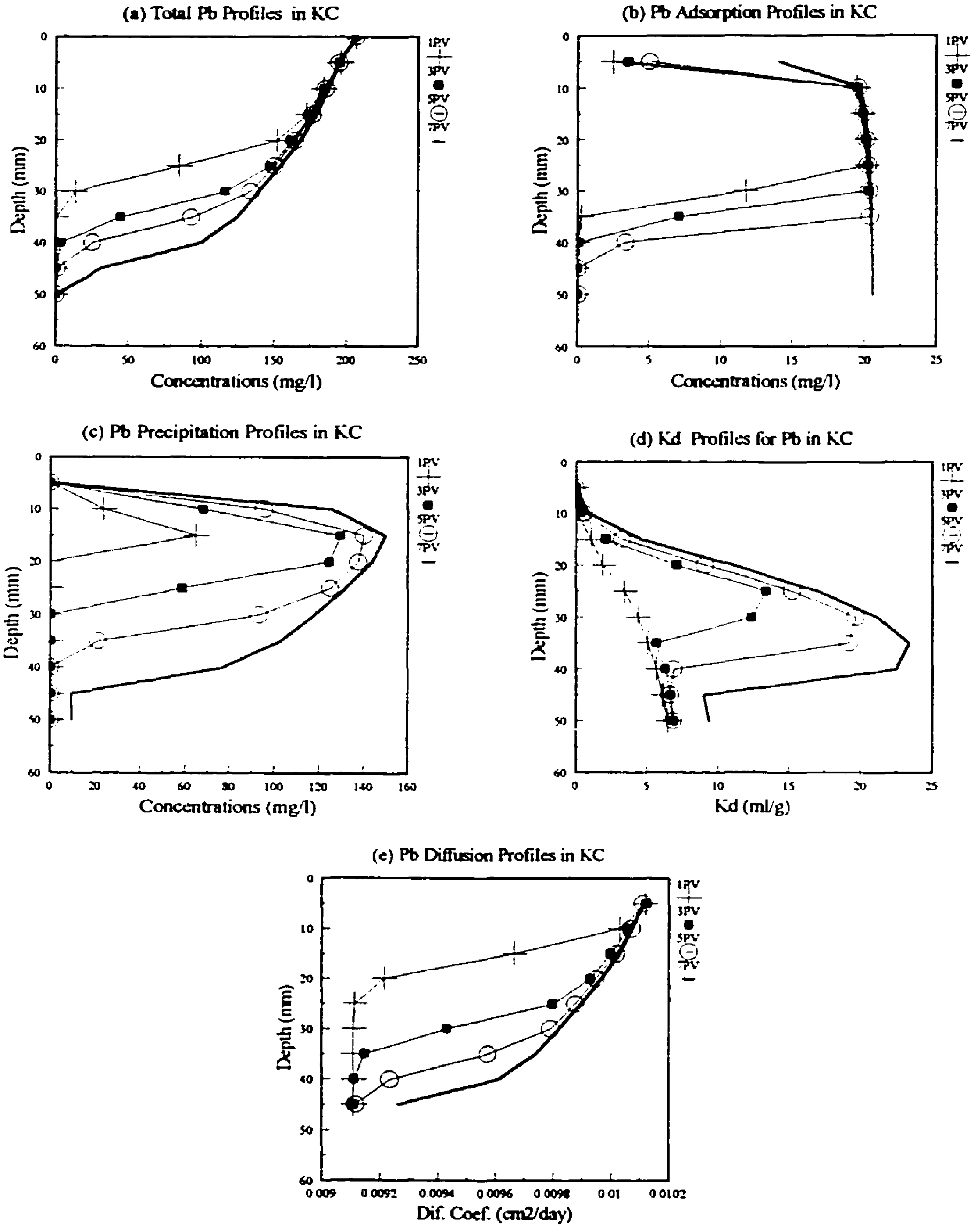
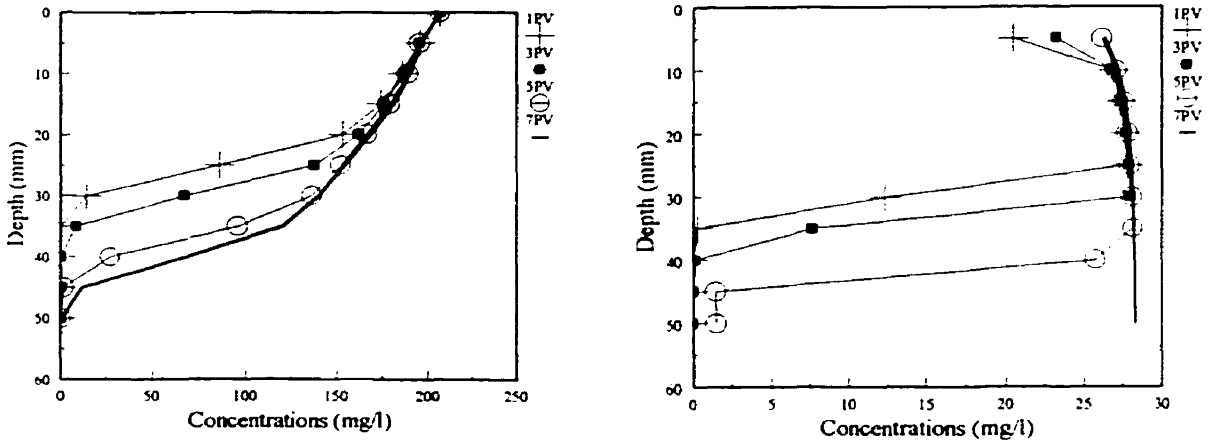
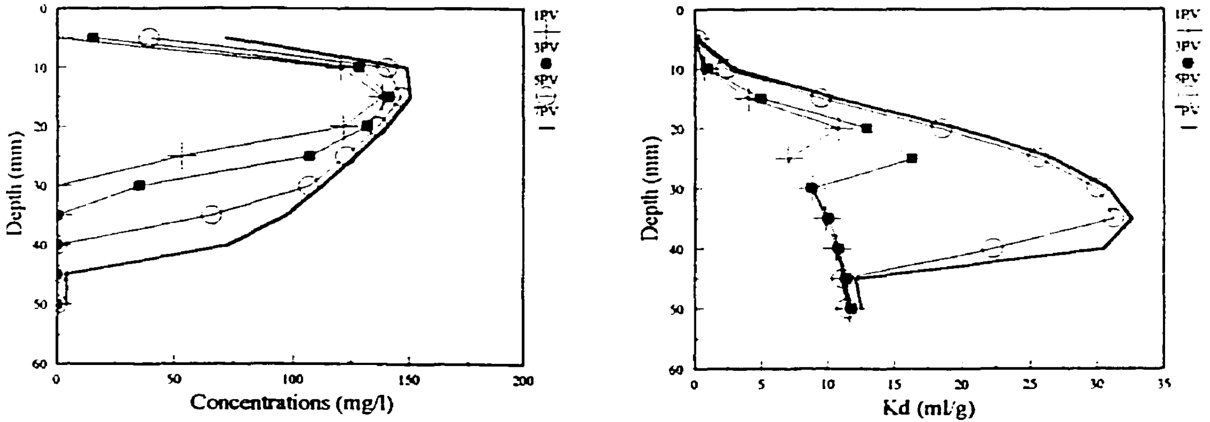


**Fig. 9.27** Gradient Effect on Pb Characteristics Profiles for KC Soil Using Gradient of 4.00.



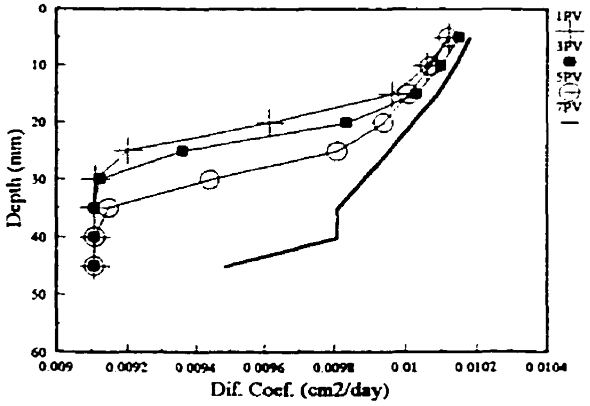
(a) Total Pb Profiles in KSC

(b) Pb Adsorption Profiles in KSC



(c) Pb Precipitation Profiles in KSC

(d) Kd Profiles for Pb in KSC



(e) Pb Diffusion Profiles in KSC

**Fig. 9.28** Gradient Effect on Pb Characteristics Profiles for KSC Soil Using Gradient of 4.00.

### 9.2.7 The Effect of Temperature

The reactivity of a chemical interaction of a multi-component system is a function of temperature. The equilibrium constants described in Equation 3.4 are functions of the system temperature and ionic strength. The values supplied in MINTEQA3.1 (Allison, 1993) thermodynamic database are referenced to 25° C and an ionic strength of zero. If the temperature is not at 25° C , a new equilibrium constant must be calculated before solving the equation.

The ionic strength constants must be calculated before solving the equation. The ionic strength affects activity coefficients which, in turn, affect the adjusted equilibrium constants. MINTEQA3.1 allows the option of specifying a fixed ionic strength or of recalculating the ionic strength from the new estimates of species concentrations at each iteration. Chemical equilibrium speciation incorporates two schemes for adjusting the equilibrium constants for temperature. If the necessary data are available in the thermodynamic database, it uses a power function of the form

$$\log K_T = A + BT + C/T + D\,\mathrm{Log}(T) + ET^2 + F/T^2 + GT^{0.5} \qquad \mathbf{(9.1)}$$

where

T = temperature (K)

A,B,... G = empirical constants stored in the thermodynamic database

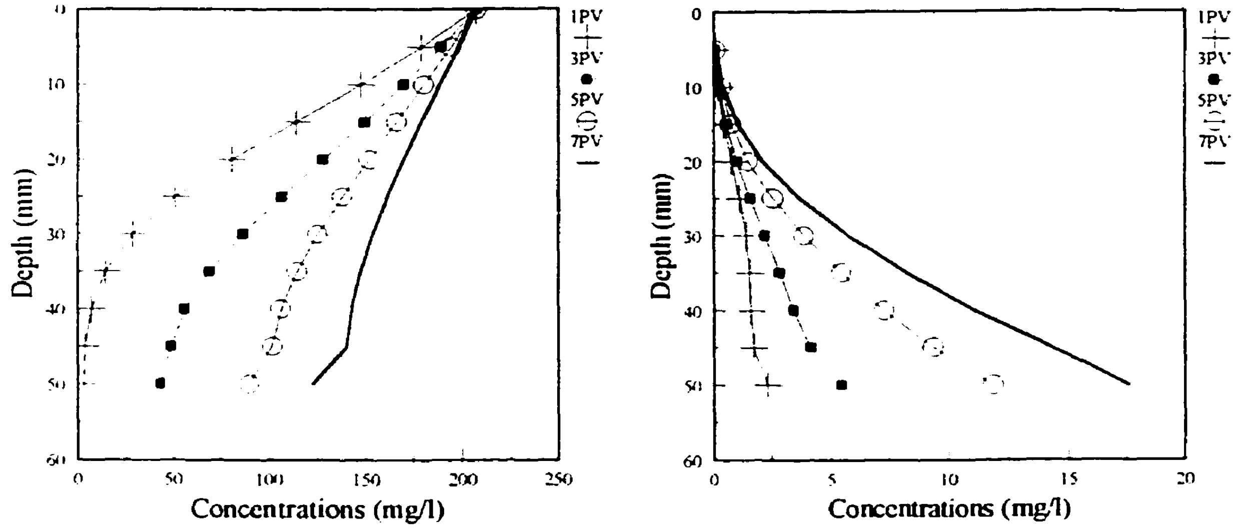
For any species that does not have the constants needed for Equation 9.1, the equilibrium constant is corrected for temperature variations from 25° C by the Van't Hoff Equation

$$\log K_T = lgK_{T_r} - \frac{\Delta H_r^o}{2.303R}\left[\frac{1}{T} - \frac{1}{T_r}\right] \qquad \textbf{(9.2)}$$

where

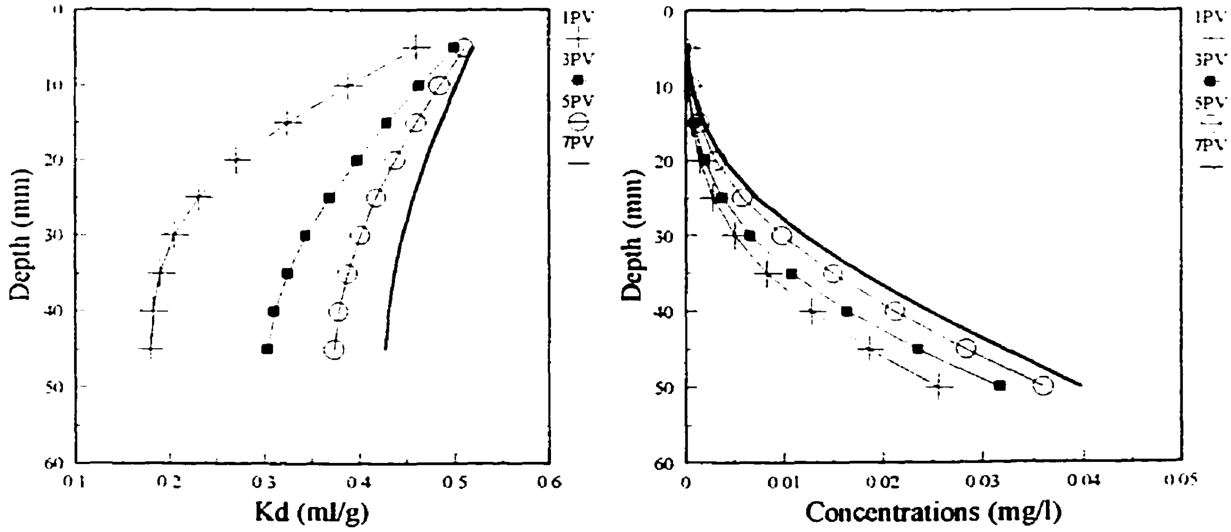
$T_r$ = reference temperature, 298.16 K
R = molar gas constant
log $K_{Tr}$ = log of the equilibrium constant at the reference temperature
T = temperature of the system to be modelled (Kelvin)
$\Delta H_r$ = standard enthalpy change of the reaction

However, in order to evaluate the sensitivity of the model to isothermal temperature, (using all other parameters constant). the reaction temperature was increased to 100° C and the COSTCHESP was simulated. The above simplification should usually be valid in the groundwater zone, but is probably not satisfactory near the ground surface where large temperature gradients are present The predicted results for the total lead transported, migrated, adsorbed, precipitated profiles and the computed distribution coefficient and diffusion coefficient profiles for kaolinite soil and kaolinite mixtures are shown in Figs 9.29 to 9.32 a-d. As expected increasing the temperature reduced the amounts of heavy metals retained for all type of the soils. As shown in Figure 9.29 to 9.32 the retention of lead into a kaolinite mixture (KS, KC, KSC) shifted from the adsorption into the precipitation form. These results are agree with previous research done by Serpaud *et al.*, 1994. Their studies show that a temperature increase from 10 degree C to 40 degree C caused decreased heavy metals (Cu, Zn, Cd and Pb) adsorption on clay soils as observed from Freundlich and Langmuir plots.



(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite



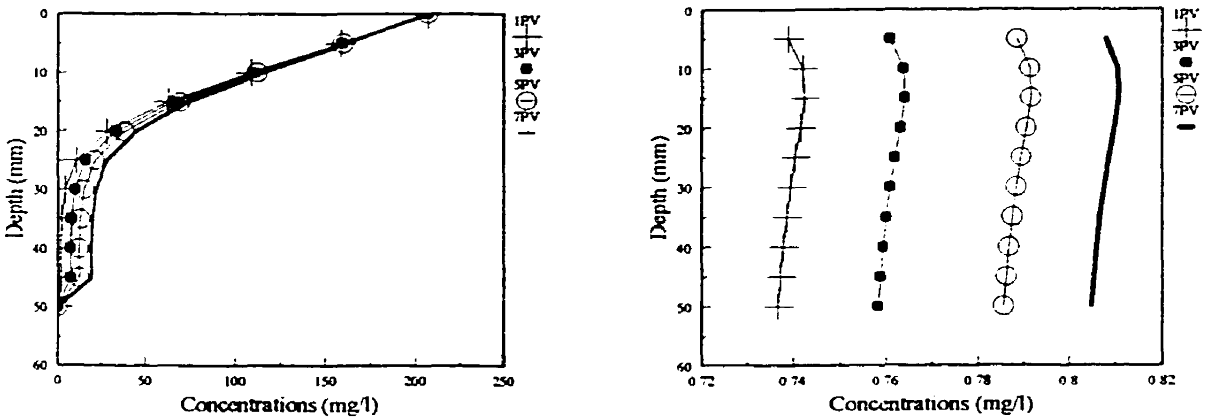
(d) Kd Profiles for Pb in Kaolinite

(d) Pb Diffusion Profiles in Kaolinite

Fig. 9.29 Predicted Temperature Effect on Pb Characteristics Profiles for Kaolinite Soil.

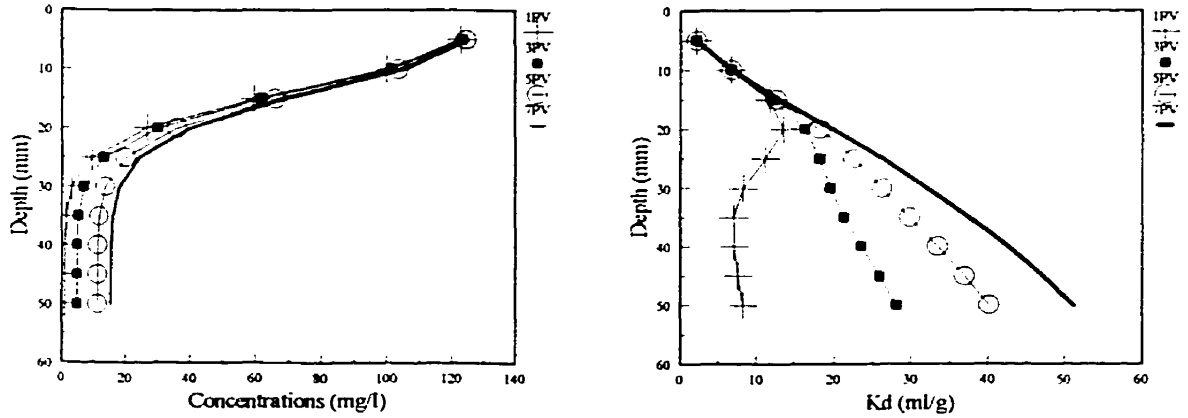
(a) Total Pb Profiles in KS

(b) Pb Adsorption Profiles in KS



(c) Pb Precipitation Profiles in KS

(d) Kd Profiles for Pb in KS



(e) Pb Diffusion Profiles in KS

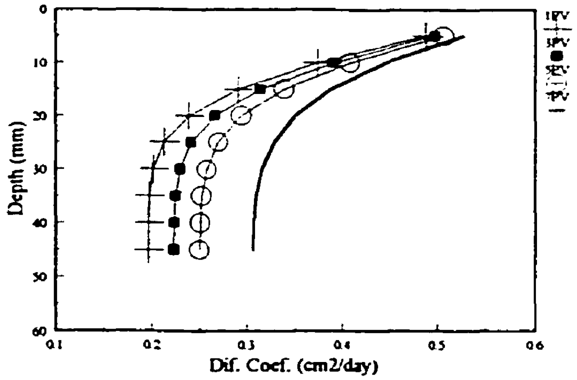
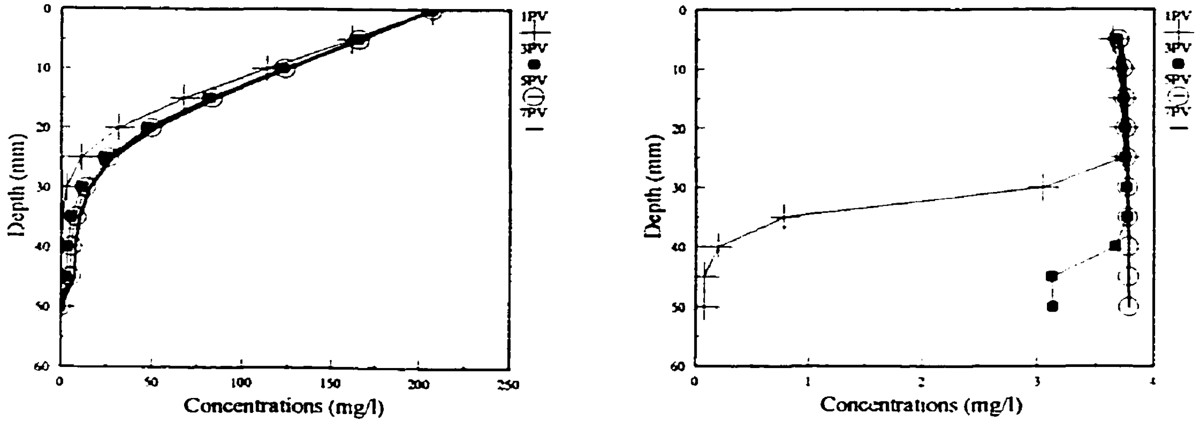
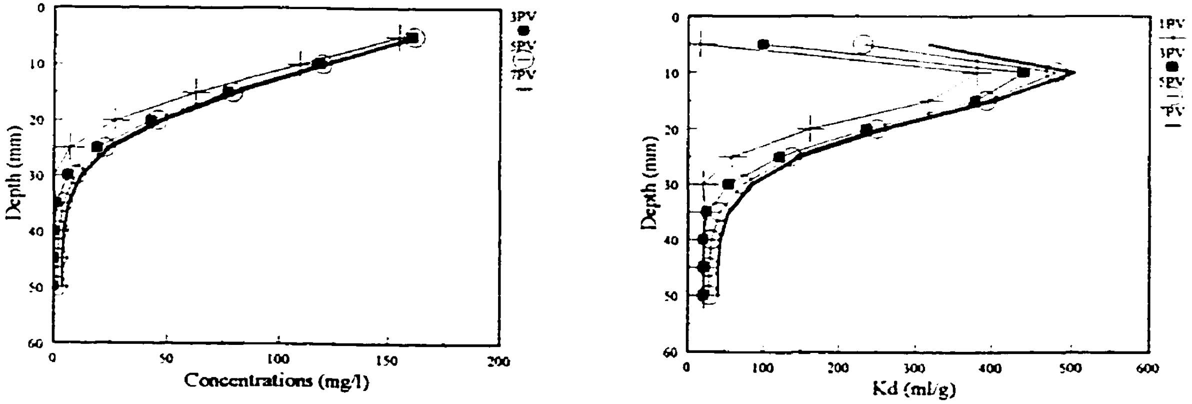


**Fig. 9.30 Temperature Effect on Pb Characteristics Profiles for KS Soil.**



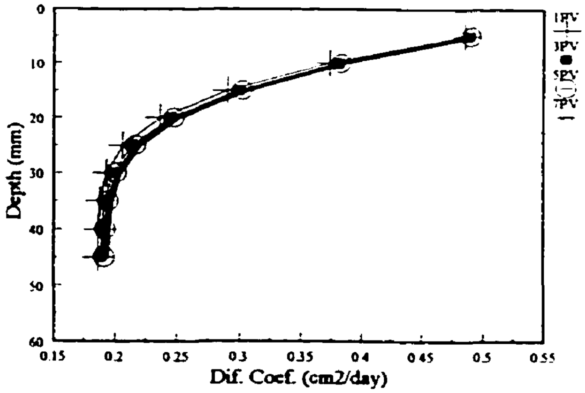
(a) Total Pb Profiles in KC

(b) Pb Adsorption Profiles in KC



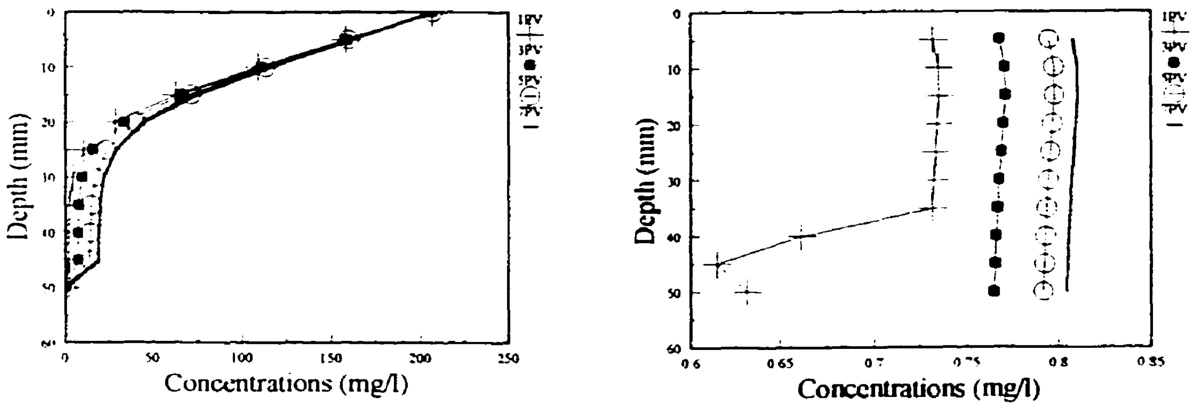
(c) Pb Precipitation Profiles in KC

(d) Kd Profiles for Pb in KC



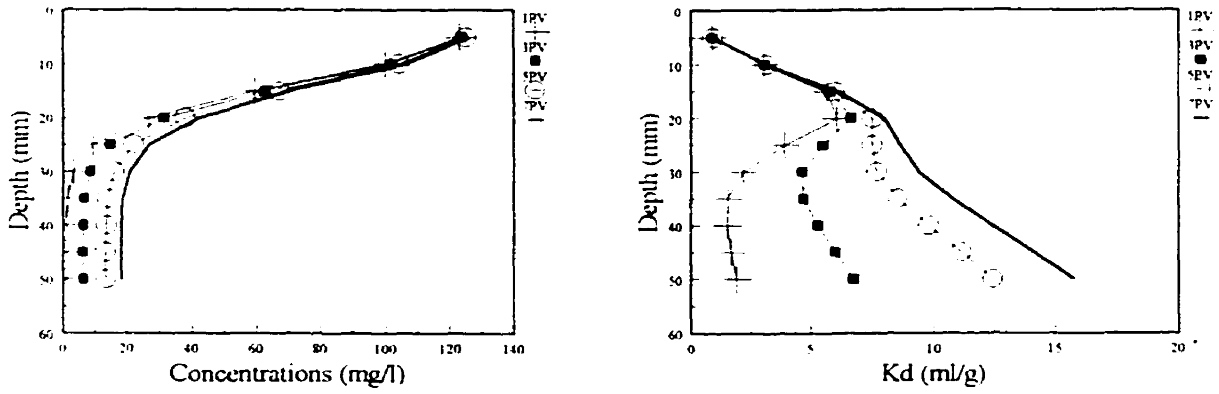
(e) Pb Diffusion Profiles in KC

**Fig. 9.31** Temperature Effect on Pb Characteristics Profiles for KC Soil.



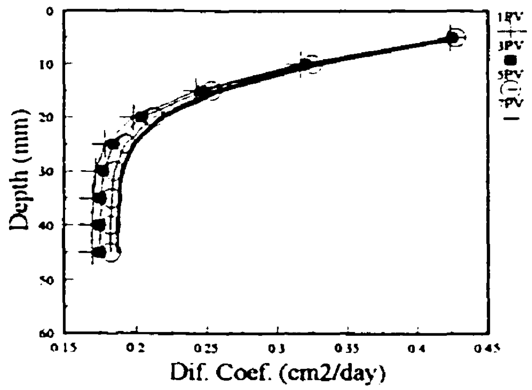
(a) Total Pb Profiles in KSC

(b) Pb Adsorption Profiles in KSC



(c) Pb Precipitation Profiles in KSC

(d) Kd Profiles for Pb in KSC



(e) Pb Diffusion Profiles in KSC

**Fig. 9.32 Predicted Temperature Effect on Pb Characteristics Profiles for KSC Soil.**

### 9.2.8 The Effect of $CO_2$ pressure

The partial pressure of carbon dioxide ($CO_2$ ) has been noted as the major chemical variable controlling the precipitation of heavy metals carbonates (Sposito, 1984). In an open system such as earth's atmosphere $P_{CO2}$ is constant (0.0003 atmosphere) so that dissolved $CO_2$ is also constant. Rainwater and melted snow in nonurban, nonindustrial areas have pH values normally between 5 and 6. The equilibrium pH for nonsaline water in contact with $CO_2$ at the earth's atmospheric value of $10^{-3.5}$ bar is 5.7 (Freeze and Cherry, 1979). Measurements of the composition of gas samples from soils at locations in North America, Europe, and elsewhere have established that the $CO_2$ partial pressure of soil atmosphere is normally much higher than that of the earth's atmosphere. Values in the range of $10^{-3}$ - $10^{-1}$ bar are typical. In a landfill environment, the partial pressure of $CO_2$ is constantly changing due to the variations of temperature, moisture conditions, microbial activity, availability of organic matter and the dissolution of calcium carbonate in the leachate. In this case, the $CO_2$ is not free to escape in the atmosphere and the partial pressure of $CO_2$ in a young leachate, for example, is obviously greater than that of atmosphere. The production of carbon dioxide occurs during bacterial oxidation of organic matter or dissolution of limestone from natural soil. In addition, the use of crushed limestone along with soil liners has been suggested as a means for immobilization of heavy metals.

Specifying a gas phase at a fixed partial pressure in the system would have much the same effect mathematically as does a solid phase. When a $CO_2$ gas phase is present, the following reaction would apply

$$CO_3^{2-}+2H^{+}-H_2O-CO_2$$

The corresponding mass action expression would be represented by

$$P_{CO_2}=(CO_3^{2-})+(2H^{+})^2(-H_2O)^{-1}K-CO_2$$

Where $P_{co2}$ is the partial pressure in atmosphere. For a system open to the atmosphere, $P_{co2}$ is fixed at $10^{-3.5}$ atmosphere (Allison, *et al*, 1993). The new equilibrium constant would be

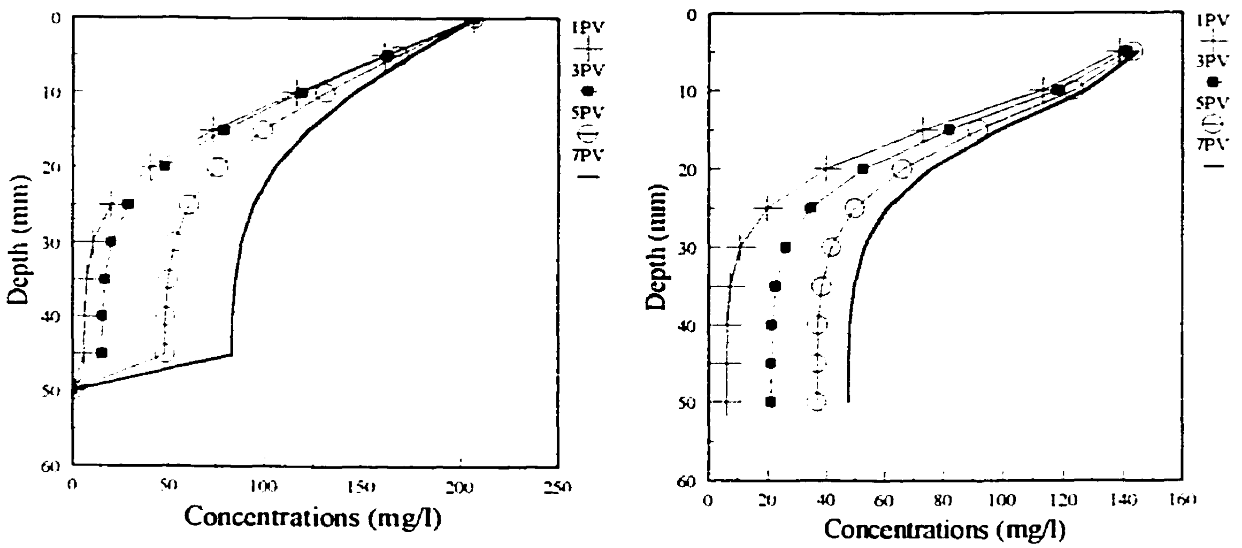
$$K^{'}=K/P_{CO2}$$

CHESP computes the adjusted equilibrium constant from the user-specified partial pressure.

To evaluate the effect of $P_{CO2}$ on the mobility of lead or zinc into kaolinite or a kaolinite mixture, COSTCHESP was simulated using the $P_{CO2}$ with a pressure which is equal to atmosphere while the other physico-chemical properties were kept constant, except the adsorption parameter which was changed for the new concentration. The predicted results for the total lead transported, migrated, adsorbed, precipitated profiles and the computed distribution coefficient and diffusion coefficient profiles for KC and KSC are shown in Figs 9.33 to 9.34a-e. The effect of $P_{co2}$ pressure was not simulated for kaolinite and KS since they do not have $CO_2$ in their composition. As shown in Figure 9.33, for KC soil as the $P_{co2}$ pressure increased the retention of lead shifted from the precipitation to the adsorption form and the precipitated lead was negligible in both types of soil.

(a) Total Pb Profiles in KC

(b) Pb Adsorption Profiles in KC



(c) Kd Profiles for Pb in KC

(d) Pb Diffusion Profiles for KC

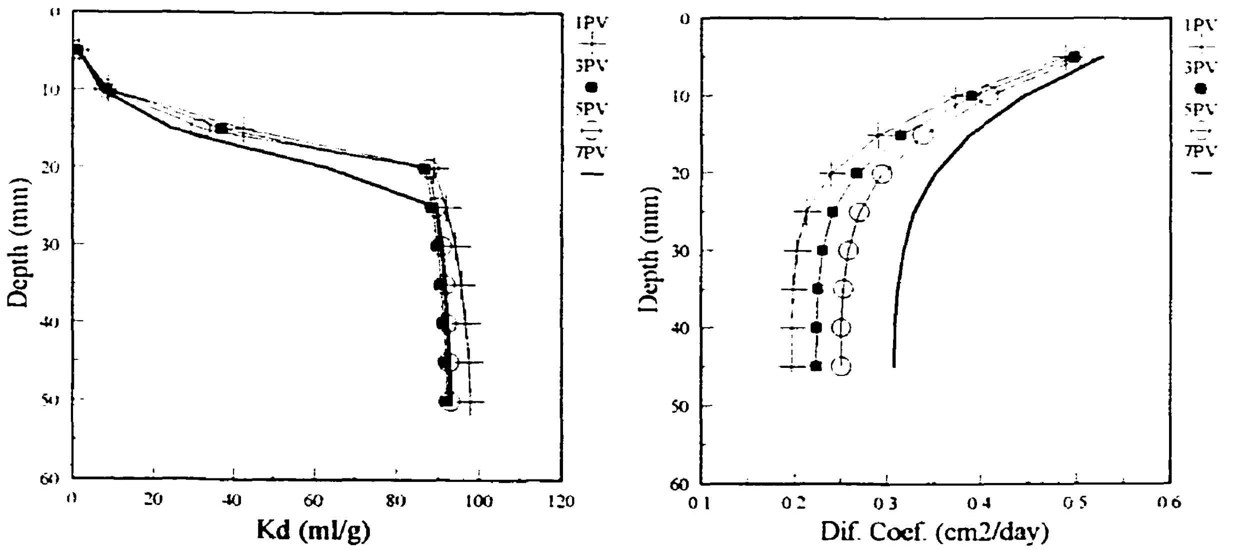


**Fig. 9.33 Predicted CO2 Pressure Effect on Pb Characteristics Profiles for KC Soil.**

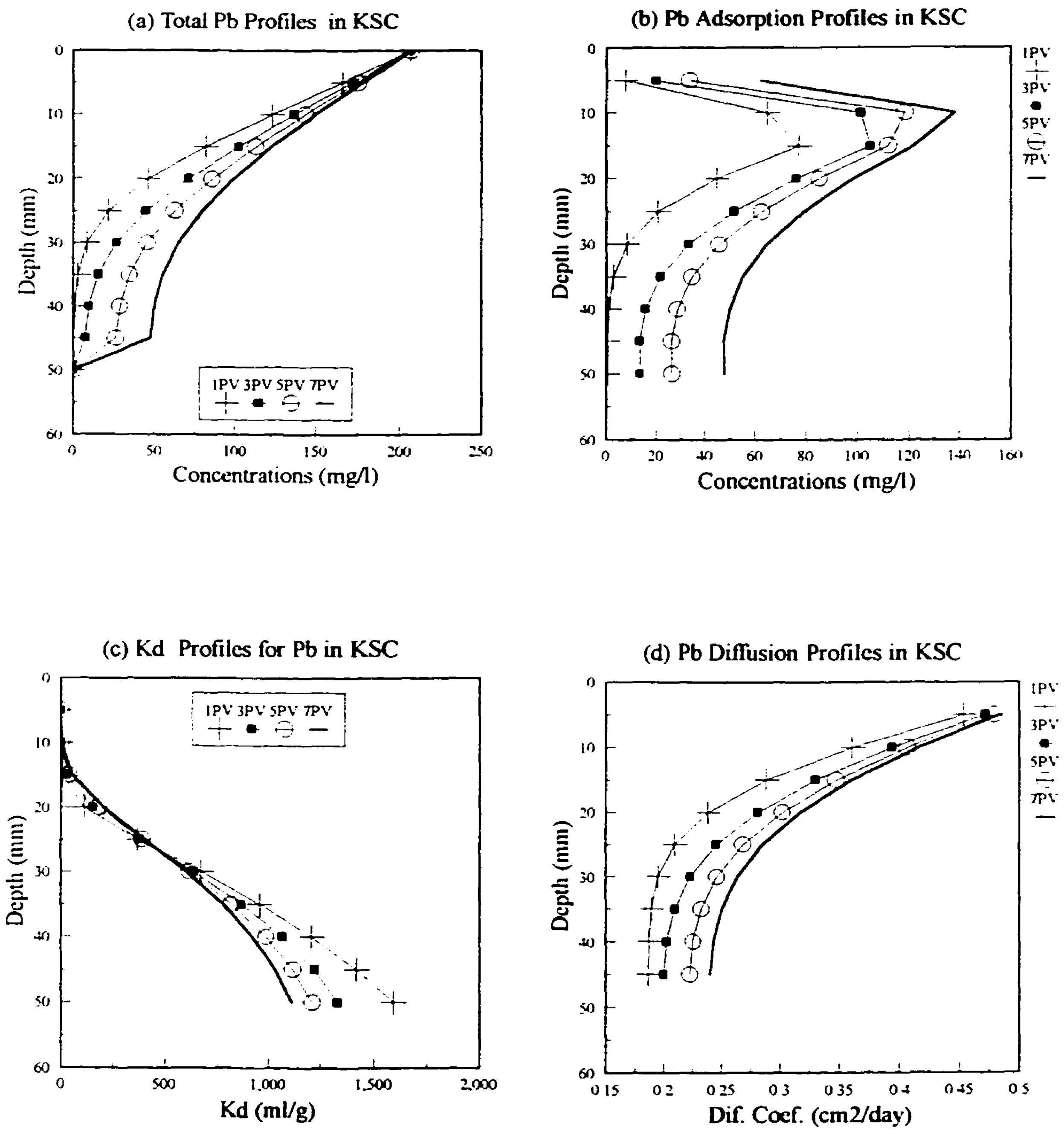
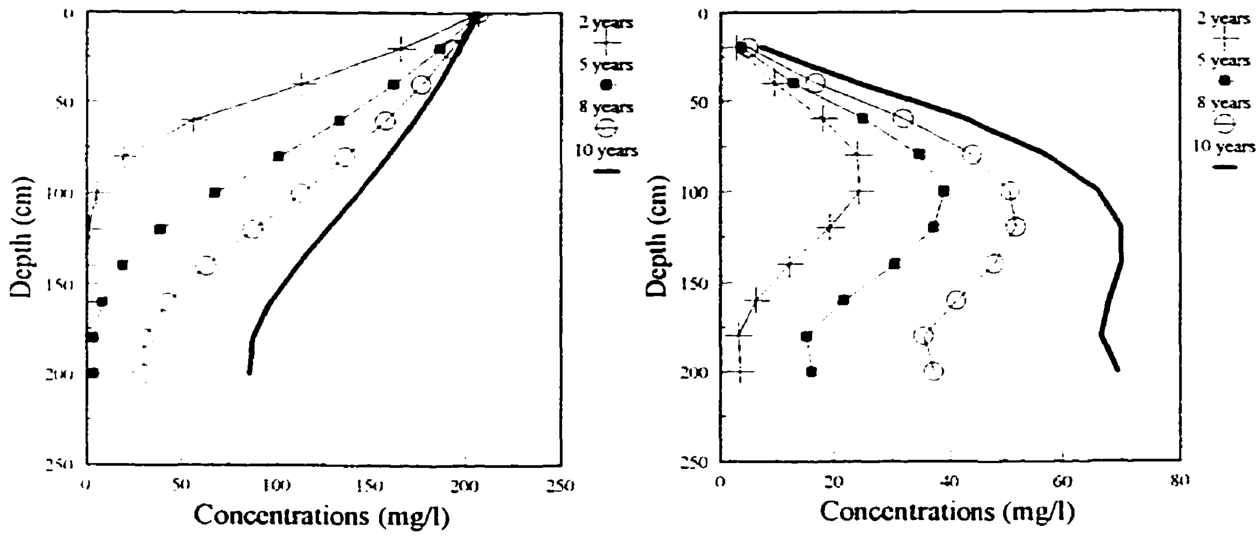


**Fig. 9.34** CO2 Pressure Effect on Pb Characteristics Profiles for KSC Soil.

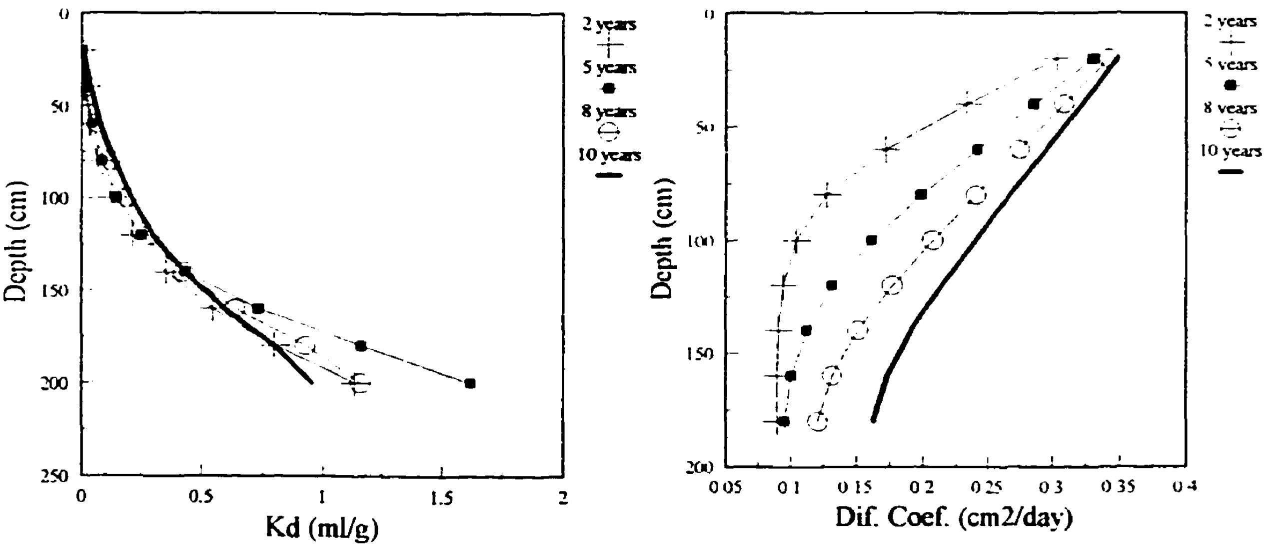
### 9.2.9 The Effect of Depth of Clay liner

Borden and Yanoschak (1990) examined chemical data from monitoring wells at 71 municipal sanitary landfills in North Carolina, U.S.A. Ground water-quality violations were found for Pb and Cr (18% of sites), and As, Cd and Zn (6% of sites). Although Yanful *et al.* (1988) studies at the confederation road landfill site near Sarina, Ontario indicate that heavy metals migrated a distance of 10-20 cm in 16 years due to high pH (7.8) of the environment and very high carbonate content (34%) of the clay subsoil.

However, in order to evaluate how the model is sensitive to the depth of clay liner (using all other parameters constant) the depth of each clay soil was enlarged to 2 m and COSTCHESP was simulated. This depth is a reasonable depth in an actual landfill. A time incerement of 10 days and space incerement of 20 cm were chosed. The prediction was made for a total of 3600 days (10 years). The predicted results of the total lead transported, adsorbed and the computed distribution coefficient and diffusion coefficient profiles in kaolinite and KS clay, after 2 years, 5 years, 8 years and ten years, are shown in Figs (9.35a-d ) and the total lead transported, adsorbed and the computed distribution coefficient and diffusion coefficient profiles in kaolinite mixtures (KS, KC, KSC) are shown in Figs 9.36a-d and 9.38a-d, respectively. As expected, the predicted migration profiles show that most of the lead was retained in the top part of the soil. Very little Pb was migrated at the bottom of the soil column in kaolinite mixtures due to the high retention of lead in clay soil. The kaolinite soil has low affinity for the adsorption of lead and thus, lead could migrate at the bottom of the clay soil.

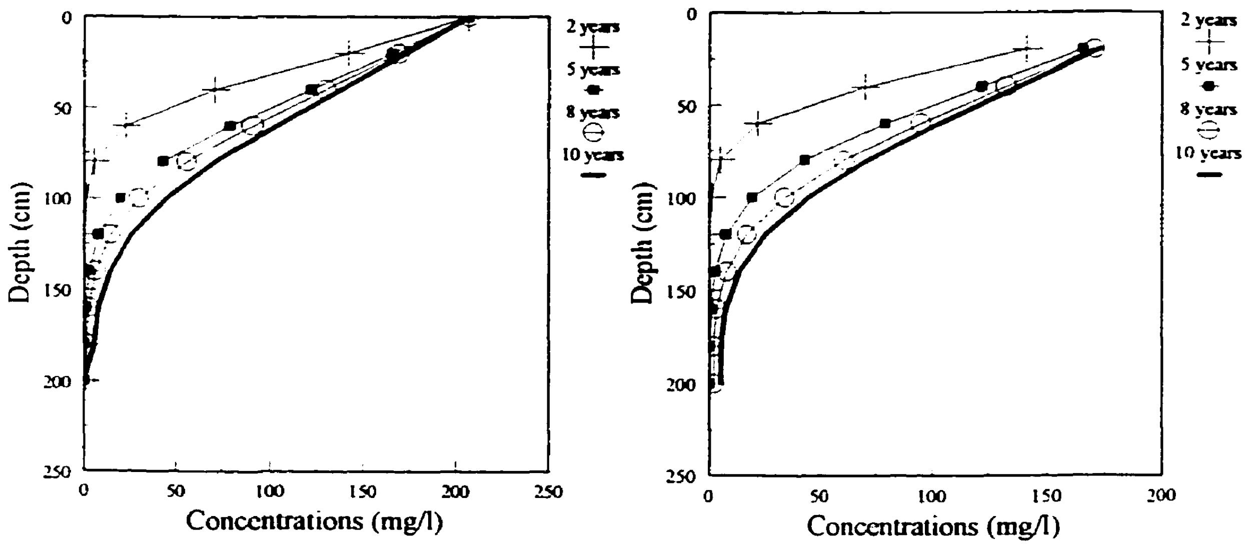

(a) Total Pb Profiles in Kaolinite

(b) Pb Adsorption Profiles in Kaolinite


(c) Kd Profiles for Pb in Kaolinite

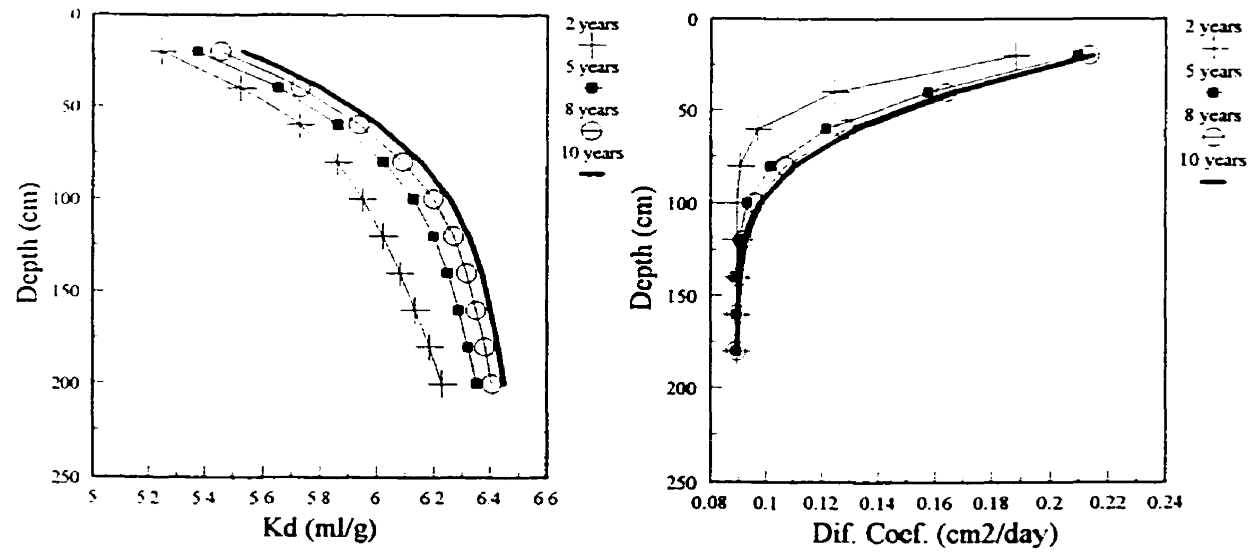
(d) Pb Diffusion Profiles in Kaolinite

Fig. 9.35 Predicted Depth Effect on Pb Characteristics Profiles for Kaolinite.



(a) Total Pb Profiles in KS

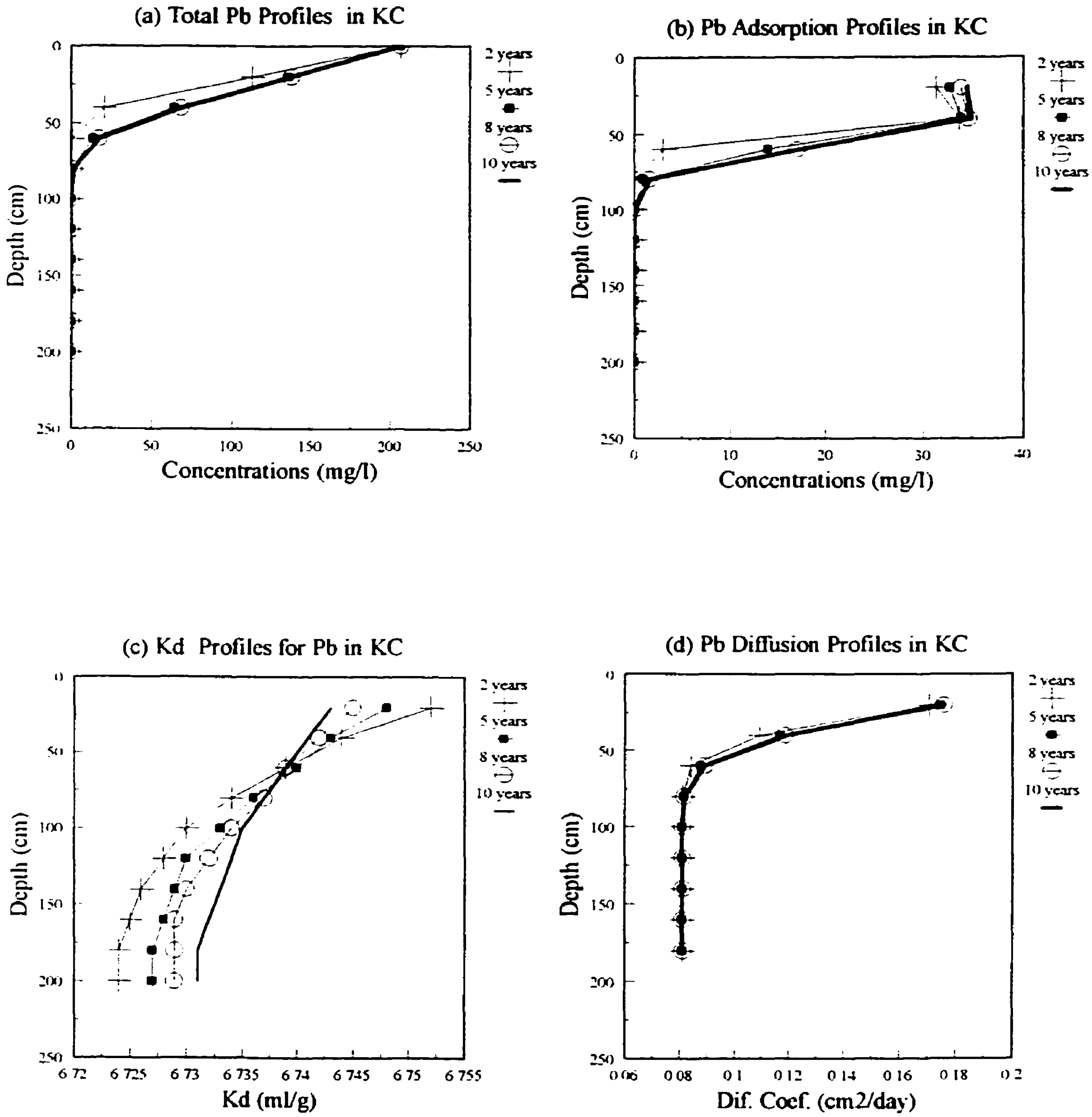
(b) Pb Adsorption Profiles in KS



(c) Kd Profiles for Pb in KS

(d) Pb Diffusion Profiles in KS

**Fig. 9.36** Depth Effect on Pb Characteristics Profiles for KS Soil.



(a) Total Pb Profiles in KC

(b) Pb Adsorption Profiles in KC

(c) Kd Profiles for Pb in KC

(d) Pb Diffusion Profiles in KC

**Fig. 9.37** Depth Effect on Pb Characteristics Profiles for KC Soil.

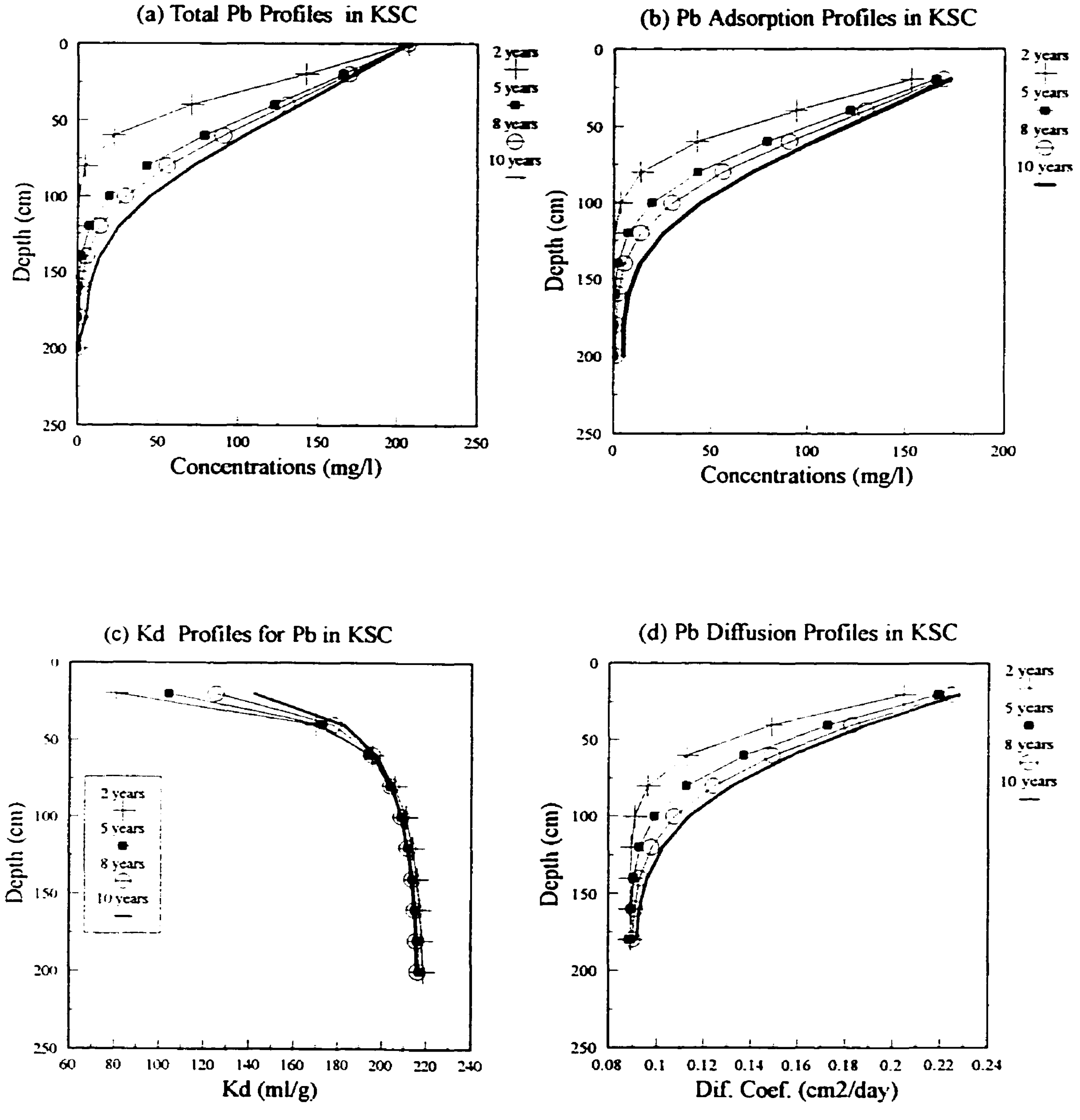


Fig. 9.38 Depth Effect on Pb Characteristics Profiles for KSC Soil.

## 9.3 Summary

In this Chapter, the importance of various parameters including; heavy metals concentrations, chloride concentrations, pH of the leachate solution, CEC, SSA, hydraulic gradient, temperature, $CO_2$ pressure and depth of clay liner to the partitioning coefficient, diffusion coefficient and the migration of heavy metals into different clay barriers has been discussed. It has been shown that these effects are more considerable in a multi-component system. It has been shown that the proposed model is very sensitive to this factor, particularly when dealing with the migration of heavy metals into kaolinite which has a very low pH and does not have any soil constituents compared to the three other soils. It was shown that the higher the heavy metal or chloride concentrations, the higher hydraulic gradient or the lower pH of the leachate solution resulted in the increase of mobility of heavy metals in all types of the soil with highest sensitivity in the kaolinite soil. The reduction of CEC or SSA decreased the adsorption in kaolinite mixture and increase of CEC or SSA reduced the mobility of heavy metals in kaolinite soil. The higher the temperature, the lower adsorption in kaolinite and kaolinite mixtures and higher precipitation if heavy metals in kaolinite mixtures. $CO_2$ pressure was found to increase the adsorption of heavy metals in carbonated soil.

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# Chapter 10

# Conclusions and Recommendations

## 10.1 Summary

This study was aimed at investigating experimentally and theoretically the coupled solute transport and geo-chemical reaction of multi- component heavy metals in clay soil. An experimental design for coupled solute transport and chemical reaction, based on the column leaching test in association with the batch equilibrium test for comparison, is proposed. A COupled Solute Transport and CHemical Equilibrium SPeciation (COSTCHESP) was developed to simulate the experiment. The proposed model accounts for most of the hydro-geochemical interactions of the multi-components with the clay liner, through the coupling of the geochemical and transport models. The reliability of the model has been verified by the laboratory experiments. Then, using the experimental data, long-term migration and retention behaviour of the heavy metals has been predicted by calibration of the proposed model. The sensitivity of the parameters in the simulated model has also been evaluated. In the following sections a summary of the experimental program, proposed model, sensitivity analysis and the conclusions drawn are given.

### 10.1.1 Batch TEST and CHESP

In the batch equilibrium test, the role of dissolved organics and inorganics in the leachate on heavy metals partitioning into different clay soils through a soil suspension test followed by sequential extraction techniques were investigated. The batch equilibrium test was carried out in order to have a rough estimation of the adsorption characteristics of each heavy metal, and to compare the partitioning coefficient, $K_d$, with the one computed through the column test. It has been shown that the presence of other contaminants, especially inorganic and organic complexing agents, affects the distribution coefficient, and it varies with soil constituents, CEC, SSA and pH of the soil solution. It was also concluded that EDTA had major a effect on the partitioning of heavy metals in different clay soils compared to chloride which had a marginal effect. CHESP could provide a reasonable simulation of the batch test, provided the required parameters were calibrated by the experimental results. Thus, the $K_d$ parameter can have an important effect on the uncertainty associated with the modelling results. $K_d$ is often used as a constant parameter to describe the partitioning of a contaminant between the ground-water solution and the solid soil matrix. In addition, the batch equilibrium test which has been used as a tool to measure the distribution coefficient does not represent the compacted clay liner in field.

### 10.1.2 Column Test and COSTCHESP Simulation

Column tests are carried out in order to simulate the coupled solute transport and chemical reaction of multi-component heavy metals. Two types of the experiments were designed for coupled processes:

1) retention of heavy metals along the clay liner (immobilization), and 2) mobilization of heavy metals from the contaminated clay liner (remediation/ mobilization). To simulate immobilization of heavy metals in a multi-component system into a clay liner, the coupled solute transport and chemical reactions were simulated through the column leaching test, using kaolinite as a clay material mixed at a predetermined ratio with amorphous silica and calcium carbonate. The prepared clay soils were leached by the solution of heavy metals mixed with dissolved organic (EDTA) and chloride, as an organic and inorganic complexing agent, in an acidic environment. This part of the study was aimed at evaluating how multi-components affect the mobility of heavy metals into different clay soils, and how different functions of the soil material contribute to heavy metals retention. The experimental results were used as a tool to determine the required parameters for the proposed model and its

calibration.

From the experimental results of heavy metals immobilization into the clay liner, it is evident that the amount of heavy metals retained in each type of soil depends, not only on the other contaminants in the solution but also, on the soil solution pH, CEC, SSA, soil constituents, and type of heavy metal. It was also concluded that a dissolved organic complexing agent could significantly change the mobility of heavy metals along the clay liner depth, while the effect of an inorganic complexation such as chloride is trivial. The partitioning coefficient was increased from the top to the bottom of the column because less lead is transported to the bottom of the column. $K_d$ was reduced as more volumes of the leachate passed through the soil because more lead is transported into the aqueous phase. In other words, the $K_d$ is time and space dependent, and it varies with the type of the soil, type of the heavy metal, its concentration and other contaminants in the solution.

To simulate the experimental program and predict the long term migration and retention behaviour of heavy metals in a clay barrier system, a Coupled Solute Transport and Chemical Equilibrium Speciation (COSTCHESP) was developed.The model consists of two main modules, a finite difference transport module (COST), and an equilibrium geochemistry module (CHESP), which is a modified version of MINTEQA3 (1993). By making use of the local equilibrium assumption, the inherent chemical nonlinearity is confined to the chemical domain. This linearizes the coupling between the physical and chemical processes and leads to a simple and efficient two-step sequential solution algorithm.

The model was able to simulate both the solute transport and the geo-chemical reaction of heavy metals with other contaminants and soil compositions in a clay barrier system. It provides the distribution of heavy metals concentrations (adsorbed, precipitated, and dissolved ) along the depth of a clay liner to assist in evaluation of the role of the various clay soil solids (clay minerals, amorphous materials, and carbonate) in heavy metals retention capability as a function of acidity of the leachate. The input of the model includes; the total aqueous leachate concentrations of all contaminants, total soluble heavy metals concentration, pH of the solution, geometry of the clay ( hydraulic head, total depth of clay, and the number of the layer) and soil constituents concentration and adsorption characteristics of the soil material (CEC, SSA). COCTCHESP was also applied for the multi-component transport of heavy metals of the actual leachate into natural soil. The predicted results show that model is capable of simulating the complex interactions between the flow, transport, and geochemical reactions of composite heavy metal with other contaminants along the depth of column soil at various times. The simulation results also indicates that an a priori selected distribution coefficient or a retardation factor cannot accurately simulate the behaviour patterns that arise from complex nonlinear chemical reactions and solute transport. The prediction results show good accord between the values predicted and the values measured. It was also concluded that using an average diffusion coefficient in most of the existing transport models is not a good assumption for the various individual contaminant constituents, regardless of soil compositions and other contaminants in solution.

For decontamination or mobilization of the heavy metals from the clay liner, EDTA at a concentration of 0.01 mole with a pH of 4.5 or sodium acetate at a concentrations of 0.2 with a pH of 5.0 was used as a permeant solution. It was shown that EDTA was very effective in desorbing lead from all types of clay soil. Sodium Acetate could not effectively mobilize the lead from the column soil. Lead appeared in the effluent for all types of clay soil at the first pore volume and could decontaminate the kaolinite or kaolinite mixture (KS, KC, KSC) to 80 precent at the 3th to 7th pore volumes, respectively. This part of the experiment was performed to determine how fast different clay soils were decontaminated from heavy metals and to compute the required parameters for the COSTCHESP. Then, using the experimental data, long term remediation of the clay liner from the heavy metals was predicted through the COSCHESP.

### 10.1.3 Sensitivity Analysis

Since different parameters have different effects on the solution, the sensitivity of the parameters in the simulated model was evaluated. The transport of the each component, especially a non conservative component, is a function of the solution composition and varies significantly with relatively small changes in the solution parameter. The importance of various parameters including; heavy metals concentrations, chloride concentrations, pH of the solution, CEC, SSA, hydraulic gradient, temperature, $CO_2$ pressure, coefficient of the hydraulic conductivity to the partitioning coefficient , diffusion coefficient and the migration of the heavy metals into different clay barriers has been discussed. It has been shown that these effects are more considerable in a multi-component system. It was shown that the proposed model is very sensitive to these factors, particularly when dealing with the migration of heavy metals into kaolinite which has a very low pH and does not have any soil constituents compared to the three other soils.

## 10.2 Main Conclusion

The study of multi-component transport of heavy metals in an actual landfill becomes very complicated due to the various physico-chemical and biological interactions which are involved. From the experimental results, it is evident that the amount of heavy metals retained in each type of soil depends on the other contaminants in the leachate, their concentrations and pH and soil properties such as pH, CEC, SSA, soil constituents, and the type of heavy metal. The mobility of each heavy metal increases as the pH, CEC and SSA of the soil decreases or the concentration of the complexing agent, organic or inorganic, was presented in the leachate.

From the experimental results of the role of soil inorganic constituents to heavy metals partitioning it may be concluded that soil constituents have a major role in attenuation of heavy metals and for the design of a clay barrier this important factor should be considered. Clay soil barriers should have high CEC, SSA, amorphous and carbonate mineral to have enough buffer capacity for the retention of heavy metals under the acidic environment.

However, due to the leachate constituent and soil composition effect on the mobility of heavy metals, the transport of the solutes in question should be modelled with the bulk solution composition. The results confirm that the distribution coefficient ($K_d$) is a function not only of the contaminant and a given material, but also of a given leachate chemistry and the physicochemical properties of the soil liner material. Whereas, most of existing transport models are based on an adsorption isotherm where physico-chemical interactions are different from the adsorption of the contaminant in the compacted clay. Thus, the $K_d$ approach for the prediction of pollutants such as heavy metals is not a proper approach for the design of clay barrier systems since it assumes in one constant a number of effects from a variety of variables, without an adequate thermodynamically based theory as a support. The effects of pH, redox conditions, ionic strength, complexation, competitive adsorption, temperature, and especially soil constituents and the mechanisms of sorption are either assumed constant or ignored.

Using an average diffusion coefficient for the various individual contaminant constituents throughout the length of the soil column in most of the existing transport models is questionable since soil compositions and other contaminants in solution and adsorption effects are not considered. Also, if one recognizes that the interactions established between the contaminant and the soil cause continuous alteration in the transmissibility characteristics of the soil, the procedure which uses the constant diffusion coefficient can only provide average values since the values of C are obtained at the outlet end of the test sample. These values can be used with some certainty for cations such as Na and Ca which may reach their break through concentrations at few pore volumes but for heavy metals which mostly must be retained in the clay they are not applicable. Thus, whereas a representative diffusion coefficient should be calculated for individual layers in the soil column, and for each pore volume passage of effluent, so long as outlet values of concentration are the only set of values obtained, we cannot calculate the different values of D with depth (length of the soil sample) and with number of pore volumes of passage of leachate.

It is now accepted that complete characterization of a disposal site is not feasible using experimental methods alone due to the long time scales involved. Consequently, the use of computer-base models can be used to supplement experimental work where conditions do not permit direct economical measurement. Coupled processes is an adequate technique could provide good estimates of the movement and attenuation of contaminants after they are released into the subsurface system. In this study a coupled solute transport and chemical reactions were simulated through the column test and an interactive numerical scheme was developed to evaluate the effect of various physico-chemical processes on the migration of heavy metals into a clay barrier. Also long term migration, adsorption/desorption and precipitation /dissolution of heavy metals along the clay barrier were predicted which account for most of the hydro geochemical interactions of multi-component heavy metals with clay. Laboratory and numerical modelling are complementary work to the development of an improved predictive capability.

## 10.3 Practical Hints

- Design of clay barrier, based on low permeability clay (EPA), questionable since soil constituents are not specified.
- Clay soil barriers should have high CEC, SSA, amorphous and carbonate content.
- Use of crushed limestone along with soil liners has been suggested as a means for immobilization of heavy metals in poor buffer capacity of clay barrier soil. Adding fly ash to clay soil may have the same influence on immobilization of heavy metals due to having amorphous silica content.
- For design of clay barrier, heavy metal, other contaminants, complexing agent (i.e., Cl, EDTA) concentrations, hydraulic gradient, pH of the leachate, temperature, $CO_2$ , CEC and SSA should be accounted for.
- In $K_d$ approach, the effects of pH, redox conditions, ionic strength, complexation, competitive adsorption, temperature, and especially soil constituents and the mechanisms of sorption are either assumed constant or ignored.
- Landfill monitoring is necessary due to remobilisation of heavy metal from the clay liner either by organic or inorganic complexing agent or acidifying of the environment.

## 10.4 Contributions

This research program has been conducted in order to study the the coupled solute transport and geo-chemical reaction of multi- component heavy metals in a compacted clay barrier, and to provide an improved understanding of the various physico-chemical interactions which are involves in the process. The contributions of the present study can be summarized as follows:

1. An experimental procedure for the simulation of multi-component transport of heavy metals into different clay soils was designed and the uncertainty of the constant distribution coefficient in the contaminant transport models has been demonstrated.
2. Based on the experimental results, a general mathematical model of multi-component transport of heavy metals through saturated clay soils in one and two dimensions has been developed. The features of the proposed model are as follows:
    a) the model is able to simulate both the solute transport and the geo-chemical reaction of heavy metals with other contaminants and soil compositions in a clay barrier system considering speciation effect, pH variation, isothermal temperature and $CO_2$ pressure effects.
    b) the model provides the distribution of heavy metals concentrations (adsorbed, precipitated, and dissolved ) along the depth of a clay liner to assist in evaluation of the role of the various clay soil solids (clay minerals, amorphous materials, and carbonate) in heavy metals retention.
    c) the diffusion/dispersion coefficient is considered in the physical process to be a function of heavy metals concentration.
    d) the ion restriction effect due to clay surface negative charges and the chemico-osmotic effect are accounted for.
    e) the site density for the adsorption term is generalized in a manner which accords with the physico-chemical process.
3. The model for soil remediation, in which, contaminated soil with heavy metals is desorbed by the addition of a complexing agent has been generalized.
4. A nonlinear optimization technique for the parameter determination in the model

has been used.

5. The sensitivity of the model to the various parameters has been demonstrated.
6. The program has two friendly users for preparation of the input for the COST and CHESP. The required parameters for the COST and CHESP can be easily computed from the column leaching test with a few pore volumes of the effluent.

The program has been written in a two-dimensional form and its applicability to field data is more realistic than the column test experiment. This is because the time step for the coupling between COST and CHESP is long enough and the clay liner depth is many times that of the column test used in the experiments.

The model is primarily targeted toward the clay liner's potential for transport and retention of the multi-component of heavy metals along the soil columns in an acidic solution but is potentially also applicable to the full range of geochemical scenarios covered including, aqueous complexation, reduction/oxidation, acid/base reactions, sorption via surface reactions and precipitation/ dissolution and should be equally useful in the study of other solute migration in respect to equilibrium assumption problems.

## 10.5 Recommendations and Suggestions for Further Studies

The overall performance of the model suggests that this computational tool could be useful in the study of a variety of problems involving flow and solute transport in soil continuum such as the selection of the best soil materials and barrier thickness that retain contaminants which are generated in landfill sites.

The residual discrepancies between experiment and model predictions could probably be explained on the basis of a more complete description of sorption equilibria and kinetic effects. In addition, clay minerals are especially notorious for providing a generous accommodation of a variety of cations. Such behaviour is impossible to capture in a model built on simple equilibrium thermodynamics alone. On the other hand, there are some limitations in terms of the time and space step in the numerical approach, i.e high changes in soil pH may results in a sudden increase or decrease of ion concentrations and thus, this sometimes requires a small element size and a short time step, which imposes some limitations on the applicability of the equilibrium assumption in the proposed model for the large scale.

As mentioned in the limitation of the proposed model, COSTCHESP could not simulate the biological activities which may be involved in the organic function of natural clay. The program was not verified in a two-dimensional form for the actual field. Even through the computed parameters for the COST and CHESP are based the pore volumes of the effluent. there is still some doubt to using the same parameter from the lab experiment for the field and only changing the boundary condition.

Experimental work of this research was performed at room temperature and more research is needed to evaluate the effect of low temperature, which is the case in North America, and high temperature which is the case for nuclear waste disposal, on coupled solute transport and geochemical reaction of heavy metal into clay barrier system. The effect of colloid transport was neglected in this study. In some cases it may significant influence on the transport and adsorption of heavy metals.

The model evaluates only the soil's capacity to retain heavy metals and may not, in some cases, reflect actual field conditions where many natural soil variations cannot be identified. The model may not be applied to unsaturated soil without some modifications. The successful application of the model will depend a great deal on our ability to describe the field system The shortcomings of geochemical modelling are obvious; more empirical laboratory and field study is necessary to further expand the applicability of the model description of the variations found in nature.

## 10.6 Personal Statement

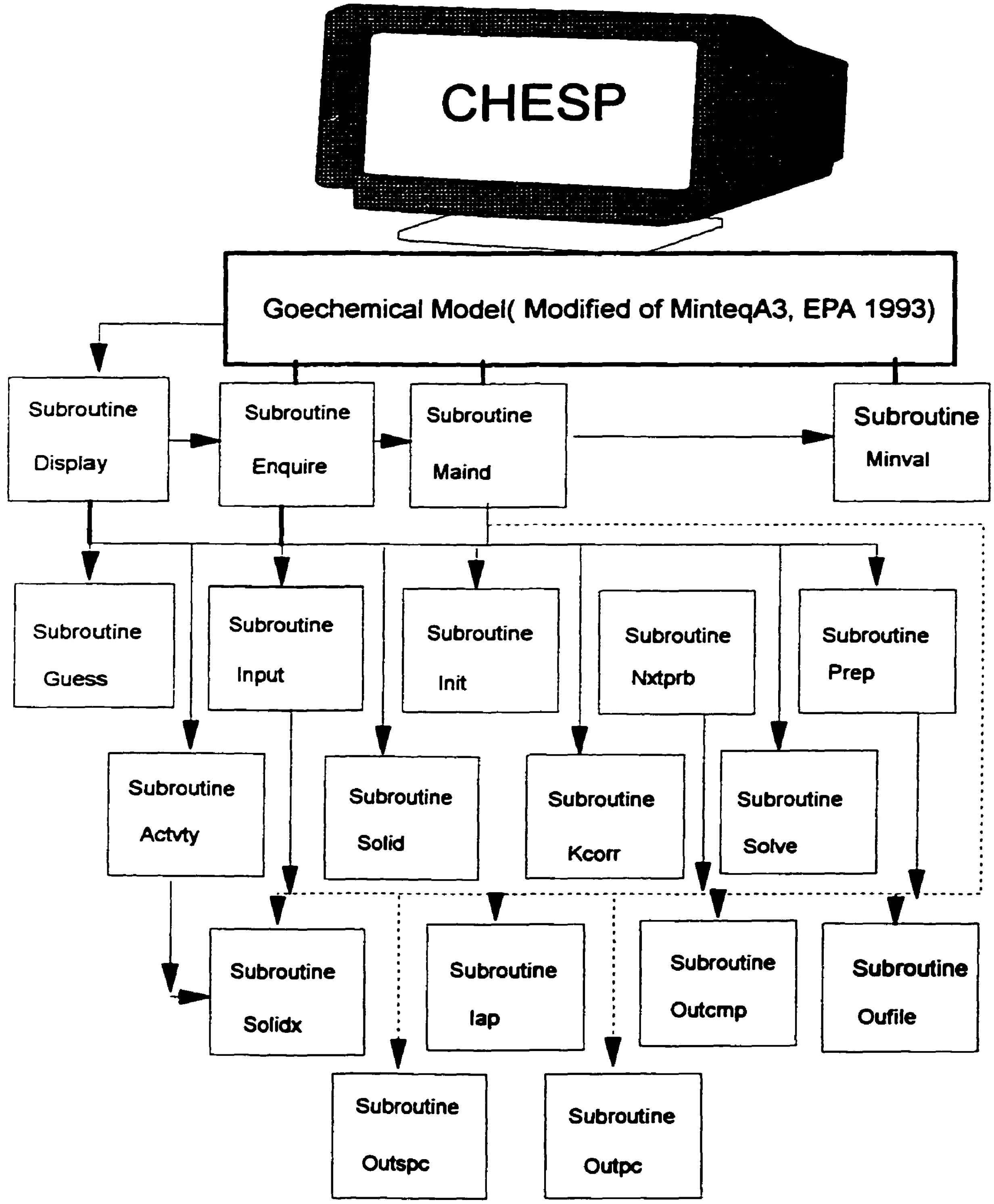
I would like to express some personal opinions about the global problem of groundwater protection in engineered landfill sites.“*There is a feeling in some environmental circles that heavy metals contained in solid wastes can be safely disposed of in landfills. This “safe " feeling is usually based on the notion that heavy metals solubilizing will subsequently form insoluble carbonates and hydroxides and will also be adsorbed on soil used as liner*”.This remark made by E. Yanful et al. (1988), which I came across in the early stages of my work was perhaps the starting point of a series discussions I had with Professor

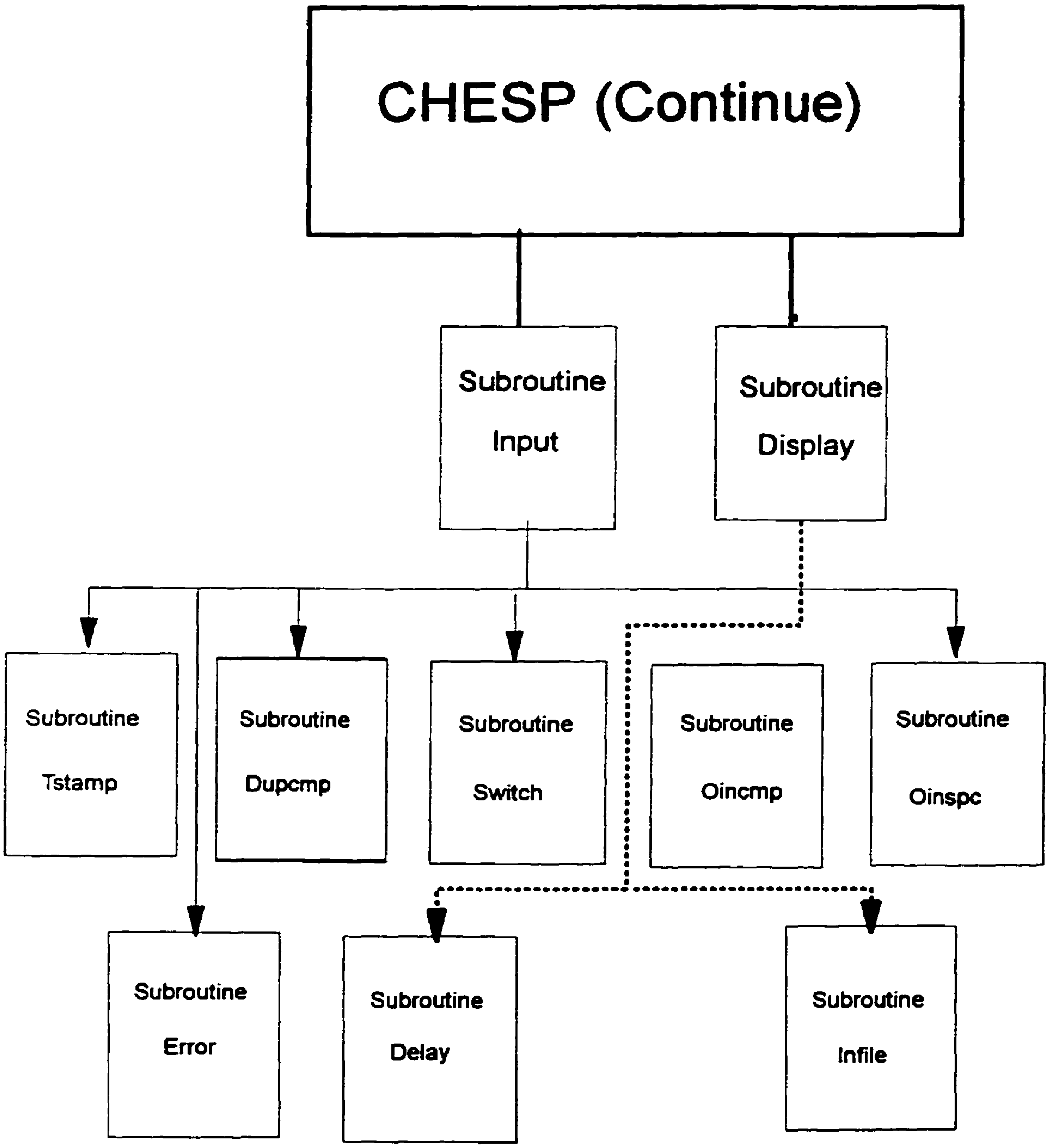
Yong and some graduate student colleagues, about the philosophy of the work we have been trying to develop. This is because the physico-chemical interactions of the heavy metals with other components in the waste materials and soil compositions is yet to be understood. It has been shown that the partitioning of heavy metals in clay soils depends on other contaminants in the waste, their concentrations, soil constituents, pH and temperature of the environment. A prime requirement in proper waste management is to predict or determine the extent of transport of contaminants, as growth rates of contaminant plumes or concentrations of target pollutants at specific times and locations from the contaminant source. A good way to gain some understanding of at least the most relevant of these complex processes and mechanisms is through mathematical modelling. This is vital to the success of predictions of the advance of contaminant plumes in the substrate, and/or distribution of concentrations of target pollutants at various points of concern and after specific time periods. On the other hand, sophisticated modelling is nothing but interesting if the parameters that feed these models are well understood and technically well determined. Consequently, the coupled experiment and models can provide great contributions to research development There is still a lot of room for the development of models which consider all bio-physico-chemical interactions of multi-component transport in landfill sites.

# Table of Contents in Appendices

# Appendix A

## *COSTCHESP DESCRIPTION*


CHESP
Goechemical Model( Modified of MinteqA3, EPA 1993)
Subroutine Display
Subroutine Enquire
Subroutine Maind
Subroutine Minval
Subroutine Guess
Subroutine Input
Subroutine Init
Subroutine Nxtprb
Subroutine Prep
Subroutine Actvty
Subroutine Solid
Subroutine Kcorr
Subroutine Solve
Subroutine Solidx
Subroutine Iap
Subroutine Outcmp
Subroutine Oufile
Subroutine Outspc
Subroutine Outpc


CHESP (Continue)
Subroutine Input
Subroutine Display
Subroutine Tstamp
Subroutine Dupcmp
Subroutine Switch
Subroutine Oincmp
Subroutine Oinspc
Subroutine Error
Subroutine Delay
Subroutine Infile

## SUNROUNTINE INBOUND

## INPUT BOUNDARY CONDITION SUNROUNTINE

Decribes characteristics, constants, geometery of the region, number of space and time steps are given and boundary conditions imposed.

## SUBROUTINE POISON

Hydraulic head are calculated by using the gauss over relaxation method

## SUBROUTINE TRANS

This subroutine calculates concentrations of conservative components at new time step using explicit finite difference merhod

## SUBROUTINE EXPLIT

This subroutine calculates concenterations at advanced time step using explicit finite difference merhod for non-conservative componens

## SUBROUTINE ENQUIRE

The purpose of this subroutine is to inquire whether the file named FILENAME exists and return the logical variable FILEXIST as .TRUE. or .FALSE. accordingly.The logical variable PREEXIST indicates whether the file is supposed to already exist. The character variable MESSG indicates whether ENQUIRE is to write an error message on the screen if a file that is supposed to already exist does not or vica versa. The character variable XERR indicates whether the disposition of the file is as it should be (XERR = 'N' for "no error") or not as it should be (XERR = 'Y' for "error").

## SUBROUTINE MINVAL

Calculate machine dependent numeric constants. Determine the number of decimal digits of REAL precision number and the smallest REAL greater than 1.0. First find the number of significant binary digits, then convert it to the number of significant decimal digits. Any machine used today is going to have more than 7 binary digits of precision (actually, we're cheating, because 1 is added to R2PREC after it is tested. This usually results in 7 decimal digits of precision, which is usually the case, whereas strictly speaking only 6 decimal digits are guaranteed, and 6 is usually the result if R2PREC is initialized to 6).

## SUBROUTINE DISPLAY

The purpose of this routine is to display the program title and obtain I/O filenames, and display execution status information and error messages on the screen while CHESPexecutes.

## SUBROUTINE MAIND

This is the main driver for chesp. The program is set up to execute multiple data sets stored in the same file. This format allows all data sets in the file to be executed even if an error occurs in one of the files.

## SUBROUTINE INFILE

The purpose of this routine is to read the input filename entered by the user in response to the input filenameprompt displayed on the screen by Subroutine DISPLAY and OPEN that file is a valid filename is specified. This routine calls ENQUIRE to check on the existence of of the file prior to OPEN. A code xerr is returned to the calling sub-program (DISPLAY) to indicate whether a good filename was entered or not or if the user chooses to exit (idicated by entering).

## SUBROUTINE OUFILE

The purpose of this routine is to read the output filename entered by the user in response to the oyput filename prompt displayed on the screen by Subroutine DISPLAY and OPEN that file. The filename is passed back to the calling subprogram.

## SUBROUTINE DELAY

The purpose of this subroutine is to provide a means of delaying execution of the calling program for "isec" seconds. The method used is to make an initial call to GETTIM, convert the hours, minutes, seconds returned to total seconds, then to make repeated calls to that same routine and, after a similar conversion, to difference the two total seconds. Stop calling GETTIM and return to the calling program when the absolute value of the difference exceeds the requested delay time, isec.

## SUBROUTINE INPUT

Subroutine input requires 4 input files.

File lun01, contains the run specific information (water analysis)

File lun02, contains thermodynamic data for all specie types except type 6 solids

File lun03, contains a list of all accepted components and the necessary auxillary thermodynamic data.

File lun04, contains the thermodynamic data for all type 6 solids.

## SUBROUTINE NXTPRB

The purpose of this routine is to generate the next problem from the initial problem specification read from the input file and stored on unit 12. This routine is called from subroutine MAIND after a speciation problem is solved but before the next in a series of identical problems begins. The series of problems are presented to CHESP as a single-problem input file with the specifications for changing the pH, eh, or total concentrations of some component, embedded within it. NXTPRB is called only for problems that are to be run at a series of fixed activities or total concentrations of some component.

## SUBROUTINE PREP

This routine is called immediately before the iterative loop in main. Its basic functions are:

1.correct logk values for temperature
2.calculate debye-huckel constants (a&b) as a function of temperature
3.convert all units to molality
4.calculate an initial cation-anion balance

## SUBROUTINE GUESS

The purpose of this subroutine is to make better activity guesses for certain components those for which an equation of some sort is provided below and for which the flag reguess is not equal to no).

## SUBROUTINE ACTVTY

This subroutine calculates

1. Activity coefficients for all species by both the davies and debye-huckel equations
2. The ionic strength
3. The ionic strength correction for the equilibrium constants by calling kcorr

## SUBROUTINE SOLID

This subroutine modifies the a,b,t and gk matrices for the presence of fixed solids.

## SUBROUTINE KCORR

This subroutine corrects the equilibrium constants for ionic strength.

**SUBROUTINE SOLVE**

This subroutine solves aqueous speciation problem which has been modified for solids in subroutine solid.

**SUBROUTINE SOLIDX**

This subroutine modifies the a,b,t,gx,and x matrices following subroutine solve. The subroutine also selects the type 4 and 5 solids which will dissolve or precipitate this iteration.

**SUBROUTINE TSTAMP**

Assign the date and time of the excucution of the program.

**SUBROUTINE ERROR**

Reads/writes the error diagnostics for CHESP errors.

**SUBROUTINE INIT**

Assign the iteration number.

**SUBROUTINE IAP**

This subroutine calculates the saturation indices for all minerals and solids in the type 6 file. The indices are calculated one at a time thus requiring memory for only one mineral.

**SUBROUTINE DUPCMP**

The purpose of this routine is to duplicate (i.e., copy) the TYPE 1 entry "i". The newly created species will have the id number "idnew" and will also be of TYPE 1 and identical to the original in all respects. This is useful for preserving the identity of a TYPE 3 species as a TYPE 1 species (Subroutine SWITCH moves fixed component species from TYPE 1 to TYPE 3 without preserving TYPE 1 identity).

**SUBROUTINE POINTER**

The purpose of this routine is to load the indices of all non-zero stoichiometry elements for each species in an array and to store the number of such elements in a corresponding vector. The array is accessed in subroutine. Solve to avoid the overhead of multiplying or adding non-zero stoichiometries in mass action and related equations by "pointing" to non-zero stoichiometries only.

## SUBROUTINE ALKCOR

The purpose of this routine is to calculate the total dissolved concentration of component 140, CO3-2, from the user-supplied value of alkalinity. The alkalinity is stored in t(j) where j = the component index corresponding to id # 140. Alkalinity as used here means that the value supplied represents the acid-neutralizing capacity of the solution as determined by titrating the solution to the CO2 equivalence endpoint. This corresponds to an operational definition implemented here which is: The alkalinity is the negative of the TOTH expression when the components are the principal components at the CO2 equivalence point.

## SUBROUTINE GUESS1

The purpose of this subroutine is to make better activity guesses for certain components.

## SUBROUTINE ADSORB

This subroutine performs all adsorption calculations for the triple layer site binding modeland for the constant capacitance model the subroutine is broken into three entry points.

Entry adsid initializes some useful constants and locates. The column headers for the electrostatic components.

Entry adinit initializes the total masses of the surface site and electrostatic components.

Entry adsjac includes the derivatives of tj/psi(j) for the electrostatic components in the jacobian.

## SUBROUTINE SIMQ

This subroutine solves the jacobian matrix via gaussian elimination and back substitution.This procedure is faster than gauss-jordan elimination by at least 50%.

## SUBROUTINE NEWX

This routine returns the equilibrium constant corrected for temperature.

## SUBROUTINE SWITCH

The purpose of this subroutine is to change the type of a specie from type l to ltype. This requires
changing the row the specie is stored in which is accomplished by calling exrow.

## SUBROUTINE COMPOSIT

This subroutine computes the concentration of a metal/ligand complex where the ligand is a composite of sites representing various functional groups such that the material as a whole exhibits a continuous distribution of log K's for binding a given metal. The distribution is assumed to be Gaussian with a known mean log K and standard deviation (sigma). Integration over the Gaussian distribution is by means of the Gaussian-Hermite quadrature using a pre-defined set of points and weights. The contributions to the gradients are also calculated. These are added to the appropriate elements of the z(i,j) array and are referred to here as "partial gradients" (Allison, 1993 ).

## SUBROUTINE EXROW

This subroutine exchanges rows in the a and b matrices along with the appropriate row headers.

## SUBROUTINE OUTPUT

This subroutine prints the input data as well as the results of the aqueous speciation and mass transfer calculations. Saturation indicies for all solids are printed in subroutine iap.

# Appendix B

## *COST Derivation*

### Coupled Solute Transport (COST) Development (Yong *et al.*, 1992)

The rates of flow (flux), J, and the thermodynamic force, X, related as

$$J_i = L_{ij} X_j$$

for water and solute fluxes in one dimension

$$\text{water flux} \quad J_w = L_{pp} \frac{\partial \psi_p}{\partial z} + L_{pc} \frac{\partial \psi_c}{\partial z}$$

$$\frac{\partial \psi_p}{\partial z} = Vol_w \frac{\partial}{\partial z}(-u)$$

$$\text{solute flux} \quad J_s = L_{cp} \frac{\partial \psi_p}{\partial z} + L_{cc} \frac{\partial \psi_c}{\partial z}$$

$$\frac{\partial \psi_c}{\partial z} = \frac{RT}{C} \frac{\partial}{\partial z}(-c) \quad \text{forces due concentration}$$

substituting for each variable and Darcy's law applied to $J_w$ and Fick's law to Js

$$\text{for } J_w \quad \frac{\partial}{\partial z}(-C) = 0 \quad \text{then} \quad L_{pp} = \frac{K_h}{\gamma_w \, Vol_w^2 \, n}$$

$$\text{for } J_s \quad \frac{\partial}{\partial z}(-u) = 0 \quad \text{then} \quad L_{cc} = \frac{C}{RT} D_m$$

$$\text{defining} \quad K_{hc} = Vol_w \frac{RT}{C} L_{pc} \qquad K_{ch} = n \, \frac{Vol_w}{C} L_{cp}$$

substituting the expressions for $L_{pc}$ and $L_{cp}$ and knowing

that u= $\gamma_w$ x h yields

$$J_w=\frac{K_h}{Vol_w\ n}\ \frac{\partial}{\partial z}(-h)+\frac{K_{hc}}{V_w}\ \frac{\partial}{\partial z}(-C)$$

$$J_s=\frac{C\ K_{ch}}{n}\ \frac{\partial}{\partial z}(-h)+D_m\frac{\partial}{\partial z}(-C)$$

$$V_z=J_wVol_w$$

$$V_z=\frac{K_h}{n}\ \frac{\partial}{\partial z}(-h)+K_{hc}\ \frac{\partial}{\partial z}(-C)$$

The solute mass flux to a fixed coordinate

$\acute{J}_s = J_s + CV_z$

$$\dot{j}_s=\frac{CK_{ch}}{n}\frac{\partial}{\partial z}(-h)+D_m\frac{\partial}{\partial z}(-C)+CV_z$$

$$\textit{obtaining}\quad \frac{\partial}{\partial z}(-h)\quad \textit{subsituting}$$

$$\dot{j}_s=\frac{K_{ch}}{K_h}CV_z+\frac{K_{ch}\ K_{hc}}{K_h}C\frac{\partial C}{\partial z}-D_m\frac{\partial C}{\partial z}+CV_z$$

The solute mass conservation equation is given by:

$$\frac{\partial C}{\partial t}+\frac{\partial \dot{j}_s}{\partial z}\pm\frac{\partial \rho_s}{\partial t}=0$$

$$\textit{Substituting}\ \dot{j}_s$$

$$\frac{\partial C}{\partial t}+(\frac{K_{ch}}{K_h}+1)\ V_z\ \frac{\partial C}{\partial z}+\frac{K_{ch}\ K_{hc}}{2K_h}\ \frac{\partial^2 C^2}{\partial z^2}=\frac{\partial}{\partial z}(D_m\frac{\partial C}{\partial}z)\pm\frac{\rho_s}{n}\ \frac{\partial s}{\partial t}$$

$K_{ch}$ (ion restriction parameter) = [$K_{hc}$ (osmotic parameter) x n(porosity)]/ (R x T)

R = gas constant
T = temperture
$V_z = V_h + V_{hc}$

$$V_h = \frac{K_h}{n}\frac{\partial}{\partial z}(-h)$$

$$also \quad for$$

$$V_{hc} = k_{hc}\,\frac{\partial}{\partial z}(c)$$

References:

Yong, R. N., Mohamed A., and Warkentin, B., (1992), "Principles of Contaminant Transport in Soils", Elsevier Publications.

# Appendix C

## Adsorption Model in CHESP Program

### Electrostatic Adsorption Models

Activity of an ion X of charge z near the surface (Boltzman expression)

$$X_s^z = X^z[e^{-\phi F/RT}]^z$$

Z = charge of ion X
$\{X_s^z\}$ = activity of an ion x of charge z near the surface
$\{X^z\}$ = corresponding activity of X in bulk solution
$\phi e^F/RT$ = Boltzman factor
F = Faraday constant
R = ideal gas constant
T = absolute temperature

### Charge Balance Equation

Obtain the difference in charge by summing the charges of all species specifically adsorbed on the plane as:

$$Y_\sigma = \sum a_{i\sigma} C_i - T_\sigma$$

where

$C_i$ = charge of specifically adsorbed components
$a_i$ = stoichiometry of the electrostatic component
$T_o$ = total charge of plane

**Total Surface Charge**

$$T_\sigma = 0.1174\ I^{0.5}\ \sinh(Z\phi F/2RT)$$

Z = valency of the symmetrical electrolyte (Z=1)
I = ionic strength

**Constant Capacitance Model**

$T_\sigma = C\ \phi$

**Input Concentrations for the Surface Site**

$SOH = (N_s\ S_A\ C_s)/\ N_A$

where

$N_s$ = surface site density ( number of site/m$^2$)
$S_A$ = specific surface are of the solid ( m$^2$/g)
$C_s$ = concentrations of solid in the suspension (g/L)
$N_A$ = Avogadro's number ($6.02 \times 10^{23}$)

**Protonation Reaction**

$SOH + H_s \rightleftharpoons SOH^+_2$

$K = \{SOH^+_2\}/\{SOH\}\ \{H^+_s\}$

$$[H_s^+] = [H^+]e^{-\phi zF/RT} \quad \textit{thus}$$

$$K = \frac{[SOH_2^+]}{[SOH]\ [H^+]\ [e^{-\phi F/RT}]}$$

**De-protonation Reaction**

$SOH - H_s^+ = SO^-$

$$K = \frac{[SO^-]\ [H^+]\ [e^{-\phi F/RT}]}{[SOH]}$$

In above equations Boltzman factor incorporated as a component

**Adsorption of Divalent Cation $M^{2+}$**

$SOH + M_s^{2+} - H_s^+ = SO.M^+$

$$K = \frac{[SO.M^+]\ [H_s^+]}{[SOH][M_s^{2+}]}$$

$$K = \frac{[SO.M^+]\ [H^+]\ [e^{-\phi zF/RT}]}{[SOH][M^{2+}]\ [e^{-\phi F/RT}]^2}$$

$$K = \frac{[SO.M^+]\ [H^+]}{[SOH]\ [M^2][e^{-\phi F/RT}]}$$

**References:**

Davis, J.A. and Kent, D. B. (1990), "Surface Complexation Modeling in Aqueous Geomistry", Reviews in Mineralogy Vol 23, Edited by Paul H. Ribbe, Mineralogical Society of America pp 177-259.

# Appendix D

## Sample of Input of CHESP and COST for All Cases

### D.1- Column Leaching Tests for Artificial Soil

### D.1.1 CHESP Input for leaching lead solution spiked with Sodium Chloride into Kaolinite

```
 Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 5 2
n           180    492    500    600    811
4  2  7
8.174E+00 (CEC)  25.00 (SSA)  1.200 0.200 81
4.087E+00 (CEC)   5.00 (SSA)  1.400 0.400 82
   330  1.000E-03   -7.00              /H+1
   180  5.000E-02   -0.83 y            /Cl-1
   500  5.000E-02   -1.82 y            /Na+1
    30  1.000E-07  -16.00 y            /Al+3
   770  1.000E-05  -16.00 y            /H4SiO4
   492  2.000E-03   -2.70              /NO3-1
   600  1.000E-03   -2.18 y            /Pb+2
   813  0.000E-01    0.00              /ADS1PSIo
   811  5.580E-02    1.20              /ADS1TYP1

 4  1
8603001   -5.7260   35.2800   1.000E-01    /KAOLINITE
 6  1
   813    0.0000    0.0000              /ADS1PSIo

 1  6
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
```

```
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8113302 SOH          0.0000    6.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
 8113301 =1SOH2+      0.0000     8.4500   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116000 =1SOpb+       0.0000   -7.9300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8115001 sona        0.0000   -5.7000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500   2.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116002 SOPbOH        0.0000   -5.97000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
```

**D.1.2- CHESP Input for leaching lead solution spiked with Sodium Chloride into Kaolinite+Silica gel (KS)**

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 5 2
n          180    492    500    600    811
4  2  7
6.574E+01  115.00 1.200 0.200 81
1.187E+01   15.00 1.400 0.400 82
   330  1.000E-03  -7.00               /H+1
   492  2.000E-03  -2.70               /NO3-1
   600  1.000E-03  -2.18 y              /Pb+
   180  5.000E-02  -0.83 y              /Cl-1
   500  5.000E-02  -1.82 y              /Na+1
    30  1.000E-07 -16.00 y              /Al+3
   821  5.370E-02  -3.86               /ADS2TYP1
```

```
   811  4.320E-02  -3.88              /ADS1TYP1
   823  0.000E-01   0.00              /ADS2PSIo
   813  0.000E-01   0.00 y            /ADS1PSIo

  4  2
8603001   -5.7260   35.2800  1.000E-01    /KAOLINITE
2077004    2.7100   -3.9100  5.000E-02    /SIO2(A,PT)
  6  2
   813    0.0000    0.0000            /ADS1PSIo
   823    0.0000    0.0000            /ADS2PSIo

  2  10
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8113302 =1SOH        0.0000    7.8600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8116000 =1SOpb+      0.0000   -7.9300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8115000 =1SOna       0.0000   -8.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8116002 =SOPbOH      0.0000   -9.97000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8213300 =2SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8213302 =2SOH        0.0000   6.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8215000 =2SOna       0.0000   -6.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
```

```
0 0.000  0  0.000  0  0.000  0
8216000 =2SOpb+      0.0000   -9.9300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000  0   0.000  0   0.000  0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0 0.000  0  0.000  0  0.000  0
8216002 =2SOPbOH      0.0000   -9.97000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000  0   0.000  0   0.000  0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0 0.000  0  0.000  0  0.000  0
```

**D.1.3- CHESP Input for leaching lead solution spiked with sodium chloride into Kaolinite+Calcium Carbonate (KC)**

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 5 2
n          180    492    500    600    811
4  1  7
1.400E+01   35.00 0.000 0.000 81
   330  1.000E-03  -7.00              /H+1
   180  5.000E-02  -0.83 y            /Cl-1
   500  1.000E-03  -1.82 y            /Na+1
   150  1.000E-03  -2.62 y            /Ca+2
   492  2.000E-03  -2.70              /NO3-1
   600  1.000E-03  -2.18 y            /Pb+2
   811  5.580E-02   1.20              /ADS1TYP1
   813  0.000E-01   0.00              /ADS1PSIo
   140  1.000E-03  -16.00             /CO3-2

 3  1
3301403    19.9550   -0.5300              /CO2 (g)
 4  2
8603001   -5.7260   35.2800   1.000E-01     /KAOLINITE
5015001    8.4750    2.5850   5.170E-02     /CALCITE
 6  1
  813    0.0000     0.0000              /ADS1PSIo

 1  6
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000  0   0.000  0   0.000  0
```

```
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8113302 SOH          0.0000   2.1600  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 330  1.000 813  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8113301 =1SOH2+      0.0000   -8.4500  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 330  1.000 813  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8116000 =1SOpb+      0.0000  -7.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -1.000 330  1.000 813  0.000 0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8115001 sona         0.0000   5.7000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 500  2.000 813  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8116002 SOPbOH       0.0000  -7.97000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
```

### D.1.4 CHESP Input for leaching lead solution spiked with Sodium Chloride into Kaolinite+Silica gel+ Calcium Carbonate (KSC)

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n         180    140    500    600    811    330
4  2  7
2.574E+01  55.00 1.200 0.200 81
1.187E+01  15.00 1.400 0.400 82
   330  1.000E-03  -7.00            /H+1
   492  2.000E-03  -2.70            /NO3-1
   600  1.000E-03  -2.18 y          /Pb+
   180  5.000E-02  -0.83 y          /Cl-1
   150  0.000E-03  -2.62 y          /Ca+2
   500  5.000E-02  -1.82 y          /Na+1
   770  0.000E-03  -2.15 y          /H4SiO4
    30  0.000E-07 -16.00 y          /Al+3
```

```
   140  5.000E-03  -16.00              /CO3-2
   821  5.370E-02   -3.86              /ADS2TYP1
   811  4.320E-02   -3.88              /ADS1TYP1
   823  0.000E-01    0.00              /ADS2PSIo
   813  0.000E-01    0.00 y             /ADS1PSIo

  3   1
3301403    19.9550    -0.5300              /CO2 (g)
  4   3
8603001    -5.7260    35.2800   1.000E-01      /KAOLINITE
2077004     2.7100    -3.9100   5.000E-04      /SIO2(A,PT)
5015001     8.4750     2.5850   5.170E-04      /CALCITE
  6   2
   813     0.0000     0.0000              /ADS1PSIo
   823     0.0000     0.0000              /ADS2PSIo

  2  10
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8113302 =1SOH        0.0000    7.8600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116000 =1SOpb+      0.0000   -6.9300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8115000 =1SOna       0.0000   -8.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116002 =SOPbOH      0.0000   -9.97000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213300 =2SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213302 =2SOH        0.0000    6.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000   0   0.000   0   0.000   0
```

```
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8215000 =2SOna      0.0000  -6.1300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 500  -1.000 330  1.000 813  0.000 0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216000 =2SOpb+     0.0000  -7.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216002 =2SOPbOH     0.0000  -9.97000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
```

### D.1.5 CHESP Input for leaching zinc solution spiked with Sodium Chloride into Kaolinite + Calcium Carbonate (KC)

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n          180    140    500    950    811    330
4  2  7
1.574E+01   35.00 1.200 0.200 81
2.187E+00   15.00 1.400 0.400 82
   330  1.000E-03  -7.00              /H+1
   492  2.000E-03  -2.70              /NO3-1
   180  5.000E-02  -0.83 y            /Cl-1
   770  1.000E-03  -2.15 y            /H4SiO4
   150  0.000E-01  -2.62 y            /Ca+2
   950  1.000E-03  -1.76 y            /Zn+2
   500  5.000E-02  -1.82 y            /Na+1
    30  1.000E-07 -16.00 y            /Al+3
   821  5.370E-02  -3.86              /ADS2TYP1
   811  4.320E-02  -3.88              /ADS1TYP1
   823  0.000E-01   0.00              /ADS2PSIo
   813  0.000E-01   0.00 y            /ADS1PSIo
   140  7.000E-03 -16.00              /CO3-2

 3  1
3301403   19.4550   -0.5300             /CO2 (g)
 4  2
```

```
8603001   -5.7260   35.2800   1.000E-01      /KAOLINITE
5015001    8.4750    2.5850   5.170E-04      /CALCITE
 6  2
   813    0.0000    0.0000              /ADS1PSIo
   823    0.0000    0.0000              /ADS2PSIo

 2  10
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8113302 =1SOH         0.0000    7.4600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8119500 =1SOzn+       0.0000   -8.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8115000 =1SOna       0.0000   -8.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
81195002 =SOznOH       0.0000   -9.17000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213300 =2SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213302 =2SOH         0.0000    8.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8215000 =2SOna        0.0000   -7.7300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8219500 =2SOzn+       0.0000   -8.7100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
```

```
8219502 =2SOznOH      0.0000   -8.67000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
```

## D.2- CHESP Input for Column Leaching Tests in Natural Soil

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n             180     500     950     600     811     330
5   2   7
2.174E+01  129.00 1.200 0.200 81
4.087E+00   50.00 1.400 0.400 82
   330  4.670E-02   -7.00 y                /H+1
   500  1.522E-02   -1.82 y                /Na+1
   410  4.263E-03   -2.38 y                /K+1
   460  1.822E-03   -2.74 y                /Mg+2
   150  2.700E-02   -2.62 y                /Ca+2
   600  6.698E-03   -2.18 y                /Pb+2
   950  1.767E-02   -1.76 y                /Zn+2
   180  1.500E-01   -0.83 y                /Cl-1
   140  0.000E-02  -16.00                  /CO3-2
   821  7.370E-02   -3.86                  /ADS2TYP1
   811  7.320E-02   -3.88                  /ADS1TYP1
   823  0.000E-01    0.00                  /ADS2PSIo
   813  0.000E-01    0.00 y                /ADS1PSIo
 3   1
3301403    19.180    -0.5300               /CO2 (g)
 4   2
2046000   -16.7920    25.8400   1.697E-02     /BRUCITE
5015001     8.4750     2.5850   1.170E-02     /CALCITE
 6   2
  813     0.0000      0.0000               /ADS1PSIo
  823     0.0000      0.0000               /ADS2PSIo

 2  18
8113300 =1SO-         0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
```

```
0 0.000 0 0.000 0 0.000 0
8113302 =1SOH       0.0000   8.4600  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 330  1.000 813  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8116000 =1SOpb+      0.0000  -6.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -1.000 330  1.000 813  0.000 0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8114100 =1SOk       0.0000   -8.1300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 410  -1.000 330  1.000 813  0.000 0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8116001 =1SOPbOH     0.0000  -9.97000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8213300 =2SO-      0.0000   -6.9100  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 821  -1.000 330  -1.000 823  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8213302 =2SOH       0.0000   7.1600  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 821  1.000 330  1.000 823  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8214100 =2SOk       0.0000   -8.1300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 410  -1.000 330  1.000 813  0.000 0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8216000 =2SOpb+      0.0000   -9.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8216002 =2SOPbOH     0.0000   -9.97000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8119500 =1SOzn+     0.0000   -6.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -1.000 330  1.000 813  0.000 0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000 0 0.000 0 0.000 0
8115000 =1SOna      0.0000   -8.1300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 500  -1.000 330  1.000 813  0.000 0  0.000  0
```

```
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8119502 =1SOznOH      0.0000    -7.17000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000  0   0.000  0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8213300 =2SO-        0.0000    -7.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000  0   0.000  0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8213302 =2SOH         0.0000    8.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000  0   0.000  0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8215000 =2SOna        0.0000    -7.7300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8219500 =2SOzn+       0.0000    -7.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000  0   0.000  0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8219502 =2SOznOH      0.0000   -8.17000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 950  -2.000 330   0.000  0   0.000  0   0.000  0
 0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
```

## D.3 Column Leaching Desorption Tests for Artificial Soil (KS) Using EDTA

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n          969    492    330    600    811    821
4  2  7
6.574E+01   95.00 1.200 0.200 81
1.187E+01   15.00 1.400 0.400 82
   330  7.000E-03   -7.00                /H+1
   492  2.000E-03   -2.70                /NO3-1
   600  1.000E-03   -2.18 y              /Pb+
   770  1.000E-07   -2.15 y              /H4SiO4
    30  1.000E-07  -16.00 y              /Al+3
```

```
   969  1.000E-02  -2.30              /EDTA-4
   821  5.370E-02  -3.86              /ADS2TYP1
   811  4.320E-02  -3.88              /ADS1TYP1
   823  0.000E-01   0.00              /ADS2PSIo
   813  0.000E-01   0.00 y            /ADS1PSIo

  4  2
8603001   -5.7260   35.2800  1.000E-01     /KAOLINITE
2077004    2.7100   -3.9100  5.000E-04     /SIO2(A,PT)
  6  2
   813    0.0000    0.0000              /ADS1PSIo
   823    0.0000    0.0000              /ADS2PSIo

  2  8
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8113302 =1SOH        0.0000    3.8600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116000 =1SOpb+      0.0000   -1.2300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8116002 =SOPbOH      0.0000   -1.17000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213300 =2SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8213302 =2SOH        0.0000    3.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8216000 =2SOpb+      0.0000   -1.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8216002 =2SOPbOH      0.0000   -1.17000   0.000   0.000 0.00 0.00 0.00   0.0000
```

```
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
```

## D.4 Column Leaching Desorption Tests for Artificial Soil (KS) Using EDTA

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n            969    492    330    600    811    821
4  2  7
6.574E+01   95.00 1.200 0.200 81
1.187E+01   15.00 1.400 0.400 82
   330  7.000E-03   -7.00                /H+1
   492  2.000E-03   -2.70                /NO3-1
   600  1.000E-03   -2.18 y              /Pb+
   770  1.000E-07   -2.15 y              /H4SiO4
    30  1.000E-07  -16.00 y              /Al+3
   969  1.000E-02   -2.30                /EDTA-4
   821  5.370E-02   -3.86                /ADS2TYP1
   811  4.320E-02   -3.88                /ADS1TYP1
   823  0.000E-01    0.00                /ADS2PSIo
   813  0.000E-01    0.00 y              /ADS1PSIo

 4  2
8603001   -5.7260   35.2800  1.000E-01     /KAOLINITE
2077004    2.7100   -3.9100  5.000E-04     /SIO2(A,PT)
 6  2
   813     0.0000    0.0000              /ADS1PSIo
   823     0.0000    0.0000              /ADS2PSIo

 2  8
8113300 =1SO-         0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0  0.000  0  0.000  0  0.000  0
8113302 =1SOH         0.0000    3.8600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
```

```
0 0.000  0  0.000  0  0.000  0
8116000 =1SOpb+       0.0000  -1.2300  0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8116002 =SOPbOH       0.0000  -1.17000  0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8213300 =2SO-       0.0000  -6.9100  0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8213302 =2SOH        0.0000   3.1600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821   1.000 330   1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216000 =2SOpb+       0.0000  -1.1300  0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216002 =2SOPbOH       0.0000  -1.17000  0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
```

## D.5 Column Leaching Desorption Tests for Artificial Soil Using Sodium Acetate

```
Diffuse Double layer
surfaces.
25.00 MOLAL  0.000  0.00000E-01
0 0 1 2 3 0 0 0 1 1 0 6 2
n          992    492    500    600    811    330
4  2  7
2.574E+01   55.00 1.200 0.200 81
1.187E+01   15.00 1.400 0.400 82
   330  1.000E-03   -7.00             /H+1
   492  2.000E-03   -2.70             /NO3-1
   600  1.000E-03   -2.18 y           /Pb+
   500  5.000E-02   -1.82 y           /Na+1
   150  0.000E-03   -2.62 y           /Ca+2
```

```
   770  0.000E-03   -2.15 y              /H4SiO4
   140  0.000E-03  -16.00                /CO3-2
    30  0.000E-07  -16.00 y              /Al+3
   821  5.370E-02   -3.86                /ADS2TYP1
   811  4.320E-02   -3.88                /ADS1TYP1
   823  0.000E-01    0.00                /ADS2PSIo
   813  0.000E-01    0.00 y              /ADS1PSIo
   992  2.000E-01   -0.70                /Acetate

  3  1
3301403   20.6550   -0.5300              /CO2 (g)
  4  3
8603001   -5.7260   35.2800  1.000E-01    /KAOLINITE
2077004    2.7100   -3.9100  5.000E-04    /SIO2(A,PT)
5015001    8.4750    2.5850  5.170E-04    /CALCITE
  6  2
   813     0.0000     0.0000             /ADS1PSIo
   823     0.0000     0.0000             /ADS2PSIo

  2  10
8113300 =1SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0  0.000  0   0.000  0   0.000  0
8113302 =1SOH         0.0000    7.8600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0  0.000  0   0.000  0   0.000  0
8116000 =1SOpb+       0.0000   -8.9300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0  0.000  0   0.000  0   0.000  0
8115000 =1SOna        0.0000   -8.1300   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 500  -1.000 330   1.000 813   0.000 0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0  0.000  0   0.000  0   0.000  0
8116002 =SOPbOH       0.0000   -9.97000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 600  -2.000 330   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
0  0.000  0   0.000  0   0.000  0
8213300 =2SO-        0.0000   -6.9100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 821  -1.000 330  -1.000 823   0.000   0   0.000   0   0.000   0
  0.000  0   0.000  0   0.000  0   0.000  0   0.000  0   0.000  0
```

```
0 0.000  0  0.000  0  0.000  0
8213302 =2SOH        0.0000  6.1600  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 821  1.000 330  1.000 823  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8215000 =2SOna       0.0000  -6.1300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 500  -1.000 330  1.000 813  0.000 0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216000 =2SOpb+      0.0000  -8.9300  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
8216002 =2SOPbOH      0.0000  -9.97000  0.000  0.000 0.00 0.00 0.00  0.0000
 0.00 3  1.000 811  1.000 600  -2.000 330  0.000  0  0.000  0  0.000  0
  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0  0.000  0
0 0.000  0  0.000  0  0.000  0
```

# Appendix E

## Sample Speciation Result by COSTCHESP

### E1 Adsorption Test

### E.1.1 Output of Column Leaching Adsorption Tests for Pb Solution (1mmol/L) Spiked with Sodium chloride (0.05 mol/L) at the Last Node after 7 Pore Volumes in Kaolinite Clay.

Table E1 Components as Species in Solution at the Last Node after 7 Pore Volumes in Kaolinite Clay.

| ID | Name | Calc Mol | Activity | Log Activity | Gamma | New logk |
|---|---|---|---|---|---|---|
| 330 | H+1 | 8.528E-08 | 6.945E-08 | -7.15836 | .81430 | .089 |
| 492 | NO3-1 | 2.000E-03 | 1.629E-03 | -2.78818 | .81430 | .089 |
| 600 | Pb+2 | 5.767E-08 | 2.536E-08 | -7.59591 | .43967 | .357 |
| 180 | Cl-1 | 5.000E-02 | 4.072E-02 | -1.39024 | .81430 | .089 |
| 150 | Ca+2 | 3.805E-04 | 1.673E-04 | -3.77651 | .43967 | .357 |
| 500 | Na+1 | 4.751E-02 | 3.868E-02 | -1.41247 | .81430 | .089 |
| 770 | H4SiO4 | 9.627E-05 | 9.745E-05 | -4.01121 | 1.01232 | -.005 |
| 30 | Al+3 | 1.594E-14 | 2.509E-15 | -14.60046 | .15741 | .803 |
| 140 | CO3-2 | 6.649E-06 | 2.924E-06 | -5.53409 | .43967 | .357 |
| 821 | ADST1 | 2.913E-02 | 2.913E-02 | -1.53564 | 1.00000 | .000 |
| 811 | ADST2 | 5.751E-03 | 5.751E-03 | -2.24025 | 1.00000 | .000 |

**Table E2** Other Species in Solution or Adsorbed at the Last Node after 7 Pore Volumes in Kaolinite Clay.

| ID | Name | Calc Mol | Activity | Log Activity | Gamma | New logk |
|---|---|---|---|---|---|---|
| 8216002 | 2SOPbOH | 3.240E-04 | 3.240E-04 | -3.48944 | 1.00000 | -7.970 |
| 3301400 | HCO3 - | 5.325E-03 | 4.336E-03 | -2.36288 | .81430 | 10.419 |
| 3301401 | H2CO3 AQ | 6.682E-04 | 6.764E-04 | -3.16981 | 1.01232 | 16.676 |
| 3300020 | OH- | 1.773E-07 | 1.444E-07 | -6.84045 | .81430 | -13.909 |
| 3307700 | H3SiO4 - | 2.030E-07 | 1.653E-07 | -6.78164 | .81430 | -9.840 |
| 3307701 | H2SiO4 -2 | 1.111E-11 | 4.885E-12 | -11.31111 | .43967 | -21.260 |
| 1503300 | CaOH + | 7.452E-10 | 6.068E-10 | -9.21696 | .81430 | -12.509 |
| 1501400 | CaHCO3 + | 9.233E-06 | 7.519E-06 | -5.12386 | .81430 | 11.434 |
| 1501401 | CaCO3 AQ | 6.866E-07 | 6.950E-07 | -6.15799 | 1.01232 | 3.147 |
| 5001400 | NaCO3 - | 2.574E-06 | 2.096E-06 | -5.67856 | .81430 | 1.357 |
| 5001401 | NaHCO3 AQ | 9.328E-05 | 9.442E-05 | -4.02491 | 1.01232 | 10.075 |
| 303300 | AlOH +2 | 8.394E-13 | 3.691E-13 | -12.43291 | . 43967 | -4.633 |
| 303301 | Al(OH)2 + | 5.057E-11 | 4.118E-11 | -10.38536 | .81430 | -10.011 |
| 303302 | Al(OH)4 - | 1.315E-09 | 1.071E-09 | -8.97025 | .81430 | -22.911 |
| 303303 | Al(OH)3 AQ | 7.360E-10 | 7.451E-10 | -9.12781 | 1.01232 | -16.005 |
| 6001800 | PbCl + | 5.047E-08 | 4.110E-08 | -7.38615 | .81430 | 1.689 |
| 6001801 | PbCl2 AQ | 2.620E-09 | 2.652E-09 | -8.57639 | 1.01232 | 1.795 |
| 6001802 | PbCl3 - | 1.051E-10 | 8.558E-11 | -10.06763 | .81430 | 1.788 |
| 6001803 | PbCl4 -2 | 3.802E-12 | 1.672E-12 | -11.77688 | .43967 | 1.737 |
| 6001400 | Pb(CO3)2-2 | 2.152E-08 | 9.460E-09 | -8.02409 | .43967 | 10.997 |
| 6003300 | PbOH + | 8.727E-09 | 7.106E-09 | -8.14836 | .81430 | -7.621 |
| 6003301 | Pb(OH)2 AQ | 3.925E-11 | 3.974E-11 | -10.40081 | 1.01232 | -17.125 |
| 6003302 | Pb(OH)3 - | 8.053E-15 | 6.558E-15 | -14.18325 | .81430 | -27.971 |
| 6003303 | Pb2OH +3 | 2.563E-14 | 4.034E-15 | -14.39427 | .15741 | -5.557 |

**Table E2** Continue

| ID | Name | Calc Mol | Activity | Log Activity | Gamma | New logk |
|---|---|---|---|---|---|---|
| 6004920 | PbNO3 + | 7.501E-10 | 6.108E-10 | -9.21409 | .81430 | 1.259 |
| 6003304 | Pb3(OH)4+2 | 2.086E-18 | 9.172E-19 | -18.03752 | .43967 | -23.523 |
| 6001401 | PbCO3 AQ | 1.273E-06 | 1.288E-06 | -5.89000 | 1.01232 | 7.235 |
| 6003305 | Pb(OH)4 -2 | 4.922E-19 | 2.164E-19 | -18.66470 | .43967 | -39.342 |
| 6001402 | PbHCO3 + | 1.002E-07 | 8.159E-08 | -7.08836 | .81430 | 13.289 |
| 8113300 | =1SO- | 1.712E-02 | 1.712E-02 | -1.76657 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 1.722E-02 | 1.722E-02 | -1.76393 | 1.00000 | 7.860 |
| 8116000 | =1SOpb+ | 1.557E-09 | 1.557E-09 | -8.8 0780 | 1.00000 | -6. 130 |
| 8115000 | =1SOna | 2.375E-05 | 2.375E-05 | -4.62436 | 1.00000 | -8.130 |
| 8116002 | =SOPbOH | 3.240E-05 | 3.240E-05 | -4.48944 | 1.00000 | -8.970 |
| 8213300 | =2SO- | 1.230E-02 | 1.230E-02 | -1.90996 | 1.00000 | -6.910 |
| 8213302 | =2SOH | 1.226E-02 | 1.226E-02 | -1.91133 | 1.00000 | 6.160 |
| 8215000 | =2SONa | 2.375E-03 | 2.375E-03 | -2.62436 | 1.00000 | -6.130 |
| 8216000 | =2SOPb+ | 3.553E-04 | 3.553E-04 | -3.44944 | 1.00000 | -7.930 |

**Table E3** Finite Solids (present at equilibrium) at the Last Node after 7 Pore Volumes in Kaolinite Clay.

| ID | Name | Calc Mol | Log Mol | New Logk | DH |
|---|---|---|---|---|---|
| 8603001 | KAOLINITE | 9.864E-02 | -2.867 | -5.726 | 35.280 |
| 8415000 | LEONHARDITE | 3.898E-04 | -3.409 | -16.490 | 85.360 |
| 5060000 | CERRUSITE | 2.868E-04 | -3.542 | 13.130 | -4.860 |
| 2003002 | DIASPORE | 1.156E-03 | -2.937 | -6.873 | 24.630 |

**Table E4** Unsaturated Solids (not present at equilibrium) at the Last Node after 7 Pore Volumes in Kaolinite Clay.

| ID | Name | Calc Mol | Log Mol | New Logk | DH |
|---|---|---|---|---|---|
| 2077003 | SIO2(A,GL) | 1.020E-01 | -.992 | 3.018 | -4.440 |
| 2003001 | BOEHMITE | 1.972E-02 | -1.705 | -8.578 | 28.130 |
| 5050001 | THERMONATR | 3.275E-09 | -8.485 | -.125 | 2.802 |
| 4160000 | COTUNNITE | 2.475E-06 | -5.606 | 4.770 | -5.600 |
| 4160002 | PHOSGENITE | 2.012E-04 | -3.696 | 19.810 | .000 |
| 2077004 | SIO2(A,PT) | 5.017E-02 | -1.300 | 2.710 | -3.910 |
| 2060000 | MASSICOT | 6.457E-07 | -6.190 | -12.910 | 16.780 |
| 2060001 | LITHARGE | 1.000E-06 | -6.000 | -12.720 | 16.380 |
| 2060002 | PBO, .3H2O | 5.492E-07 | -6.260 | -12.980 | .000 |
| 5060001 | PB2OCO3 | 1.230E-06 | -5.910 | .500 | 11.460 |
| 5060002 | PB3O2CO3 | 1.950E-11 | -10.710 | -11.020 | 26.430 |
| 8260000 | PBSIO3 | 2.457E-05 | -4.610 | -7.320 | 9.260 |
| 8060000 | PB2SIO4 | 4.682E-11 | -10.330 | -19.760 | 26.000 |
| 2060004 | PB(OH)2 © | 3.708E-02 | -1.431 | -8.150 | 13.990 |
| 4160003 | LAURIONITE | 3.535E-03 | -2.452 | -.623 | .000 |
| 4160004 | PB2(OH)3CL | 1.252E-04 | -3.902 | -8.793 | .000 |
| 5060003 | HYDCERRUSITE | 8.302E-03 | -2.081 | 17.460 | .000 |
| 2060005 | PB2O(OH)2 | 1.735E-13 | -12.761 | -26.200 | .000 |
| 8450001 | ANALCIME | 7.584E-03 | -2.120 | -6.719 | 22.840 |
| 8603000 | HALLOYSITE | 5.395E-04 | -3.268 | -8.994 | 39.730 |
| 5015000 | ARAGONITE | 1.060E-01 | -.975 | 8.336 | 2.615 |
| 5015001 | CALCITE | 1.460E-01 | -.836 | 8.475 | 2.585 |
| 8450002 | LOW ALBITE | 9.956E-03 | -2.002 | -2.592 | 17.400 |
| 8450003 | ANALBITE | 1.214E-03 | -2.916 | -3.506 | 20.000 |

**Table E4 Continue**

| ID | Name | Calc Mol | Log Mol | New Logk | DH |
|---|---|---|---|---|---|
| 8415001 | ANORTHITE | 6.871E-10 | -9.163 | -25.430 | 70.660 |
| 8603002 | PYROPHYLLITE | 2.021E-01 | -.694 | 1.598 | .000 |
| 8415002 | LAUMONTITE | 6.090E-07 | -6.215 | -14.460 | 50.450 |
| 8415003 | WAIRAKITE | 2.378E-11 | -10.624 | -18.870 | 63.150 |
| 2015000 | LIME | 5.526E-23 | -22.258 | -32.797 | 46.265 |
| 2015001 | PORTLANDITE | 7.305E-13 | -12.136 | -22.675 | 30.690 |
| 8215002 | WOLLASTONITE | 3.418E-07 | -6.466 | -12.996 | 19.498 |
| 8215003 | P-WOLLSTANIT | 4.828E-08 | -7.316 | -13.846 | 21.068 |
| 8015001 | CA-OLIVINE | 2.632E-21 | -20.580 | -37.649 | 54.695 |
| 8015002 | LARNITE | 8.476E-23 | -22.072 | -39.141 | 57.238 |
| 8015007 | CA3SIO5 | 0.000E+00 | -46.258 | -73.867 | 106.335 |
| 8450004 | NEPHELINE | 2.462E-06 | -5.609 | -14.218 | 33.204 |
| 8015006 | GEHLENITE | 9.863E-27 | -26.006 | -56.822 | 116.125 |
| 2003000 | ALOH3(A) | 3.106E-04 | -3.508 | -10.380 | 27.045 |
| 2077000 | CHALCEDONY | 3.261E-01 | -.487 | 3.523 | -4.615 |
| 2077001 | CRISTOBALITE | 3.779E-01 | -.423 | 3.587 | -5.500 |
| 2077002 | QUARTZ | 9.918E-01 | -.004 | 4.006 | -6.220 |
| 2003003 | GIBBSITE © | 1.265E-02 | -1.898 | -8.770 | 22.800 |
| 3003000 | Al2O3 | 5.845E-10 | -9.233 | -22.980 | .000 |
| 4150000 | HALITE | 4.124E-05 | -4.385 | -1.582 | -.918 |
| 8450000 | MAGADIITE | 9.434E-09 | -8.025 | 14.300 | .000 |
| 3050000 | NATRON | 8.789E-08 | -7.056 | 1.311 | -15.745 |

### E. 1.2 Output of Column Leaching Adsorption Tests for Zinc Solution (1 cmol/L) Spiked with Sodium Chloride (0.05 mol /L) at the Last Node after 7 Pore Volumes in Kaolinite Clay

**Table E5- Type I** - Components as Species in Solution at the Last Node after 7 Pore Volumes in Kaolinite Clay

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 330 | H+1 | 2.327E-04 | 1.872E-04 | -3.72759 | .80463 | .094 |
| 492 | NO3-1 | 2.000E-02 | 1.609E-02 | -1.79337 | .80463 | .094 |
| 180 | Cl-1 | 4.996E-02 | 4.020E-02 | -1.39579 | .80463 | .094 |
| 770 | H4SiO4 | 1.845E-04 | 1.872E-04 | -3.72780 | 1.01445 | -.006 |
| 950 | Zn+2 | 6.869E-04 | 2.879E-04 | -3.54074 | .41916 | .378 |
| 500 | Na+1 | 5.000E-02 | 4.023E-02 | -1.39547 | .80463 | .094 |
| 30 | Al+3 | 1.812E-04 | 2.561E-05 | -4.59151 | .14137 | .850 |
| 821 | ADS2TYP1 | 2.913E-02 | 2.913E-02 | -1.53564 | 1.00000 | .000 |
| 811 | ADS1TYP1 | 2.686E-02 | 2.686E-02 | -1.57081 | 1.00000 | .000 |

**Table E6 -Type II** - Other Species in Solution or Adsorbed at the Last Node after 7 Pore Volumes in Kaolinite Clay

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 8219502 | =2SOznOH | 1.491E-06 | 1.491E-06 | -5.82638 | 1.00000 | -8.170 |
| 9503303 | Zn(OH)4 -2 | 3.504E-30 | 1.469E-30 | -29.83300 | .41916 | -40.821 |
| 9501804 | ZnOHCl AQ | 2.013E-09 | 2.042E-09 | -8.68985 | 1.01445 | -7.486 |
| 3300020 | OH- | 6.654E-11 | 5.354E-11 | -10.27131 | .80463 | -13.904 |
| 3307700 | H3SiO4 - | 1.464E-10 | 1.178E-10 | -9.92900 | .80463 | -9.834 |
| 3307701 | H2SiO4 -2 | 3.079E-18 | 1.291E-18 | -17.88924 | .41916 | -21.239 |
| 303300 | AlOH +2 | 3.333E-06 | 1.397E-06 | -5.85483 | .41916 | -4.612 |

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 303301 | Al(OH)2 + | 7.182E-08 | 5.779E-08 | -7.23814 | .80463 | -10.006 |
| 303302 | Al(OH)4 - | 2.568E-13 | 2.066E-13 | -12.68477 | .80463 | -22.906 |
| 303303 | Al(OH)3 AQ | 3.822E-10 | 3.877E-10 | -9.41146 | 1.01445 | -16.006 |
| 9501800 | ZnCl + | 3.871E-05 | 3.115E-05 | -4.50654 | .80463 | .524 |
| 9501801 | ZnCl2 AQ | 1.293E-06 | 1.311E-06 | -5.88233 | 1.01445 | .444 |
| 9501802 | ZnCl3 - | 7.350E-08 | 5.914E-08 | -7.22813 | .80463 | .594 |
| 9501803 | ZnCl4 -2 | 2.836E-09 | 1.189E-09 | -8.92492 | .41916 | .577 |
| 9503300 | ZnOH + | 2.091E-09 | 1.682E-09 | -8.77406 | .80463 | -8.866 |
| 9503301 | Zn(OH)2 AQ | 1.017E-13 | 1.032E-13 | -12.98637 | 1.01445 | -16.905 |
| 9503302 | Zn(OH)3 - | 2.161E-21 | 1.739E-21 | -20.75968 | .80463 | -28.305 |
| 8113300 | =1SO- | 7.656E-03 | 7.656E-03 | -2.11598 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 8.401E-03 | 8.401E-03 | -2.07565 | 1.00000 | 5.860 |
| 8115000 | =1SOna | 4.279E-08 | 4.279E-08 | -7.36870 | 1.00000 | -8.130 |
| 8119500 | =SOZnOH | 1.491E-07 | 1.491E-07 | -6.82638 | 1.00000 | -9.170 |
| 8213300 | =2SO- | 1.227E-02 | 1.227E-02 | -1.91105 | 1.00000 | -6.910 |
| 8213302 | =2SOH | 1.230E-02 | 1.230E-02 | -1.91024 | 1.00000 | 6.160 |
| 8215000 | =2SONa | 4.279E-06 | 4.279E-06 | -5.36870 | 1.00000 | -6.130 |
| 8219500 | =2SOZn+ | 2.714E-04 | 2.714E-04 | -3.56638 | 1.00000 | -5.910 |

```
Type III - SPECIES WITH FIXED ACTIVITY
 ID      NAME      CALC MOL      LOG MOL   NEW LOGK    DH
  2       H2O      8.876E-05      -4.052        .001   .000

-----------------------------------------------------------------
Type IV - FINITE SOLIDS (presumed present at equilibrium)
 ID            NAME     CALC MOL   LOG MOL     NEW LOGK     DH
8603001  KAOLINITE    9.991E-02    -4.035          -5.726   35.280

-----------------------------------------------------------------
```

**Table E7 -Type V** - Possible Solids at the Last Node after 7 Pore_ Volumes in Kaolinite Clay

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8450000 | MAGADIITE | 3.513E-10 | -9.454 | 14.300 | .000 |
| 2077002 | QUARTZ | 1.905E+00 | .280 | 4.006 | -6.220 |
| 2077003 | SIO2(A,GL) | 1.959E-01 | -.708 | 3.018 | -4.440 |
| 2077004 | SIO2(A,PT) | 9.638E-02 | -1.016 | 2.710 | -3.910 |
| 4195000 | ZNCL2 | 4.342E-14 | -13.362 | -7.030 | 17.480 |
| 2095000 | ZN(OH)2 (A) | 2.902E-09 | -8.537 | -12.450 | .000 |
| 2095001 | ZN(OH)2 (C) | 5.160E-09 | -8.287 | -12.200 | .000 |
| 2095002 | ZN(OH)2 (B) | 1.454E-08 | -7.837 | -11.750 | .000 |
| 2095003 | ZN(OH)2 (G) | 1.595E-08 | -7.797 | -11.710 | .000 |
| 2095004 | ZN(OH)2 (E) | 2.586E-08 | -7.587 | -11.500 | .000 |
| 4195001 | ZN2(OH)3CL | 3.183E-13 | -12.497 | -15.200 | .000 |
| 4195002 | N5(OH)8CL2 | 6.579E-30 | -29.182 | -38.500 | .000 |
| 5195000 | ZNNO3)2,6H2O | 2.674E-11 | -10.573 | -3.440 | -5.510 |
| 2095005 | ZNO(ACTIVE) | 4.014E-08 | -7.396 | -11.310 | .000 |
| 2095006 | ZINCITE | 5.937E-08 | -7.226 | -11.140 | 21.860 |
| 8295000 | ZNSIO3 | 1.809E-03 | -2.742 | -2.930 | 18.270 |
| 8095000 | WILLEMITE | 5.903E-12 | -11.229 | -15.330 | 33.370 |
| 8450001 | ANALCIME | 5.619E-06 | -5.250 | -6.719 | 22.840 |
| 8603000 | HALLOYSITE | 5.395E-04 | -3.268 | -8.994 | 39.730 |
| 2003000 | ALOH3(A) | 1.616E-04 | -3.791 | -10.380 | 27.045 |
| 8450002 | LOW ALBITE | 1.418E-05 | -4.848 | -2.592 | 17.400 |
| 8450003 | ANALBITE | 1.728E-06 | -5.762 | -3.506 | 20.000 |
| 8603002 | PYROPHYLLIT | 7.463E-01 | -.127 | 1.598 | .000 |

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8450004 | NEPHELINE | 9.497E-10 | -9.022 | -14.218 | 33.204 |
| 2003001 | BOEHMITE | 1.027E-02 | -1.989 | -8.578 | 28.130 |
| 2077000 | CHALCEDONY | 6.266E-01 | -.203 | 3.523 | -4.615 |
| 2077001 | CRISTOBALITE | 7.261E-01 | -.139 | 3.587 | -5.500 |
| 2003002 | DIASPORE | 5.205E-01 | -.284 | -6.873 | 24.630 |
| 2003003 | GIBBSITE (C) | 6.585E-03 | -2.181 | -8.770 | 22.800 |
| 3003000 | Al2O3 | 1.584E-10 | -9.800 | -22.980 | .000 |
| 4150000 | HALITE | 4.234E-05 | -4.373 | -1.582 | -.918 |

```
Type VI - EXCLUDED SPECIES (not included in mole balance)
 ID      NAME       CALC MOL     LOG MOL   NEW LOGK    DH
   813  ADS1PSIo    2.305E-03     -2.637        .000   .000
   823  ADS2PSIo    1.560E-03     -2.807        .000   .000


          PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
        TYPE I and TYPE II (dissolved and adsorbed) species


+H+1
+          52.1   PERCENT BOUND IN SPECIES #   330  H+1

+        >1000.   PERCENT BOUND IN SPECIES #8113302  =1SOH

+        >1000.   PERCENT BOUND IN SPECIES #8213302  =2SOH


+NO3-1
+         100.0   PERCENT BOUND IN SPECIES #   492  NO3-1


+Cl-1
+          99.9   PERCENT BOUND IN SPECIES #   180  Cl-1
```

```
 +H4SiO4
+          100.0   PERCENT BOUND IN SPECIES #    770   H4SiO4

+Zn+2
+           68.7   PERCENT BOUND IN SPECIES #    950   Zn+2

+            3.9   PERCENT BOUND IN SPECIES #9501800   ZnCl +

+           27.1   PERCENT BOUND IN SPECIES #8219500   =2SOZn+

+Na+1
+          100.0   PERCENT BOUND IN SPECIES #    500   Na+1

+ADS1PSIo
+         >1000.   PERCENT BOUND IN SPECIES #8113302   =1SOH

+ADS2TYP1
+           54.2   PERCENT BOUND IN SPECIES #    821   ADS2TYP1

+           22.9   PERCENT BOUND IN SPECIES #8213300   =2SO-

+           22.9   PERCENT BOUND IN SPECIES #8213302   =2SOH

+ADS1TYP1
+           62.2   PERCENT BOUND IN SPECIES #    811   ADS1TYP1

+           17.7   PERCENT BOUND IN SPECIES #8113300   =1SO-

+           19.4   PERCENT BOUND IN SPECIES #8113302   =1SOH

+ADS2PSIo
+         >1000.   PERCENT BOUND IN SPECIES #8213302   =2SOH

+Al+3
+           98.2   PERCENT BOUND IN SPECIES #     30   Al+3

+            1.8   PERCENT BOUND IN SPECIES # 303300   AlOH +2

+H2O
+           95.7   PERCENT BOUND IN SPECIES # 303300   AlOH +2

+            4.1   PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +
```

```
PART 5 of OUTPUT FILE
DATE OF CALCULATIONS: 27-MAR-96  TIME: 16:45:38
```

**Table E8** Equilibrated Mass Distribution at the Last Node after 7 Pore Volumes in Kaolinite Clay

| ID | NAME | DISSOLVED | | SORBED | | PRECIPITATED | |
|---|---|---|---|---|---|---|---|
| | | MOL/KG | PERCENT | MOL/KG | PERCENT | MOL/KG | PERCENT |
| 330 | H+1 | 2.004E-04 | 74.4 | 6.894E-05 | 25.6 | 0.000E+00 | .0 |
| 492 | NO3-1 | 2.000E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 180 | Cl-1 | 5.000E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 950 | Zn+2 | 6.755E-04 | 67.6 | 3.245E-04 | 32.4 | 0.000E+00 | .0 |
| 500 | Na+1 | 5.000E-02 | 100.0 | 4.885E-06 | .0 | 0.000E+00 | .0 |
| 770 | H4SiO4 | 9.682E-05 | .0 | 0.000E+00 | .0 | 1.999E-01 | 100.0 |
| 30 | Al+3 | 2.435E-04 | .1 | 0.000E+00 | .0 | 1.998E-01 | 99.9 |
| 2 | H2O | 5.208E-06 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |

```
0    Charge Balance: SPECIATED
0     Sum of CATIONS =  5.224E-02 Sum of ANIONS   6.996E-02
0       PERCENT DIFFERENCE =   1.450E+01   (ANIONS - CATIONS)/(ANIONS +
CATIONS)
0    EQUILIBRIUM IONIC STRENGTH (m) =   6.246E-02
0    EQUILIBRIUM pH                 =   3.781

******* DIFFUSE LAYER ADSORPTION MODEL ********

 **** Parameters For Adsorbent Number 1 ****
 Electrostatic Variables:  psi0 =  .152896     sig0 =  .286779
                           psib =  .000000     sigb =  .000000
                           psid =  .000000     sigd =  .000000
 Adsorbent Concentration (g/l):  15.740
 Specific Surface Area (sq. meters/g):   15.00

 **** Parameters For Adsorbent Number 2 ****
 Electrostatic Variables:  psi0 =  .162872     sig0 =  .348522
                           psib =  .000000     sigb =  .000000
                           psid =  .000000     sigd =  .000000
 Adsorbent Concentration (g/l):   1.187
```

```
 Specific Surface Area (sq. meters/g):   5.00
_________________________ PART 6 of OUTPUT FILE _______________________
DATE OF CALCULATIONS: 27-MAR-96  TIME: 16:45:39
Saturation indices and stoichiometry of all minerals
  ID #     NAME      Sat. Index      Stoichiometry in [brackets]
 2003000 ALOH3(A)      -3.511    [ 1.000]  30  [ 3.000]   2  [ -3.000] 330
 2003001 BOEHMITE      -1.709    [ -3.000] 330  [ 1.000]  30  [ 2.000]   2
 2077000 CHALCEDONY     -.483    [ -2.000]   2  [ 1.000] 770
 2077001 CRISTOBALITE   -.419    [ -2.000]   2  [ 1.000] 770
 2003002 DIASPORE       -.004    [ -3.000] 330  [ 1.000]  30  [ 2.000]   2
 2003003 GIBBSITE (C)  -1.901    [ -3.000] 330  [ 1.000]  30  [ 3.000]   2
 3003000 Al2O3         -9.240    [ 2.000]  30  [ 3.000]   2  [ -6.000] 330
 4150000 HALITE        -4.373    [ 1.000] 500  [ 1.000] 180
 8450000 MAGADIITE    -11.361    [ -1.000] 330  [ -9.000]   2  [ 1.000] 500
                                 [ 7.000] 770
 2077002 QUARTZ          .000    [ -2.000]   2  [ 1.000] 770
 2077003 SIO2(A,GL)     -.988    [ -2.000]   2  [ 1.000] 770
 2077004 SIO2(A,PT)    -1.296    [ -2.000]   2  [ 1.000] 770
 4195000 ZNCL2        -13.395    [ 1.000] 950  [ 2.000] 180
 2095000 ZN(OH)2 (A)   -8.462    [ -2.000] 330  [ 1.000] 950  [ 2.000]   2
 2095001 ZN(OH)2 (C)   -8.212    [ -2.000] 330  [ 1.000] 950  [ 2.000]   2
 2095002 ZN(OH)2 (B)   -7.762    [ -2.000] 330  [ 1.000] 950  [ 2.000]   2
 2095003 ZN(OH)2 (G)   -7.722    [ -2.000] 330  [ 1.000] 950  [ 2.000]   2
 2095004 ZN(OH)2 (E)   -7.512    [ -2.000] 330  [ 1.000] 950  [ 2.000]   2
 4195001 ZN2(OH)3CL   -12.400    [ -3.000] 330  [ 2.000] 950  [ 3.000]   2
                                 [ 1.000] 180
 4195002 ZN5(OH)8CL2  -28.912    [ -8.000] 330  [ 5.000] 950  [ 8.000]   2
                                 [ 2.000] 180
 5195000 ZNNO3)2,6H2O -10.605    [ 1.000] 950  [ 2.000] 492  [ 6.000]   2
 2095005 ZNO(ACTIVE)   -7.321    [ -2.000] 330  [ 1.000] 950  [ 1.000]   2
 2095006 ZINCITE       -7.151    [ -2.000] 330  [ 1.000] 950  [ 1.000]   2
 8295000 ZNSIO3        -2.947    [ -2.000] 330  [ -1.000]   2  [ 1.000] 950
                                 [ 1.000] 770
 8095000 WILLEMITE    -11.358    [ -4.000] 330  [ 2.000] 950  [ 1.000] 770
 8450001 ANALCIME      -5.477    [ 1.000] 500  [ 1.000]  30  [ 2.000] 770
                                 [ -1.000]   2  [ -4.000] 330
 8603000 HALLOYSITE    -3.268    [ 2.000]  30  [ 2.000] 770  [ 1.000]   2
                                 [ -6.000] 330
 8603001 KAOLINITE       .000    [ 2.000]  30  [ 2.000] 770  [ 1.000]   2
                                 [ -6.000] 330
 8450002 LOW ALBITE    -5.355    [ 1.000] 500  [ 1.000]  30  [ 3.000] 770
                                 [ -4.000] 330  [ -4.000]   2
 8450003 ANALBITE      -6.269    [ 1.000] 500  [ 1.000]  30  [ 3.000] 770
                                 [ -4.000] 330  [ -4.000]   2
 8603002 PYROPHYLLITE   -.687    [ 2.000]  30  [ 4.000] 770  [ -4.000]   2
                                 [ -6.000] 330
 8450004 NEPHELINE     -8.969    [ -4.000] 330  [ 1.000] 770  [ 1.000]  30
```

### E.1.3 Output of Column Leaching Adsorption Tests for Zinc Solution (1 mmol/L) Spiked with Sodium chloride (0.05 mol/L) at the Last Node after 7 Pore Volumes in Kaolinite+ Carbonate + Silica gel (KSC)

**Table E9 Type I** - Components as Species in Solution at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 330 | H+1 | 1.144E-07 | 9.269E-08 | -7.03298 | .81023 | .091 |
| 492 | NO3-1 | 2.000E-03 | 1.620E-03 | -2.79037 | .81023 | .091 |
| 180 | Cl-1 | 5.000E-02 | 4.051E-02 | -1.39246 | .81023 | .091 |
| 770 | H4SiO4 | 9.619E-05 | 9.745E-05 | -4.01120 | 1.01318 | -.006 |
| 150 | Ca+2 | 4.938E-04 | 2.128E-04 | -3.67203 | .43095 | .366 |
| 950 | Zn+2 | 1.296E-11 | 5.584E-12 | -11.25306 | .43095 | .366 |
| 500 | Na+1 | 4.975E-02 | 4.031E-02 | -1.39462 | .81023 | .091 |
| 30 | Al+3 | 3.965E-14 | 5.966E-15 | 14.22433 | .15047 | .823 |
| 821 | ADS2TYP1 | 1.464E-02 | 1.464E-02 | -1.83434 | 1.00000 | .000 |
| 811 | ADS1TYP1 | 5.950E-03 | 5.950E-03 | -2.22546 | 1.00000 | .000 |
| 140 | CO3-2 | 9.456E-06 | 4.075E-06 | -5.38985 | .43095 | .366 |

**Table E10 Type II** - Other Species in Solution or Adsorbed at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 8219502 | =2SOznOH | 2.615E-08 | 2.615E-08 | -7.58257 | 1.00000 | -8.170 |
| 3301400 | HCO3 - | 9.957E-03 | 8.068E-03 | -2.09326 | .81023 | 10.421 |
| 3301401 | H2CO3 AQ | 1.658E-03 | 1.680E-03 | -2.77480 | 1.01318 | 16.675 |
| 3300020 | OH- | 1.335E-07 | 1.082E-07 | -6.96582 | .81023 | -13.907 |
| 3307700 | H3SiO4 - | 1.529E-07 | 1.239E-07 | -6.90701 | .81023 | -9.837 |
| 3307701 | H2SiO4 -2 | 6.364E-12 | 2.742E-12 | -11.56186 | .43095 | -21.251 |
| 1503300 | CaOH + | 7.137E-10 | 5.783E-10 | -9.23785 | .81023 | -12.507 |

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 1501400 | CaHCO3 + | 2.196E-05 | 1.779E-05 | -4.74976 | .81023 | 11.436 |
| 1501401 | CaCO3 AQ | 1.216E-06 | 1.232E-06 | -5.90927 | 1.01318 | 3.147 |
| 5001400 | NaCO3 - | 3.758E-06 | 3.045E-06 | -5.51647 | .81023 | 1.359 |
| 5001401 | NaHCO3 AQ | 1.807E-04 | 1.830E-04 | -3.73744 | 1.01318 | 10.074 |
| 303300 | AlOH +2 | 1.526E-12 | 6.574E-13 | -12.18215 | .43095 | -4.624 |
| 303301 | Al(OH)2 + | 6.783E-11 | 5.496E-11 | -10.25998 | .81023 | -10.009 |
| 303302 | Al(OH)4 - | 9.903E-10 | 8.024E-10 | -9.09562 | .81023 | -22.909 |
| 303303 | Al(OH)3 AQ | 7.354E-10 | 7.451E-10 | -9.12780 | 1.01318 | -16.006 |
| 9501800 | ZnCl + | 7.514E-13 | 6.088E-13 | -12.21552 | .81023 | .521 |
| 9501801 | ZnCl2 AQ | 2.549E-14 | 2.582E-14 | -13.58798 | 1.01318 | .444 |
| 9501802 | ZnCl3 - | 1.449E-15 | 1.174E-15 | -14.93045 | .81023 | .591 |
| 9501803 | ZnCl4 -2 | 5.517E-17 | 2.377E-17 | -16.62391 | .43095 | .565 |
| 9503300 | ZnOH + | 8.138E-14 | 6.593E-14 | -13.18089 | .81023 | -8.869 |
| 9503301 | Zn(OH)2 AQ | 8.065E-15 | 8.171E-15 | -14.08771 | 1.01318 | -16.905 |
| 9503302 | Zn(OH)3 - | 3.434E-19 | 2.783E-19 | -18.55553 | .81023 | -28.308 |
| 9503303 | Zn(OH)4 -2 | 1.102E-24 | 4.749E-25 | -24.32336 | .43095 | -40.833 |
| 9501804 | ZnOHCl AQ | 7.961E-14 | 8.066E-14 | -13.09335 | 1.01318 | -7.486 |
| 9501400 | ZnHCO3 + | 6.539E-12 | 5.298E-12 | -11.27589 | .81023 | 12.491 |
| 9501401 | ZnCO3 AQ | 4.481E-12 | 4.540E-12 | -11.34291 | 1.01318 | 5.294 |
| 9501402 | Zn(CO3)2-2 | 9.179E-13 | 3.956E-13 | -12.40276 | .43095 | 9.996 |
| 8113300 | =1SO- | 3.531E-02 | 3.531E-02 | -1.45215 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 3.558E-02 | 3.558E-02 | -1.44877 | 1.00000 | 8.460 |
| 8115000 | =1SOna | 1.918E-05 | 1.918E-05 | -4.71710 | 1.00000 | -8.130 |
| 8119500 | =SoznOH | 2.615E-09 | 2.615E-09 | -8.58257 | 1.00000 | -9.170 |
| 8213300 | =2SO- | 1.951E-02 | 1.951E-02 | -1.70979 | 1.00000 | -7.910 |

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 8213302 | =2SOH | 1.955E-02 | 1.955E-02 | -1.70889 | 1.00000 | 8.160 |
| 8215000 | =2SOna | 4.818E-05 | 4.818E-05 | -4.31710 | 1.00000 | -7.730 |
| 8219500 | =2SOzn+ | 4.758E-09 | 4.758E-09 | -8.32257 | 1.00000 | -8.910 |

**Table E11- Type III** - Species with Fixed Activity at the Last Node after 7 Pore Volumes

| 0 ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2 | H2O | -6.485E-03 | -2.188 | .001 | .000 |
| 3301403 | CO2 (g) | -6.315E-03 | -2.200 | 19.455 | -.530 |

**Table E12- Type IV** - FINITE SOLIDS (present at equilibrium) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8603001 | KAOLINITE | 9.998E-02 | -4.635 | -5.726 | 35.280 |
| 2003002 | DIASPORE | 4.644E-05 | -4.333 | -6.873 | 24.630 |

**Table E13- Type V** - Undersaturated Solids (not present at equilibrium) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2077004 | SIO2(A,PT) | 5.016E-02 | -1.300 | 2.710 | -3.910 |
| 3050000 | NATRON | 1.330E-07 | -6.876 | 1.311 | -15.745 |
| 2077002 | QUARTZ | 9.917E-01 | -.004 | 4.006 | -6.220 |
| 2077003 | SIO2(A,GL) | 1.020E-01 | -.992 | 3.018 | -4.440 |
| 2003001 | BOEHMITE | 1.972E-02 | -1.705 | -8.578 | 28.130 |
| 5050001 | THERMONATR | 4.956E-09 | -8.305 | -.125 | 2.802 |
| 4195000 | ZNCL2 | 8.551E-22 | -21.068 | -7.030 | 17.480 |
| 5095000 | SMITHSONITE | 2.276E-07 | -6.643 | 10.000 | 4.360 |
| 5095001 | ZNCO3, 1H2O | 4.133E-07 | -6.384 | 10.260 | .000 |
| 2095000 | ZN(OH)2 (A) | 2.298E-10 | -9.639 | -12.450 | .000 |
| 2095001 | ZN(OH)2 (C) | 4.086E-10 | -9.389 | -12.200 | .000 |
| 2095002 | ZN(OH)2 (B) | 1.152E-09 | -8.939 | -11.750 | .000 |
| 2095003 | ZN(OH)2 (G) | 1.263E-09 | -8.899 | -11.710 | .000 |
| 2095004 | ZN(OH)2 (E) | 2.048E-09 | -8.689 | -11.500 | .000 |
| 4195001 | ZN2(OH)3CL | 9.953E-19 | -18.002 | -15.200 | .000 |
| 4195002 | ZN5(OH)8CL2 | 0.000E+00 | -41.293 | -38.500 | .000 |
| 5195000 | ZNNO3)2,6H2O | 5.265E-21 | -20.279 | -3.440 | -5.510 |
| 2095005 | ZNO(ACTIVE) | 3.178E-09 | -8.498 | -11.310 | .000 |
| 2095006 | ZINCITE | 4.700E-09 | -8.328 | -11.140 | 21.860 |
| 8295000 | ZNSIO3 | 7.456E-05 | -4.128 | -2.930 | 18.270 |
| 8095000 | WILLEMITE | 1.926E-14 | -13.715 | -15.330 | 33.370 |
| 8450001 | ANALCIME | 5.920E-03 | -2.228 | -6.719 | 22.840 |
| 8603000 | HALLOYSITE | 5.395E-04 | -3.268 | -8.994 | 39.730 |

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 5015000 | ARAGONITE | 1.880E-01 | -.726 | 8.336 | 2.615 |
| 8415000 | LEONHARDITE | 5.099E-01 | -.293 | -16.490 | 85.360 |
| 8450002 | LOW ALBITE | 7.772E-03 | -2.109 | -2.592 | 17.400 |
| 8450003 | ANALBITE | 9.474E-04 | -3.023 | -3.506 | 20.000 |
| 8415001 | ANORTHITE | 4.906E-10 | -9.309 | -25.430 | 70.660 |
| 8603002 | PYROPHYLLITE | 2.021E-01 | -.694 | 1.598 | .000 |
| 8415002 | LAUMONTITE | 4.348E-07 | -6.362 | -14.460 | 50.450 |
| 8415003 | WAIRAKITE | 1.698E-11 | -10.770 | -18.870 | 63.150 |
| 2015000 | LIME | 3.946E-23 | -22.404 | -32.797 | 46.265 |
| 2015001 | PORTLANDITE | 5.216E-13 | -12.283 | -22.675 | 30.690 |
| 8215002 | WOLLASTONITE | 2.441E-07 | -6.612 | -12.996 | 19.498 |
| 8215003 | P-WOLLSTANIT | 3.448E-08 | -7.462 | -13.846 | 21.068 |
| 8015001 | CA-OLIVINE | 1.342E-21 | -20.872 | -37.649 | 54.695 |
| 8015002 | LARNITE | 4.322E-23 | -22.364 | -39.141 | 57.238 |
| 8015007 | CA3SIO5 | 0.000E+00 | -46.697 | -73.867 | 106.335 |
| 8450004 | NEPHELINE | 1.922E-06 | -5.716 | -14.218 | 33.204 |
| 8015006 | GEHLENITE | 5.029E-27 | -26.299 | -56.822 | 116.125 |
| 2003000 | ALOH3(A) | 3.106E-04 | -3.508 | -10.380 | 27.045 |
| 2077000 | CHALCEDONY | 3.261E-01 | -.487 | 3.523 | -4.615 |
| 2077001 | CRISTOBALITE | 3.779E-01 | -.423 | 3.587 | -5.500 |
| 5015001 | CALCITE | 2.589E-01 | -.587 | 8.475 | 2.585 |
| 2003003 | GIBBSITE (C) | 1.265E-02 | -1.898 | -8.770 | 22.800 |
| 3003000 | Al2O3 | 5.845E-10 | -9.233 | -22.980 | .000 |
| 4150000 | HALITE | 4.275E-05 | -4.369 | -1.582 | -.918 |
| 8450000 | MAGADIITE | 7.365E-09 | -8.133 | 14.300 | .000 |

## PART 4 of OUTPUT FILE

```
          PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
        TYPE I and TYPE II (dissolved and adsorbed) species

+H+1
+        72.6   PERCENT BOUND IN SPECIES #3301400   HCO3 -

+        24.2   PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+         1.3   PERCENT BOUND IN SPECIES #5001401   NaHCO3 AQ

+       259.3   PERCENT BOUND IN SPECIES #8113302   =1SOH

+       142.4   PERCENT BOUND IN SPECIES #8213302   =2SOH

+NO3-1
+       100.0   PERCENT BOUND IN SPECIES #    492   NO3-1

+Cl-1
+       100.0   PERCENT BOUND IN SPECIES #    180   Cl-1

+ADS1TYP1
+         7.7   PERCENT BOUND IN SPECIES #    811   ADS1TYP1

+        45.9   PERCENT BOUND IN SPECIES #8113300   =1SO-

+        46.3   PERCENT BOUND IN SPECIES #8113302   =1SOH

+ADS2PSIo
+      >1000.   PERCENT BOUND IN SPECIES #8213302   =2SOH

 +Zn+2
+        77.9   PERCENT BOUND IN SPECIES #8219502   =2SOznOH

+         7.8   PERCENT BOUND IN SPECIES #8119500   =SOznOH

+        14.2   PERCENT BOUND IN SPECIES #8219500   =2SOZn+

+Na+1
+        99.5   PERCENT BOUND IN SPECIES #    500   Na+1

+ADS1PSIo
+      >1000.   PERCENT BOUND IN SPECIES #8113302   =1SOH
```

```
+ADS2TYP1
+          27.3   PERCENT BOUND IN SPECIES #   821   ADS2TYP1

+          36.3   PERCENT BOUND IN SPECIES #8213300   =2SO-

+          36.4   PERCENT BOUND IN SPECIES #8213302   =2SOH

+Ca+2
+          95.5   PERCENT BOUND IN SPECIES #   150   Ca+2

+           4.2  PERCENT BOUND IN SPECIES #1501400   CaHCO3 +

+H4SiO4
+          99.8   PERCENT BOUND IN SPECIES #   770   H4SiO4

+CO3-2
+          84.2   PERCENT BOUND IN SPECIES #3301400   HCO3 -

+          14.0   PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+           1.5  PERCENT BOUND IN SPECIES #5001401   NaHCO3 AQ

+Al+3
+           3.8  PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

+          55.2   PERCENT BOUND IN SPECIES # 303302   Al(OH)4 -

+          41.0   PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

+H2O
+          95.0   PERCENT BOUND IN SPECIES #3300020   OH-

+           2.8  PERCENT BOUND IN SPECIES # 303302   Al(OH)4 -

+           1.6  PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

__________________________ PART 5 of OUTPUT FILE _______________________
   DATE OF CALCULATIONS:  1-APR-96  TIME: 17:22:35
```

**Table E14** -Equilibrated Mass Distribution at the Last Node after 7 Pore Volumes

| IDX | NAME | DISSOLVED | | SORBED | | PRECIPITATED | |
|---|---|---|---|---|---|---|---|
| | | MOL/KG | PERCENT | MOL/KG | PERCENT | MOL/KG | PERCENT |
| 330 | H+1 | 1.348E-02 | 98.2 | 2.488E-04 | 1.8 | 0.000E+00 | .0 |
| 492 | NO3-1 | 2.000E-03 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 180 | Cl-1 | 5.000E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 950 | Zn+2 | 2.584E-11 | .1 | 3.352E-08 | 99.9 | 0.000E+00 | .0 |
| 500 | Na+1 | 4.993E-02 | 99.9 | 6.737E-05 | .1 | 0.000E+00 | .0 |
| 150 | Ca+2 | 5.170E-04 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 770 | H4SiO4 | 9.634E-05 | .0 | 0.000E+00 | .0 | 2.000E-01 | 100.0 |
| 140 | CO3-2 | 1.183E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 30 | Al+3 | 1.795E-09 | .0 | 0.000E+00 | .0 | 2.000E-01 | 100.0 |
| 2 | H2O | 1.405E-07 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |

```
0   Charge Balance: SPECIATED
0    Sum of CATIONS =  5.076E-02 Sum of ANIONS   6.198E-02
0      PERCENT DIFFERENCE =    9.951E+00  (ANIONS - CATIONS)/(ANIONS +
CATIONS)
0   EQUILIBRIUM IONIC STRENGTH (m) =   5.687E-02
0   EQUILIBRIUM pH              =   7.033

 ******* DIFFUSE LAYER ADSORPTION MODEL ********

  **** Parameters For Adsorbent Number 1 ****
  Electrostatic Variables:  psi0 =  .038472    sig0 =  .022974
                            psib =  .000000    sigb =  .000000
                            psid =  .000000    sigd =  .000000
  Adsorbent Concentration (g/l):  25.740
  Specific Surface Area (sq. meters/g):   45.00

  **** Parameters For Adsorbent Number 2 ****
  Electrostatic Variables:  psi0 =  .059250    sig0 =  .039925
                            psib =  .000000    sigb =  .000000
                            psid =  .000000    sigd =  .000000
```

```
 Adsorbent Concentration (g/l):  2.187
 Specific Surface Area (sq. meters/g):  45.00
  DATE ID NUMBER:        960401
   TIME ID NUMBER:       17223541
   ACCESSORY OUTPUT FILE: n

____________________ PART 6 of OUTPUT FILE ______________________
  DATE OF CALCULATIONS: 1-APR-96  TIME: 17:22:35

0Saturation indices and stoichiometry of all minerals
  ID #     NAME     Sat. Index     Stoichiometry in [brackets]
  2003000 ALOH3(A)      -3.508   [ 1.000]  30 [ 3.000]   2 [-3.000] 330
  5015000 ARAGONITE      -.726   [ 1.000] 150 [ 1.000] 140
  2003001 BOEHMITE      -1.705   [-3.000] 330 [ 1.000]  30 [ 2.000]   2
  5015001 CALCITE        -.587   [ 1.000] 150 [ 1.000] 140
  2077000 CHALCEDONY     -.487   [-2.000]   2 [ 1.000] 770
  2077001 CRISTOBALITE   -.423   [-2.000]   2 [ 1.000] 770
  2003002 DIASPORE        .000   [-3.000] 330 [ 1.000]  30 [ 2.000]   2
  2003003 GIBBSITE (C)  -1.898   [-3.000] 330 [ 1.000]  30 [ 3.000]   2
  3003000 Al2O3         -9.233   [ 2.000]  30 [ 3.000]   2 [-6.000] 330
  4150000 HALITE        -4.369   [ 1.000] 500 [ 1.000] 180
  8450000 MAGADIITE     -8.133   [-1.000] 330 [-9.000]   2 [ 1.000] 500
                                 [ 7.000] 770
  3050000 NATRON        -6.876   [ 2.000] 500 [ 1.000] 140 [10.000]   2
  2077002 QUARTZ         -.004   [-2.000]   2 [ 1.000] 770
  2077003 SIO2(A,GL)     -.992   [-2.000]   2 [ 1.000] 770
  2077004 SIO2(A,PT)    -1.300   [-2.000]   2 [ 1.000] 770
  5050001 THERMONATR    -8.305   [ 2.000] 500 [ 1.000] 140 [ 1.000]   2
  4195000 ZNCL2        -21.068   [ 1.000] 950 [ 2.000] 180
  5095000 SMITHSONITE   -6.643   [ 1.000] 950 [ 1.000] 140
  5095001 ZNCO3, 1H2O   -6.384   [ 1.000] 950 [ 1.000] 140 [ 1.000]   2
  2095000 ZN(OH)2 (A)   -9.639   [-2.000] 330 [ 1.000] 950 [ 2.000]   2
  2095001 ZN(OH)2 (C)   -9.389   [-2.000] 330 [ 1.000] 950 [ 2.000]   2
  2095002 ZN(OH)2 (B)   -8.939   [-2.000] 330 [ 1.000] 950 [ 2.000]   2
  2095003 ZN(OH)2 (G)   -8.899   [-2.000] 330 [ 1.000] 950 [ 2.000]   2
  2095004 ZN(OH)2 (E)   -8.689   [-2.000] 330 [ 1.000] 950 [ 2.000]   2
  4195001 ZN2(OH)3CL   -18.002   [-3.000] 330 [ 2.000] 950 [ 3.000]   2
                                 [ 1.000] 180
  4195002 ZN5(OH)8CL2  -41.293   [-8.000] 330 [ 5.000] 950 [ 8.000]   2
                                 [ 2.000] 180
  5195000 ZNNO3)2,6H2O -20.279   [ 1.000] 950 [ 2.000] 492 [ 6.000]   2
  2095005 ZNO(ACTIVE)   -8.498   [-2.000] 330 [ 1.000] 950 [ 1.000]   2
  2095006 ZINCITE       -8.328   [-2.000] 330 [ 1.000] 950 [ 1.000]   2
  8295000 ZNSIO3        -4.128   [-2.000] 330 [-1.000]   2 [ 1.000] 950
                                 [ 1.000] 770
  8095000 WILLEMITE    -13.715   [-4.000] 330 [ 2.000] 950 [ 1.000] 770
```

```
8450001 ANALCIME     -2.228   [ 1.000] 500 [ 1.000]  30 [ 2.000] 770
                   [ -1.000]  2 [ -4.000] 330
8603000 HALLOYSITE   -3.268   [ 2.000]  30 [ 2.000] 770 [ 1.000]  2
                   [ -6.000] 330
8603001 KAOLINITE     .000   [ 2.000]  30 [ 2.000] 770 [ 1.000]  2
                   [ -6.000] 330
8415000 LEONHARDITE   -.293   [ -1.000]  2 [-16.000] 330 [ 2.000] 150
                   [ 8.000] 770 [ 4.000]  30

 ID #   NAME    Sat. Index     Stoichiometry in [brackets]
8450002 LOW ALBITE   -2.109   [ 1.000] 500 [ 1.000]  30 [ 3.000] 770
                   [ -4.000] 330 [ -4.000]  2
8450003 ANALBITE     -3.023   [ 1.000] 500 [ 1.000]  30 [ 3.000] 770
                   [ -4.000] 330 [ -4.000]  2
8415001 ANORTHITE    -9.309   [ 1.000] 150 [ 2.000]  30 [ 2.000] 770
                   [ -8.000] 330
8603002 PYROPHYLLITE  -.694   [ 2.000]  30 [ 4.000] 770 [ -4.000]  2
                   [ -6.000] 330
8415003 WAIRAKITE   -10.770   [ 1.000] 150 [ 2.000]  30 [ 4.000] 770
                   [ -8.000] 330 [ -2.000]  2
2015000 LIME        -22.404   [ -2.000] 330 [ 1.000] 150 [ 1.000]  2
2015001 PORTLANDITE -12.283   [ -2.000] 330 [ 1.000] 150 [ 2.000]  2
8215002 WOLLASTONITE -6.612   [ -1.000]  2 [ -2.000] 330 [ 1.000] 770
                   [ 1.000] 150
8215003 P-WOLLSTANIT -7.462   [ -1.000]  2 [ -2.000] 330 [ 1.000] 770
                   [ 1.000] 150
8015001 CA-OLIVINE  -20.872   [ -4.000] 330 [ 1.000] 770 [ 2.000] 150
8015002 LARNITE     -22.364   [ -4.000] 330 [ 1.000] 770 [ 2.000] 150
8015007 CA3SIO5     -46.697   [ -6.000] 330 [ 1.000] 770 [ 3.000] 150
                   [ 1.000]  2
8450004 NEPHELINE    -5.716   [ -4.000] 330 [ 1.000] 770 [ 1.000]  30
                   [ 1.000] 500
8015006 GEHLENITE   -26.299   [-10.000] 330 [ 2.000]  30 [ 1.000] 770
                   [ 2.000] 150 [ 3.000]
```

## E2 Adsorption Column Test in Natural Soil

### E.2.1 Output of Column Leaching Adsorption Tests for the Last Node in Naural Soil

**Table E15** Components as Species in Solution at the Last Node after 5 Pore Volumes in Natural Clay.

| Id | Name | Calc mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 330 | H+1 | 4.056E-06 | 3.043E-06 | -5.51669 | .75019 | .125 |
| 500 | Na+1 | 1.520E-02 | 1.140E-02 | -1.94300 | .75019 | .125 |
| 410 | K+1 | 4.263E-03 | 3.198E-03 | -2.49512 | .75019 | .125 |
| 460 | Mg+2 | 1.879E-02 | 5.952E-03 | -2.22534 | .31673 | .499 |
| 150 | Ca+2 | 1.219E-02 | 3.861E-03 | -2.41332 | .31673 | .499 |
| 600 | Pb+2 | 3.829E-04 | 1.213E-04 | -3.91622 | .31673 | .499 |
| 950 | Zn+2 | 4.597E-03 | 1.456E-03 | -2.83687 | .31673 | .499 |
| 180 | Cl-1 | 1.410E-01 | 1.058E-01 | -.97566 | .75019 | .125 |
| 140 | CO3-2 | 5.381E-15 | 1.704E-15 | -14.76843 | .31673 | .499 |
| 821 | ADS2 | 3.998E-02 | 3.998E-02 | -1.39817 | 1.00000 | .000 |
| 811 | ADS1 | 5.056E-03 | 5.056E-03 | -2.29619 | 1.00000 | .000 |

**Table E16** Other Species in Solution or Adsorbed Components as Species in Solution at the Last Node after 5 Pore Volumes in Natural Clay.

| Id | Name | Calc mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 8219502 | =2SOZnOH | 5.374E-03 | 5.374E-03 | -2.26968 | 1.00000 | -8.170 |
| 3301400 | HCO3 - | 1.477E-10 | 1.108E-10 | -9.95556 | .75019 | 10.454 |
| 3301401 | H2CO3 AQ | 7.310E-10 | 7.572E-10 | -9.12081 | 1.03580 | 16.666 |
| 3300020 | OH- | 4.382E-09 | 3.288E-09 | -8.48312 | .75019 | -13.873 |
| 4603300 | MgOH + | 4.268E-09 | 3.202E-09 | -8.49457 | .75019 | -11.659 |
| 4601400 | MgCO3 AQ | 9.347E-15 | 9.682E-15 | -14.01405 | 1.03580 | 2.964 |
| 4601401 | MgHCO3 + | 1.022E-11 | 7.668E-12 | -11.11534 | .75019 | 11.520 |
| 1503300 | CaOH + | 4.250E-10 | 3.188E-10 | -9.49644 | .75019 | -12.473 |
| 1501400 | CaHCO3 + | 5.909E-12 | 4.433E-12 | -11.35335 | .75019 | 11.470 |
| 1501401 | CaCO3 AQ | 9.028E-15 | 9.351E-15 | -14.02914 | 1.03580 | 3.137 |
| 5001400 | NaCO3 - | 4.802E-16 | 3.602E-16 | -15.44343 | .75019 | 1.393 |
| 5001401 | NaHCO3 AQ | 6.864E-13 | 7.110E-13 | -12.14812 | 1.03580 | 10.065 |
| 9501800 | ZnCl + | 5.525E-04 | 4.145E-04 | -3.38252 | .75019 | .555 |
| 9501801 | ZnCl2 AQ | 4.431E-05 | 4.590E-05 | -4.33818 | 1.03580 | .435 |
| 9501802 | ZnCl3 - | 7.261E-06 | 5.447E-06 | -5.26384 | .75019 | .625 |
| 9501803 | ZnCl4 -2 | 9.095E-07 | 2.881E-07 | -6.54050 | .31673 | .698 |
| 9503300 | ZnOH + | 6.964E-07 | 5.224E-07 | -6.28199 | .75019 | -8.835 |
| 9503301 | Zn(OH)2 AQ | 1.899E-09 | 1.967E-09 | -8.70611 | 1.03580 | -16.914 |

**Table E16** Continue. Other Species in Solution or Adsorbed Components as Species in Solution at the Last Node after 5 Pore Volumes in Natural Clay.

| Id | Name | Calc mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 9503302 | Zn(OH)3 - | 2.714E-15 | 2.036E-15 | -14.69123 | .75019 | -28.274 |
| 9503303 | Zn(OH)4 -2 | 3.334E-22 | 1.056E-22 | -21.97635 | .31673 | -40.700 |
| 9501804 | ZnOHCl AQ | 1.611E-06 | 1.669E-06 | -5.77765 | 1.03580 | -7.495 |
| 9501400 | ZnHCO3 + | 2.528E-11 | 1.897E-11 | -10.72199 | .75019 | 12.525 |
| 9501401 | ZnCO3 AQ | 4.780E-13 | 4.951E-13 | -12.30530 | 1.03580 | 5.285 |
| 9501402 | Zn(CO3)2-2 | 5.696E-23 | 1.804E-23 | -22.74373 | .31673 | 10.129 |
| 6001800 | PbCl + | 6.807E-04 | 5.106E-04 | -3.29188 | .75019 | 1.725 |
| 6001801 | PbCl2 AQ | 8.264E-05 | 8.560E-05 | -4.06754 | 1.03580 | 1.785 |
| 6001802 | PbCl3 - | 9.564E-06 | 7.175E-06 | -5.14419 | .75019 | 1.824 |
| 6001803 | PbCl4 -2 | 1.149E-06 | 3.640E-07 | -6.43885 | .31673 | 1.879 |
| 6001400 | Pb(CO3)2-2 | 4.855E-23 | 1.538E-23 | -22.81309 | .31673 | 11.139 |
| 6003300 | PbOH + | 1.032E-06 | 7.739E-07 | -6.11134 | .75019 | -7.585 |
| 6003301 | Pb(OH)2 AQ | 9.512E-11 | 9.852E-11 | -10.00646 | 1.03580 | -17.135 |
| 6003302 | Pb(OH)3 - | 4.935E-16 | 3.702E-16 | -15.43158 | .75019 | -27.935 |
| 6003303 | Pb2OH +3 | 2.792E-08 | 2.101E-09 | -8.67756 | .07526 | -5.237 |
| 6003304 | Pb3(OH)4+2 | 8.515E-14 | 2.697E-14 | -13.56915 | .31673 | -23.381 |
| 6001401 | PbCO3 AQ | 3.468E-12 | 3.592E-12 | -11.44465 | 1.03580 | 7.225 |
| 6003305 | Pb(OH)4 -2 | 8.782E-22 | 2.782E-22 | -21.55571 | .31673 | -39.200 |
| 6001402 | PbHCO3 + | 1.329E-11 | 9.969E-12 | -11.00134 | .75019 | 13.325 |

**Table E16** Continue. Other Species in Solution or Adsorbed Components as Species in Solution at the Last Node after 5 Pore Volumes in Natural Clay.

| Id | Name | Calc mol | Activity | Log Activity | Gamma | New Logk |
|---|---|---|---|---|---|---|
| 8113300 | =1SO- | 2.658E-02 | 2.658E-02 | -1.57545 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 3.413E-02 | 3.413E-02 | -1.46692 | 1.00000 | 8.460 |
| 8116000 | =1SOpb+ | 2.367E-09 | 2.367E-09 | -8.62572 | 1.00000 | -7.930 |
| 8114100 | =1SOk | 3.939E-08 | 3.939E-08 | -7.40462 | 1.00000 | -8.130 |
| 8116001 | =1SOPbOH | 7.095E-06 | 7.095E-06 | -5.14903 | 1.00000 | -9.970 |
| 8213300 | =2SO- | 1.662E-02 | 1.662E-02 | -1.77945 | 1.00000 | -7.910 |
| 8213302 | =2SOH | 1.710E-02 | 1.710E-02 | -1.76689 | 1.00000 | 7.160 |
| 8214100 | =2SOk | 3.939E-09 | 3.939E-09 | -8.40462 | 1.00000 | -9.130 |
| 8216000 | =2SOpb+ | 7.780E-06 | 7.780E-06 | -5.10903 | 1.00000 | -9.930 |
| 8216002 | =2SOPbOH | 7.095E-06 | 7.095E-06 | -5.14903 | 1.00000 | -9.970 |
| 8119500 | =1SOzn+ | 9.425E-11 | 9.425E-11 | -10.02572 | 1.00000 | -9.330 |
| 8115000 | =1SOna | 1.404E-07 | 1.404E-07 | -6.85250 | 1.00000 | -8.130 |
| 8119502 | =1SOznOH | 5.374E-03 | 5.374E-03 | -2.26968 | 1.00000 | -8.170 |
| 8215000 | =2SOna | 3.528E-07 | 3.528E-07 | -6.45250 | 1.00000 | -7.730 |
| 8219500 | =2SOzn+ | 9.780E-04 | 9.780E-04 | -3.00968 | 1.00000 | -8.910 |

**Table E17** Finite Solid at the Last Node after 5 Pore Volumes in Natural Clay(present at equilibrium).

| Id | Name | Calc mol | Log mol | New logk | DH |
|---|---|---|---|---|---|
| 4160003 | LAURIONITE | 5.176E-03 | -2.286 | -.623 | .000 |

**Table E18** - Udersaturated Solids at the Last Node after 5 Pore Volumes in Natural Clay (not present at equilibrium).

| Id | Name | Calc mol | Log mol | New logk | DH |
|---|---|---|---|---|---|
| 5015001 | CALCITE | 1.964E-09 | -8.707 | 8.475 | 2.585 |
| 2095002 | ZN(OH)2 (B) | 2.773E-04 | -3.557 | -11.750 | .000 |
| 2095003 | ZN(OH)2 (G) | 3.040E-04 | -3.517 | -11.710 | .000 |
| 2095004 | ZN(OH)2 (E) | 4.930E-04 | -3.307 | -11.500 | .000 |
| 4195001 | ZN2(OH)3CL | 4.957E-06 | -5.305 | -15.200 | .000 |
| 4195002 | ZN5(OH)8CL2 | 3.044E-11 | -10.517 | -38.500 | .000 |
| 2095005 | ZNO(ACTIVE) | 7.668E-04 | -3.115 | -11.310 | .000 |
| 2095006 | ZINCITE | 1.134E-03 | -2.945 | -11.140 | 21.860 |
| 4160000 | COTUNNITE | 7.988E-02 | -1.098 | 4.770 | -5.600 |
| 4160002 | PHOSGENITE | 1.811E-05 | -4.742 | 19.810 | .000 |
| 5060000 | CERRUSITE | 2.788E-06 | -5.555 | 13.130 | -4.860 |
| 2060000 | MASSICOT | 1.605E-06 | -5.795 | -12.910 | 16.780 |
| 2060001 | LITHARGE | 2.485E-06 | -5.605 | -12.720 | 16.380 |
| 2060002 | PBO, .3H2O | 1.364E-06 | -5.865 | -12.980 | .000 |
| 5060001 | PB2OCO3 | 8.525E-12 | -11.069 | .500 | 11.460 |
| 5060002 | PB3O2CO3 | 3.358E-16 | -15.474 | -11.020 | 26.430 |
| 2060004 | PB(OH)2 © | 9.195E-02 | -1.036 | -8.150 | 13.990 |
| 2046000 | BRUCITE | 1.029E-08 | -7.988 | -16.792 | 25.840 |
| 4160004 | PB2(OH)3CL | 8.781E-02 | -1.056 | -8.793 | .000 |
| 5060003 | HYDCERRUSITE | 1.600E-13 | -12.796 | 17.460 | .000 |
| 2060005 | PB2O(OH)2 | 1.069E-12 | -11.971 | -26.200 | .000 |

**Table E18** Continue - Udersaturated Solids (not present at equilibrium)

| Id | Name | Calc mol | Log mol | New logk | DH |
|---|---|---|---|---|---|
| 2015000 | LIME | 6.626E-25 | -24.179 | -32.797 | 46.265 |
| 2015001 | PORTLANDITE | 8.739E-15 | -14.059 | -22.675 | 30.690 |
| 2046001 | PERICLASE | 1.978E-13 | -12.704 | -21.510 | 36.135 |
| 5015000 | ARAGONITE | 1.427E-09 | -8.846 | 8.336 | 2.615 |
| 5046000 | ARTINITE | 1.604E-18 | -17.795 | -9.600 | 28.742 |
| 5015002 | DOLOMITE | 6.675E-18 | -17.176 | 17.000 | 8.290 |
| 4150000 | HALITE | 3.158E-05 | -4.501 | -1.582 | -.918 |
| 5015003 | HUNTITE | 0.000E+00 | -38.195 | 29.968 | 25.760 |
| 5046001 | HYDRMAGNESIT | 0.000E+00 | -50.412 | 8.766 | 52.210 |
| 5046002 | MAGNESITE | 1.084E-09 | -8.965 | 8.029 | 6.169 |
| 3050000 | NATRON | 4.350E-18 | -17.362 | 1.311 | -15.745 |
| 5046003 | NESQUEHONITE | 4.186E-12 | -11.378 | 5.621 | 5.789 |
| 5050001 | THERMONATR | 1.655E-19 | -18.781 | -.125 | 2.802 |
| 4195000 | ZNCL2 | 1.520E-12 | -11.818 | -7.030 | 17.480 |
| 5095000 | SMITHSONITE | 2.481E-08 | -7.605 | 10.000 | 4.360 |
| 5095001 | ZNCO3, 1H2O | 4.497E-08 | -7.347 | 10.260 | .000 |
| 2095000 | ZN(OH)2 (A) | 5.532E-05 | -4.257 | -12.450 | .000 |
| 2095001 | ZN(OH)2 © | 9.838E-05 | -4.007 | -12.200 | .000 |

**Table E19** Species with fixed activity

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2 | H2O | 4.546E-02 | -1.342 | .002 | .000 |
| 3301403 | CO2 (g) | 1.670E-02 | -1.777 | 25.800 | -.530 |

```
 Type IV - FINITE SOLIDS (present at equilibrium)
  ID           NAME        CALC MOL      LOG MOL   NEW LOGK    DH
 4160003 LAURIONITE     5.176E-03       -2.286         -.623     .000
 ----------------------------------------------------------------------
0 Type VI - EXCLUDED SPECIES (not included in mole balance)
0  ID          NAME        CALC MOL      LOG MOL   NEW LOGK    DH
   823   ADS2PSIo       9.727E-03      -2.012        .000        .000
   813   ADS1PSIo       7.690E-03      -2.114        .000        .000
_______________________ PART 4 of OUTPUT FILE ____________________________

             PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
            TYPE I and TYPE II (dissolved and adsorbed) species
+H+1
+           69.5    PERCENT BOUND IN SPECIES #8219502  =2SOznOH

+          171.9    PERCENT BOUND IN SPECIES #8113300  =1SO-

+          107.5    PERCENT BOUND IN SPECIES #8213300  =2SO-

+           69.5    PERCENT BOUND IN SPECIES #8119502  =1SOznOH

+           12.6    PERCENT BOUND IN SPECIES #8219500  =2SOzn+

 +Na+1
+          100.0    PERCENT BOUND IN SPECIES #    500  Na+1

+K+1
+          100.0    PERCENT BOUND IN SPECIES #    410  K+1

+ADS1TYP1
+            6.5   PERCENT BOUND IN SPECIES #    811   ADS1TYP1

+            6.9   PERCENT BOUND IN SPECIES #8219502   =2SOZnOH

+           34.3    PERCENT BOUND IN SPECIES #8113300   =1SO-

+           44.0    PERCENT BOUND IN SPECIES #8113302   =1SOH

+            6.9   PERCENT BOUND IN SPECIES #8119502   =1SOZnOH

+            1.3   PERCENT BOUND IN SPECIES #8219500   =2SOZn+
```

```
+ADS2PSIo
+          >1000.   PERCENT BOUND IN SPECIES #8213302  =2SOH

+Pb+2
+           32.4   PERCENT BOUND IN SPECIES #   600  Pb+2

+           57.7   PERCENT BOUND IN SPECIES #6001800  PbCl +

+            7.0   PERCENT BOUND IN SPECIES #6001801  PbCl2 AQ

+Zn+2
+           27.2   PERCENT BOUND IN SPECIES #   950  Zn+2

+           31.7   PERCENT BOUND IN SPECIES #8219502  =2SOznOH

+            3.3   PERCENT BOUND IN SPECIES #9501800  ZnCl +

+           31.7   PERCENT BOUND IN SPECIES #8119502  =1SOznOH

+            5.8   PERCENT BOUND IN SPECIES #8219500  =2SOzn+

+Mg+2
+          100.0   PERCENT BOUND IN SPECIES #   460  Mg+2

+ADS1PSIo
+          452.3   PERCENT BOUND IN SPECIES #8113302  =1SOH

+ADS2TYP1
+           54.2   PERCENT BOUND IN SPECIES #   821  ADS2TYP1

+           22.5   PERCENT BOUND IN SPECIES #8213300  =2SO-

+           23.2   PERCENT BOUND IN SPECIES #8213302  =2SOH

+Ca+2
+          100.0   PERCENT BOUND IN SPECIES #   150  Ca+2


+Cl-1
+           98.9   PERCENT BOUND IN SPECIES #   180  Cl-1
```

```
+CO3-2
+          15.7   PERCENT BOUND IN SPECIES #3301400   HCO3 -

+          77.9   PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+           1.1   PERCENT BOUND IN SPECIES #4601401   MgHCO3 +

+           2.7   PERCENT BOUND IN SPECIES #9501400   ZnHCO3 +

+           1.4   PERCENT BOUND IN SPECIES #6001402   PbHCO3 +

+H2O
+          20.6   PERCENT BOUND IN SPECIES #9503300   ZnOH +

+          47.7   PERCENT BOUND IN SPECIES #9501804   ZnOHCl AQ

+          30.5   PERCENT BOUND IN SPECIES #6003300   PbOH +
```

**Table E20** Equilibrated Mass Distribution at the Last Node after 7 Pore Volumes

| IDX NAME | DISSOLVED | | SORBED | | PRECIPITATED | |
|---|---|---|---|---|---|---|
| | MOL/KG | PERCENT | MOL/KG | PERCENT | MOL/KG | PERCENT |
| 330 H+1 | 6.782E-07 | .0 | -1.546E-02 | 100.0 | 0.000E+00 | .0 |
| 500 Na+1 | 1.520E-02 | 100.0 | 4.932E-07 | .0 | 0.000E+00 | .0 |
| 410 K+1 | 4.263E-03 | 100.0 | 4.333E-08 | .0 | 0.000E+00 | .0 |
| 600 Pb+2 | 1.158E-03 | 18.2 | 2.197E-05 | .3 | 5.176E-03 | 81.4 |
| 950 Zn+2 | 5.204E-03 | 30.7 | 1.173E-02 | 69.3 | 0.000E+00 | .0 |
| 460 Mg+2 | 1.879E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 150 Ca+2 | 1.219E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 180 Cl-1 | 1.425E-01 | 96.5 | 0.000E+00 | .0 | 5.176E-03 | 3.5 |
| 140 CO3-2 | 9.380E-10 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 2 H2O | 3.380E-06 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |

```
0    Charge Balance: SPECIATED
```

```
0     Sum of CATIONS =  9.262E-02 Sum of ANIONS   1.410E-01
0       PERCENT DIFFERENCE =    2.071E+01  (ANIONS - CATIONS)/(ANIONS +
CATIONS)
0    EQUILIBRIUM IONIC STRENGTH (m) =   1.528E-01
0    EQUILIBRIUM pH                =   5.517

 ******* DIFFUSE LAYER ADSORPTION MODEL ********

  **** Parameters For Adsorbent Number 1 ****
  Electrostatic Variables:  psi0 =  .125061     sig0 =  .259595
                     psib =  .000000     sigb =  .000000
                     psid =  .000000     sigd =  .000000
  Adsorbent Concentration (g/l):  21.740
  Specific Surface Area (sq. meters/g):  129.00

**** Parameters For Adsorbent Number 2 ****
  Electrostatic Variables:  psi0 =  .119026     sig0 =  .230353
                     psib =  .000000     sigb =  .000000
                     psid =  .000000     sigd =  .000000
  Adsorbent Concentration (g/l):  4.087
  Specific Surface Area (sq. meters/g):  50.00
   DATE ID NUMBER:          960404
    TIME ID NUMBER:        22252114
_________________________________________
Saturation indices and stoichiometry of all minerals
0   ID #    NAME     Sat. Index      Stoichiometry in [brackets]
  5015000 ARAGONITE      -8.846    [  1.000] 150  [  1.000] 140
  5046000 ARTINITE      -17.795   [ -2.000] 330  [  2.000] 460  [  1.000] 140
                          [  5.000]   2
  2046000 BRUCITE        -7.988    [  1.000] 460  [  2.000]   2  [ -2.000] 330
  5015001 CALCITE        -8.707    [  1.000] 150  [  1.000] 140
  5015002 DOLOMITE      -17.176    [  1.000] 150  [  1.000] 460  [  2.000] 140
  4150000 HALITE         -4.501    [  1.000] 500  [  1.000] 180
  5015003 HUNTITE       -38.195    [  3.000] 460  [  1.000] 150  [  4.000] 140
  5046001 HYDRMAGNESIT  -50.412    [  5.000] 460  [  4.000] 140  [ -2.000] 330
                          [  6.000]   2
  5046002 MAGNESITE      -8.965    [  1.000] 460  [  1.000] 140
  3050000 NATRON        -17.362    [  2.000] 500  [  1.000] 140  [ 10.000]   2
  5046003 NESQUEHONITE  -11.378    [  1.000] 460  [  1.000] 140  [  3.000]   2
  5050001 THERMONATR    -18.781    [  2.000] 500  [  1.000] 140  [  1.000]   2
  4195000 ZNCL2         -11.818    [  1.000] 950  [  2.000] 180
  5095000 SMITHSONITE    -7.605    [  1.000] 950  [  1.000] 140
  5095001 ZNCO3, 1H2O    -7.347    [  1.000] 950  [  1.000] 140  [  1.000]   2
```

```
2095000 ZN(OH)2 (A)    -4.257   [ -2.000] 330  [  1.000] 950  [  2.000]   2
2095001 ZN(OH)2 (C)    -4.007   [ -2.000] 330  [  1.000] 950  [  2.000]   2
2095002 ZN(OH)2 (B)    -3.557   [ -2.000] 330  [  1.000] 950  [  2.000]   2
2095003 ZN(OH)2 (G)    -3.517   [ -2.000] 330  [  1.000] 950  [  2.000]   2
2095004 ZN(OH)2 (E)    -3.307   [ -2.000] 330  [  1.000] 950  [  2.000]   2
4195001 ZN2(OH)3CL     -5.305   [ -3.000] 330  [  2.000] 950  [  3.000]   2
                       [  1.000] 180
4195002 ZN5(OH)8CL2   -10.517   [ -8.000] 330  [  5.000] 950  [  8.000]   2
                       [  2.000] 180
2095005 ZNO(ACTIVE)    -3.115   [ -2.000] 330  [  1.000] 950  [  1.000]   2
2095006 ZINCITE        -2.945   [ -2.000] 330  [  1.000] 950  [  1.000]   2
4160000 COTUNNITE      -1.098   [  1.000] 600  [  2.000] 180
4160002 PHOSGENITE     -4.742   [  2.000] 600  [  2.000] 180  [  1.000] 140
5060000 CERRUSITE      -5.555   [  1.000] 600  [  1.000] 140
2060000 MASSICOT       -5.795   [ -2.000] 330  [  1.000] 600  [  1.000]   2
2060001 LITHARGE       -5.605   [ -2.000] 330  [  1.000] 600  [  1.000]   2
2060002 PBO, .3H2O     -5.865   [ -2.000] 330  [  1.000] 600  [  1.330]   2
5060001 PB2OCO3       -11.069   [ -2.000] 330  [  2.000] 600  [  1.000]   2
                       [  1.000] 140
5060002 PB3O2CO3      -15.474   [ -4.000] 330  [  3.000] 600  [  1.000] 140
                       [  2.000]   2
2060004 PB(OH)2 (C)    -1.036   [ -2.000] 330  [  1.000] 600  [  2.000]   2
4160003 LAURIONITE       .000   [ -1.000] 330  [  1.000] 600  [  1.000] 180
                       [  1.000]   2
4160004 PB2(OH)3CL     -1.056   [ -3.000] 330  [  2.000] 600  [  3.000]   2
                       [  1.000] 180
```

## E3 Desorption Column Test

### E.3.1 Output of Column Leaching Desorption Tests for Lead Contaminated Soil (KSC Clay) at the Last Node after 5 Pore Volumes Using EDTA

**Table E21** Type I - Components as Species in Solution at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTVTY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 330 | H+1 | 9.133E-08 | 7.552E-08 | -7.12192 | .82695 | .083 |
| 492 | NO3-1 | 2.000E-03 | 1.654E-03 | -2.78149 | .82695 | .083 |
| 600 | Pb+2 | 6.074E-16 | 2.841E-16 | -15.54658 | .46765 | .330 |
| 150 | Ca+2 | 3.195E-10 | 1.494E-10 | -9.82565 | .46765 | .330 |
| 770 | H4SiO4 | 9.760E-05 | 9.858E-05 | -4.00622 | 1.00997 | -.004 |
| 30 | Al+3 | 1.763E-14 | 3.188E-15 | -14.49647 | .18085 | .743 |
| 140 | CO3-2 | 8.391E-06 | 3.924E-06 | -5.40628 | .46765 | .330 |
| 969 | EDTA-4 | 3.952E-05 | 1.890E-06 | -5.72352 | .04783 | 1.320 |
| 821 | ADS2TYP1 | 2.913E-02 | 2.913E-02 | -1.53564 | 1.00000 | .000 |
| 811 | ADS1TYP1 | 1.101E-02 | 1.101E-02 | -1.95827 | 1.00000 | .000 |

**Table E22 Tpe II** - other Species in Solution or Adsorbed at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 8216002 | =2SOPbOH | 3.707E-05 | 3.707E-05 | -4.43102 | 1.00000 | -1.170 |
| 1509690 | Ca EDTA | 1.517E-03 | 7.093E-04 | -3.14917 | .46765 | 12.730 |
| 1509691 | CaHEDTA | 2.579E-07 | 2.133E-07 | -6.67108 | .82695 | 16.083 |
| 3300020 | OH- | 1.608E-07 | 1.330E-07 | -6.87620 | .82695 | -13.915 |
| 3307700 | H3SiO4 - | 1.860E-07 | 1.538E-07 | -6.81309 | .82695 | -9.846 |
| 3307701 | H2SiO4 -2 | 8.935E-12 | 4.178E-12 | -11.37901 | .46765 | -21.287 |
| 1503300 | CaOH + | 6.035E-16 | 4.991E-16 | -15.30184 | .82695 | -12.515 |
| 1501400 | CaHCO3 + | 1.185E-11 | 9.800E-12 | -11.00875 | .82695 | 11.428 |
| 1501401 | CaCO3 AQ | 8.248E-13 | 8.331E-13 | -12.07932 | 1.00997 | 3.148 |
| 303300 | AlOH +2 | 9.235E-13 | 4.319E-13 | -12.36466 | .46765 | -4.660 |
| 303301 | Al(OH)2 + | 5.366E-11 | 4.438E-11 | -10.35286 | .82695 | -10.017 |
| 303302 | Al(OH)4 - | 1.184E-09 | 9.789E-10 | -9.00925 | .82695 | -22.917 |
| 303303 | Al(OH)3 AQ | 7.322E-10 | 7.395E-10 | -9.13106 | 1.00997 | -16.004 |
| 6001400 | Pb(CO3)2-2 | 4.083E-16 | 1.909E-16 | -15.71914 | .46765 | 10.970 |
| 6003300 | PbOH + | 8.866E-17 | 7.332E-17 | -16.13477 | .82695 | -7.627 |
| 6003301 | Pb(OH)2 AQ | 3.739E-19 | 3.776E-19 | -18.42297 | 1.00997 | -17.124 |
| 6003302 | Pb(OH)3 - | 6.940E-23 | 5.739E-23 | -22.24117 | .82695 | -27.977 |
| 6003303 | Pb2OH +3 | 2.578E-30 | 4.663E-31 | -30.33135 | .18085 | -5.617 |
| 6004920 | PbNO3 + | 8.403E-18 | 6.949E-18 | -17.15807 | .82695 | 1.253 |
| 6003304 | Pb3(OH)4+2 | 1.984E-42 | 9.279E-43 | -42.03252 | .46765 | -23.550 |
| 6001401 | PbCO3 AQ | 1.918E-14 | 1.937E-14 | -13.71286 | 1.00997 | 7.236 |
| 6003305 | Pb(OH)4 -2 | 3.730E-27 | 1.744E-27 | -26.75836 | .46765 | -39.369 |
| 6001402 | PbHCO3 + | 1.613E-15 | 1.334E-15 | -14.87477 | .82695 | 13.283 |

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTIVITY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 3301400 | HCO3 - | 7.654E-03 | 6.329E-03 | -2.19863 | .82695 | 10.412 |
| 3301401 | H2CO3 AQ | 1.063E-03 | 1.074E-03 | -2.96911 | 1.00997 | 16.677 |
| 6009692 | PBHEDTA | 2.347E-19 | 1.941E-19 | -18.71202 | .82695 | 9.763 |
| 6009693 | PBH2EDTA | 5.032E-30 | 5.082E-30 | -29.29393 | 1.00997 | 6.216 |
| 6009691 | PBEDTA | 8.709E-04 | 4.073E-04 | -3.39010 | .46765 | 18.210 |
| 3309691 | EDTAH | 7.199E-03 | 1.302E-03 | -2.88544 | .18085 | 10.703 |
| 3309692 | EDTAH2 | 3.739E-04 | 1.748E-04 | -3.75735 | .46765 | 16.540 |
| 3309693 | EDTAH3 | 7.133E-09 | 5.898E-09 | -8.22927 | .82695 | 18.943 |
| 3309694 | EDTAH4 | 5.182E-14 | 5.234E-14 | -13.28118 | 1.00997 | 20.926 |
| 3309695 | EDTA H5 | 1.635E-18 | 1.352E-18 | -17.86910 | .82695 | 23.547 |
| 8113300 | =1SO- | 3.281E-02 | 3.281E-02 | -1.48399 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 3.292E-02 | 3.292E-02 | -1.48255 | 1.00000 | 7.860 |
| 8116000 | =1SOpb+ | 3.864E-12 | 3.864E-12 | -11.41293 | 1.00000 | -1.030 |
| 8116002 | =SOPbOH | 4.666E-05 | 4.666E-05 | -4.33102 | 1.00000 | -1.070 |
| 8213300 | =2SO- | 1.230E-02 | 1.230E-02 | -1.91007 | 1.00000 | -6.910 |
| 8213302 | =2SOH | 1.227E-02 | 1.227E-02 | -1.91122 | 1.00000 | 6.160 |
| 8216000 | =2SOpb+ | 4.064E-05 | 4.064E-05 | -4.39102 | 1.00000 | -1.130 |

**Table E23 Type III** - Species with Fixed Activity at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2 | H2O | -8.404E-03 | -2.075 | .000 | .000 |
| 3301403 | CO2 (g) | -8.208E-03 | -2.086 | 19.650 | -.530 |

**Table E24 Type IV** - Finite Solids (present at equilibrium) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8603001 | KAOLINITE | 1.000E-01 | -7.310 | -5.726 | 35.280 |
| 2077002 | QUARTZ | 4.022E-04 | -3.396 | 4.006 | -6.220 |

**Table E25- Type V** - Undersaturated Solids (not present at equilibrium) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 5015001 | CALCITE | 1.750E-07 | -6.757 | 8.475 | 2.585 |
| 2077003 | SIO2(A,GL) | 1.028E-01 | -.988 | 3.018 | -4.440 |
| 2003001 | BOEHMITE | 1.955E-02 | -1.709 | -8.578 | 28.130 |
| 5060000 | CERRUSITE | 1.504E-08 | -7.823 | 13.130 | -4.860 |
| 2060000 | MASSICOT | 6.125E-15 | -14.213 | -12.910 | 16.780 |
| 2060001 | LITHARGE | 9.487E-15 | -14.023 | -12.720 | 16.380 |
| 2060002 | PBO, .3H2O | 5.213E-15 | -14.283 | -12.980 | .000 |
| 5060001 | PB2OCO3 | 1.755E-22 | -21.756 | .500 | 11.460 |
| 5060002 | PB3O2CO3 | 2.639E-35 | -34.579 | -11.020 | 26.430 |
| 8260000 | PBSIO3 | 2.350E-13 | -12.629 | -7.320 | 9.260 |
| 8060000 | PB2SIO4 | 4.249E-27 | -26.372 | -19.760 | 26.000 |
| 2060004 | PB(OH)2 (C) | 3.524E-10 | -9.453 | -8.150 | 13.990 |
| 5060003 | HYDCERRUSITE | 1.784E-26 | -25.749 | 17.460 | .000 |
| 2060005 | PB2O(OH)2 | 1.564E-29 | -28.806 | -26.200 | .000 |
| 8603000 | HALLOYSITE | 5.395E-04 | -3.268 | -8.994 | 39.730 |
| 5015000 | ARAGONITE | 1.271E-07 | -6.896 | 8.336 | 2.615 |
| 8415000 | LEONHARDITE | 5.940E-13 | -12.226 | -16.490 | 85.360 |

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8415001 | ANORTHITE | 5.180E-16 | -15.286 | -25.430 | 70.660 |
| 8603002 | PYROPHYLLITE | 2.052E-01 | -.688 | 1.598 | .000 |
| 8415002 | LAUMONTITE | 4.697E-13 | -12.328 | -14.460 | 50.450 |
| 8415003 | WAIRAKITE | 1.828E-17 | -16.738 | -18.870 | 63.150 |
| 2015000 | LIME | 4.179E-29 | -28.379 | -32.797 | 46.265 |
| 2015001 | PORTLANDITE | 5.533E-19 | -18.257 | -22.675 | 30.690 |
| 8215002 | WOLLASTONITE | 2.607E-13 | -12.584 | -12.996 | 19.498 |
| 8215003 | P-WOLLSTANIT | 3.682E-14 | -13.434 | -13.846 | 21.068 |
| 8015001 | CA-OLIVINE | 1.518E-33 | -32.819 | -37.649 | 54.695 |
| 8015002 | LARNITE | 4.888E-35 | -34.311 | -39.141 | 57.238 |
| 8015007 | CA3SIO5 | 0.000E+00 | -64.619 | -73.867 | 106.335 |
| 8015006 | GEHLENITE | 0.000E+00 | -38.254 | -56.822 | 116.125 |
| 2003000 | ALOH3(A) | 3.083E-04 | -3.511 | -10.380 | 27.045 |
| 2077000 | CHALCEDONY | 3.289E-01 | -.483 | 3.523 | -4.615 |
| 2077001 | CRISTOBALITE | 3.811E-01 | -.419 | 3.587 | -5.500 |
| 2003002 | DIASPORE | 9.910E-01 | -.004 | -6.873 | 24.630 |
| 2003003 | GIBBSITE © | 1.256E-02 | -1.901 | -8.770 | 22.800 |
| 3003000 | Al2O3 | 5.731E-10 | -9.242 | -22.980 | .000 |
| 2077004 | SIO2(A,PT) | 5.058E-02 | -1.296 | 2.710 | -3.910 |

**Table E26- Type VI** - Excluded Species (not included in mole balance) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 823 | ADS2PSIo | 3.858E+00 | .586 | .000 | .000 |
| 813 | ADS1PSIo | 5.466E-01 | -.262 | .000 | .000 |

```
______________________________ PART 4 of OUTPUT FILE ________________________
 DATE OF CALCULATIONS:  9-APR-96  TIME: 20: 6:44

          PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
        TYPE I and TYPE II (dissolved and adsorbed) species

+H+1
+          43.6   PERCENT BOUND IN SPECIES #3301400   HCO3 -

+          12.1   PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+          41.0   PERCENT BOUND IN SPECIES #3309691   EDTAH

+           4.3   PERCENT BOUND IN SPECIES #3309692   EDTAH2

+         187.5   PERCENT BOUND IN SPECIES #8113302   =1SOH

+          69.9   PERCENT BOUND IN SPECIES #8213302   =2SOH

+NO3-1
+         100.0   PERCENT BOUND IN SPECIES #    492   NO3-1

+Pb+2
+           3.7   PERCENT BOUND IN SPECIES #8216002   =2SOPbOH

+          87.5   PERCENT BOUND IN SPECIES #6009691   PBEDTA

+           4.7   PERCENT BOUND IN SPECIES #8116002   =SOPbOH

+           4.1   PERCENT BOUND IN SPECIES #8216000   =2SOpb+

+ADS2TYP1
+          54.2   PERCENT BOUND IN SPECIES #    821   ADS2TYP1

+          22.9   PERCENT BOUND IN SPECIES #8213300   =2SO-

+          22.8   PERCENT BOUND IN SPECIES #8213302   =2SOH

+ADS1TYP1
+          14.3   PERCENT BOUND IN SPECIES #    811   ADS1TYP1

+          42.7   PERCENT BOUND IN SPECIES #8113300   =1SO-

+          42.8   PERCENT BOUND IN SPECIES #8113302   =1SOH


+ADS2PSIo
```

```
+          >1000.   PERCENT BOUND IN SPECIES #8213300  =2SO-

+ADS1PSIo
+          >1000.   PERCENT BOUND IN SPECIES #8113302  =1SOH

+EDTA-4
+            15.2   PERCENT BOUND IN SPECIES #1509690  Ca EDTA

+             8.7   PERCENT BOUND IN SPECIES #6009691  PBEDTA

+            72.0   PERCENT BOUND IN SPECIES #3309691  EDTAH

+             3.7   PERCENT BOUND IN SPECIES #3309692  EDTAH2

+Ca+2
+           100.0   PERCENT BOUND IN SPECIES #1509690  Ca EDTA

+H4SiO4
+            99.8   PERCENT BOUND IN SPECIES #     770  H4SiO4

+CO3-2
+            87.7   PERCENT BOUND IN SPECIES #3301400  HCO3 -

+            12.2   PERCENT BOUND IN SPECIES #3301401  H2CO3 AQ

+Al+3
+             2.7   PERCENT BOUND IN SPECIES # 303301  Al(OH)2 +

+            60.1   PERCENT BOUND IN SPECIES # 303302  Al(OH)4 -

+            37.2   PERCENT BOUND IN SPECIES # 303303  Al(OH)3 AQ

+H2O
+            95.8   PERCENT BOUND IN SPECIES #3300020  OH-

+             2.8   PERCENT BOUND IN SPECIES # 303302  Al(OH)4 -

+             1.3   PERCENT BOUND IN SPECIES # 303303  Al(OH)3 AQ
```

Table E27 Equilibrated Mass Distribution at the Last Node after 7 Pore Volumes.

| IDX | NAME | DISSOLVED | | SORBED | | PRECIPITATED | |
|---|---|---|---|---|---|---|---|
| | | MOL/KG | PERCENT | MOL/KG | PERCENT | MOL/KG | PERCENT |
| 330 | H+1 | 1.773E-02 | 101.0 | -1.718E-04 | -1.0 | 0.000E+00 | .0 |
| 492 | NO3-1 | 2.000E-03 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 600 | Pb+2 | 8.709E-04 | 87.5 | 1.244E-04 | 12.5 | 0.000E+00 | .0 |
| 969 | EDTA-4 | 1.000E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 150 | Ca+2 | 1.517E-03 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 770 | H4SiO4 | 9.779E-05 | .0 | 0.000E+00 | .0 | 2.004E-01 | 100.0 |
| 140 | CO3-2 | 8.725E-03 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 30 | Al+3 | 1.971E-09 | .0 | 0.000E+00 | .0 | 2.000E-01 | 100.0 |
| 2 | H2O | 1.679E-07 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |

```
0   Charge Balance: SPECIATED
0     Sum of CATIONS =  9.203E-08 Sum of ANIONS   3.695E-02
0       PERCENT DIFFERENCE =    1.000E+02   (ANIONS - CATIONS)/(ANIONS +
CATIONS)
0   EQUILIBRIUM IONIC STRENGTH (m) =   4.308E-02
0   EQUILIBRIUM pH                 =   7.122

 ******* DIFFUSE LAYER ADSORPTION MODEL ********
  **** Parameters For Adsorbent Number 1 ****
  Electrostatic Variables:  psi0 =  .015520     sig0 =  .007472
                            psib =  .000000     sigb =  .000000
                            psid =  .000000     sigd =  .000000
  Adsorbent Concentration (g/l):  25.740
  Specific Surface Area (sq. meters/g):   55.00

  **** Parameters For Adsorbent Number 2 ****
  Electrostatic Variables:  psi0 = -.034686     sig0 = -.017725
                            psib =  .000000     sigb =  .000000
                            psid =  .000000     sigd =  .000000
  Adsorbent Concentration (g/l):  11.870
  Specific Surface Area (sq. meters/g):   15.00
   1
```

## PART 6 of OUTPUT FILE

```
 DATE OF CALCULATIONS:  9-APR-96  TIME: 20: 6:44
0Saturation indices and stoichiometry of all minerals
  ID #    NAME      Sat. Index      Stoichiometry in [brackets]
  2003000 ALOH3(A)      -3.511   [ 1.000]  30 [ 3.000]   2 [ -3.000] 330
  5015000 ARAGONITE      -6.896   [ 1.000] 150 [ 1.000] 140
  2003001 BOEHMITE      -1.709   [ -3.000] 330 [ 1.000]  30 [ 2.000]   2
  5015001 CALCITE       -6.757   [ 1.000] 150 [ 1.000] 140
  2077000 CHALCEDONY     -.483   [ -2.000]   2 [ 1.000] 770
  2077001 CRISTOBALITE   -.419   [ -2.000]   2 [ 1.000] 770
  2003002 DIASPORE       -.004   [ -3.000] 330 [ 1.000]  30 [ 2.000]   2
  2003003 GIBBSITE (C)  -1.901   [ -3.000] 330 [ 1.000]  30 [ 3.000]   2
  3003000 Al2O3         -9.242   [ 2.000]  30 [ 3.000]   2 [ -6.000] 330
  2077002 QUARTZ          .000   [ -2.000]   2 [ 1.000] 770
  2077003 SIO2(A,GL)     -.988   [ -2.000]   2 [ 1.000] 770
  2077004 SIO2(A,PT)    -1.296   [ -2.000]   2 [ 1.000] 770
  5060000 CERRUSITE     -7.823   [ 1.000] 600 [ 1.000] 140
  2060000 MASSICOT     -14.213   [ -2.000] 330 [ 1.000] 600 [ 1.000]   2
  2060001 LITHARGE     -14.023   [ -2.000] 330 [ 1.000] 600 [ 1.000]   2
  2060002 PBO, .3H2O   -14.283   [ -2.000] 330 [ 1.000] 600 [ 1.330]   2
  5060001 PB2OCO3      -21.756   [ -2.000] 330 [ 2.000] 600 [ 1.000]   2
                        [ 1.000] 140
  5060002 PB3O2CO3     -34.579   [ -4.000] 330 [ 3.000] 600 [ 1.000] 140
                        [ 2.000]   2
  8260000 PBSIO3       -12.629   [ -1.000]   2 [ -2.000] 330 [ 1.000] 600
                        [ 1.000] 770
  8060000 PB2SIO4      -26.372   [ -4.000] 330 [ 2.000] 600 [ 1.000] 770
  2060004 PB(OH)2 (C)   -9.453   [ -2.000] 330 [ 1.000] 600 [ 2.000]   2
  5060003 HYDCERRUSITE -25.749   [ -2.000] 330 [ 3.000] 600 [ 2.000] 140
                        [ 2.000]   2
  2060005 PB2O(OH)2    -28.806   [ -4.000] 330 [ 2.000] 600 [ 3.000]   2
  8603000 HALLOYSITE    -3.268   [ 2.000]  30 [ 2.000] 770 [ 1.000]   2
                        [ -6.000] 330
  8603001 KAOLINITE       .000   [ 2.000]  30 [ 2.000] 770 [ 1.000]   2
                        [ -6.000] 330
  8415000 LEONHARDITE  -12.226   [ -1.000]   2 [-16.000] 330 [ 2.000] 150
                        [ 8.000] 770 [ 4.000]  30
  8415001 ANORTHITE    -15.286   [ 1.000] 150 [ 2.000]  30 [ 2.000] 770
                        [ -8.000] 330
  8603002 PYROPHYLLITE   -.688   [ 2.000]  30 [ 4.000] 770 [ -4.000]   2
                        [ -6.000] 330
  8415003 WAIRAKITE    -16.738   [ 1.000] 150 [ 2.000]  30 [ 4.000] 770
                        [ -8.000] 330 [ -2.000]   2
```

```
2015000 LIME         -28.379   [ -2.000] 330 [  1.000] 150 [  1.000]  2
2015001 PORTLANDITE  -18.257   [ -2.000] 330 [  1.000] 150 [  2.000]  2
8215002 WOLLASTONITE -12.584   [ -1.000]  2 [ -2.000] 330 [  1.000] 770
                        [  1.000] 150
```

## E3 Desorption Test

### E.3.2 Output of Column Leaching Desorption Tests for Lead Contaminated KC Soil at the Last Node after 7 Pore Volumes Using Sodium Acetate

**Table E28** **Type I** Components as Species in Solution at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTVTY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 330 | H+1 | 5.794E-07 | 5.292E-07 | -6.27640 | .91324 | .039 |
| 492 | NO3-1 | 2.000E-03 | 1.826E-03 | -2.73839 | .91324 | .039 |
| 600 | Pb+2 | 1.688E-07 | 1.174E-07 | -6.93032 | .69557 | .158 |
| 500 | Na+1 | 9.808E-04 | 8.957E-04 | -3.04785 | .91324 | .039 |
| 150 | Ca+2 | 4.689E-04 | 3.261E-04 | -3.48662 | .69557 | .158 |
| 770 | H4SiO4 | 9.752E-05 | 9.769E-05 | -4.01016 | 1.00169 | -.001 |
| 140 | CO3-2 | 1.136E-08 | 7.901E-09 | -8.10230 | .69557 | .158 |
| 30 | Al+3 | 2.505E-12 | 1.107E-12 | -11.95599 | .44185 | .355 |
| 821 | ADS2TYP1 | 2.913E-02 | 2.913E-02 | -1.53564 | 1.00000 | .000 |
| 811 | ADS1TYP1 | 1.100E-02 | 1.100E-02 | -1.95848 | 1.00000 | .000 |
| 992 | Acetate | 9.677E-03 | 8.837E-03 | -2.05368 | .91324 | .039 |

**Table E29- Type II** Other Species in Solution or Adsorbed at the Last Node after 7 Pore Volumes.

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTVTY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 8216002 | =2SOPbOH | 4.943E-07 | 4.943E-07 | -6.30599 | 1.00000 | -9.970 |
| 5009920 | NaACETATE | 5.221E-06 | 5.230E-06 | -5.28152 | 1.00169 | -.181 |
| 1509920 | CaACETATE | 4.777E-05 | 4.362E-05 | -4.36029 | .91324 | 1.219 |
| 3300020 | OH- | 2.078E-08 | 1.898E-08 | -7.72170 | .91324 | -13.959 |
| 3307700 | H3SiO4 - | 2.382E-08 | 2.175E-08 | -7.66254 | .91324 | -9.889 |
| 3307701 | H2SiO4 -2 | 1.213E-13 | 8.434E-14 | -13.07397 | .69557 | -21.459 |
| 1503300 | CaOH + | 1.703E-10 | 1.555E-10 | -9.80832 | .91324 | -12.559 |
| 1501400 | CaHCO3 + | 3.305E-07 | 3.018E-07 | -6.52023 | .91324 | 11.385 |
| 1501401 | CaCO3 AQ | 3.656E-09 | 3.662E-09 | -8.43631 | 1.00169 | 3.152 |
| 5001400 | NaCO3 - | 1.436E-10 | 1.312E-10 | -9.88215 | .91324 | 1.307 |
| 5001401 | NaHCO3 AQ | 4.495E-08 | 4.502E-08 | -7.34655 | 1.00169 | 10.079 |
| 303300 | AlOH +2 | 3.076E-11 | 2.139E-11 | -10.66970 | .69557 | -4.832 |
| 303301 | Al(OH)2 + | 3.436E-10 | 3.138E-10 | -9.50340 | .91324 | -10.061 |
| 303302 | Al(OH)4 - | 1.544E-10 | 1.410E-10 | -9.85081 | .91324 | -22.961 |
| 303303 | Al(OH)3 AQ | 7.450E-10 | 7.463E-10 | -9.12711 | 1.00169 | -16.001 |
| 6001400 | Pb(CO3)2-2 | 4.600E-13 | 3.199E-13 | -12.49492 | .69557 | 10.798 |
| 6003300 | PbOH + | 4.736E-09 | 4.325E-09 | -8.36402 | .91324 | -7.671 |
| 6003301 | Pb(OH)2 AQ | 3.174E-12 | 3.179E-12 | -11.49773 | 1.00169 | -17.121 |
| 6003302 | Pb(OH)3 - | 7.551E-17 | 6.896E-17 | -16.16143 | .91324 | -28.021 |
| 6003303 | Pb2OH +3 | 2.573E-14 | 1.137E-14 | -13.94434 | .44185 | -6.005 |
| 6004920 | PbNO3 + | 3.473E-09 | 3.172E-09 | -8.49871 | .91324 | 1.209 |
| 6003304 | Pb3(OH)4+2 | 3.907E-20 | 2.718E-20 | -19.56577 | .69557 | -23.722 |
| 6001401 | PbCO3 AQ | 1.609E-08 | 1.612E-08 | -7.79262 | 1.00169 | 7.239 |

| ID | NAME | CALC MOL | ACTIVITY | LOG ACTVTY | GAMMA | NEW LOGK |
|---|---|---|---|---|---|---|
| 6003305 | Pb(OH)4 -2 | 4.301E-22 | 2.991E-22 | -21.52413 | .69557 | -39.541 |
| 6001402 | PbHCO3 + | 8.519E-09 | 7.780E-09 | -8.10902 | .91324 | 13.239 |
| 3301400 | HCO3 - | 9.779E-05 | 8.930E-05 | -4.04914 | .91324 | 10.369 |
| 3301401 | H2CO3 AQ | 1.060E-04 | 1.061E-04 | -3.97411 | 1.00169 | 16.680 |
| 3309921 | H ACETATE | 2.687E-04 | 2.691E-04 | -3.57008 | 1.00169 | 4.759 |
| 6009921 | PBACETATE | 8.422E-07 | 7.691E-07 | -6.11399 | .91324 | 2.909 |
| 6009922 | PBACETATE | 1.101E-07 | 1.102E-07 | -6.95767 | 1.00169 | 4.079 |
| 6009923 | PBACETATE3 | 3.452E-10 | 3.152E-10 | -9.50135 | .91324 | 3.629 |
| 6009924 | PBACETATE4 | 2.586E-12 | 1.799E-12 | -11.74502 | .69557 | 3.558 |
| 8113300 | =1SO- | 3.280E-02 | 3.280E-02 | -1.48410 | 1.00000 | -6.910 |
| 8113302 | =1SOH | 3.290E-02 | 3.290E-02 | -1.48285 | 1.00000 | 7.860 |
| 8116000 | =1SOpb+ | 2.868E-12 | 2.868E-12 | -11.54239 | 1.00000 | -8.930 |
| 8115000 | =1SOna | 1.381E-07 | 1.381E-07 | -6.85992 | 1.00000 | -8.130 |
| 8116002 | =SOPbOH | 4.943E-07 | 4.943E-07 | -6.30599 | 1.00000 | -9.970 |
| 8213300 | =2SO- | 1.228E-02 | 1.228E-02 | -1.91073 | 1.00000 | -6.910 |
| 8213302 | =2SOH | 1.229E-02 | 1.229E-02 | -1.91055 | 1.00000 | 6.160 |
| 8215000 | =2SONa | 1.381E-05 | 1.381E-05 | -4.85992 | 1.00000 | -6.130 |
| 8216000 | =2SOPb+ | 5.420E-06 | 5.420E-06 | -5.26599 | 1.00000 | -8.930 |

**Table E 30- Type III - Species with Fixed Activity at the Last Node after 7 Pore Volumes**

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2 | H2O | 1.665E-04 | -3.779 | .000 | .000 |
| 3301403 | CO2 (g) | 3.128E-04 | -3.505 | 20.655 | -.530 |

**Table E31**- Type IV - Finite Solids (present at equilibrium) at the Last Node after 7 Pore Volumes

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8603001 | KAOLINITE | 9.995E-02 | -4.312 | -5.726 | 35.280 |
| 2003002 | DIASPORE | 9.755E-05 | -4.011 | -6.873 | 24.630 |

**Table E 32- Type V** - UNDERSATURATED SOLIDS (not present at equilibrium)

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 2077002 | QUARTZ | 9.910E-01 | -.004 | 4.006 | -6.220 |
| 2077003 | SIO2(A,GL) | 1.019E-01 | -.992 | 3.018 | -4.440 |
| 2077004 | SIO2(A,PT) | 5.012E-02 | -1.300 | 2.710 | -3.910 |
| 5050001 | THERMONATR | 4.752E-15 | -14.323 | -.125 | 2.802 |
| 5060000 | CERRUSITE | 1.251E-02 | -1.903 | 13.130 | -4.860 |
| 2060000 | MASSICOT | 5.157E-08 | -7.288 | -12.910 | 16.780 |
| 2060001 | LITHARGE | 7.987E-08 | -7.098 | -12.720 | 16.380 |
| 2060002 | PBO, .3H2O | 4.389E-08 | -7.358 | -12.980 | .000 |
| 5060001 | PB2OCO3 | 1.230E-09 | -8.910 | .500 | 11.460 |
| 5060002 | PB3O2CO3 | 1.556E-15 | -14.808 | -11.020 | 26.430 |
| 8260000 | PBSIO3 | 1.961E-06 | -5.708 | -7.320 | 9.260 |
| 8060000 | PB2SIO4 | 2.984E-13 | -12.525 | -19.760 | 26.000 |
| 2060004 | PB(OH)2 (C) | 2.967E-03 | -2.528 | -8.150 | 13.990 |
| 5060003 | HYDCERRUSITE | 1.040E-07 | -6.983 | 17.460 | .000 |
| 2060005 | PB2O(OH)2 | 1.108E-15 | -14.955 | -26.200 | .000 |
| 8450001 | ANALCIME | 2.304E-05 | -4.637 | -6.719 | 22.840 |
| 8603000 | HALLOYSITE | 5.395E-04 | -3.268 | -8.994 | 39.730 |
| 5015000 | ARAGONITE | 5.586E-04 | -3.253 | 8.336 | 2.615 |
| 8415000 | LEONHARDITE | 1.133E-03 | -2.946 | -16.490 | 85.360 |

| ID | NAME | CALC MOL | LOG MOL | NEW LOGK | DH |
|---|---|---|---|---|---|
| 8450002 | LOW ALBITE | 3.018E-05 | -4.520 | -2.592 | 17.400 |
| 8450003 | ANALBITE | 3.679E-06 | -5.434 | -3.506 | 20.000 |
| 8415001 | ANORTHITE | 2.303E-11 | -10.638 | -25.430 | 70.660 |
| 8603002 | PYROPHYLLITE | 2.015E-01 | -.696 | 1.598 | .000 |
| 8415002 | LAUMONTITE | 2.051E-08 | -7.688 | -14.460 | 50.450 |
| 8415003 | WAIRAKITE | 7.983E-13 | -12.098 | -18.870 | 63.150 |
| 2015000 | LIME | 1.858E-24 | -23.731 | -32.797 | 46.265 |
| 2015001 | PORTLANDITE | 2.460E-14 | -13.609 | -22.675 | 30.690 |
| 8215002 | WOLLASTONITE | 1.149E-08 | -7.940 | -12.996 | 19.498 |
| 8215003 | P-WOLLSTANIT | 1.622E-09 | -8.790 | -13.846 | 21.068 |
| 8015001 | CA-OLIVINE | 2.973E-24 | -23.527 | -37.649 | 54.695 |
| 8015002 | LARNITE | 9.577E-26 | -25.019 | -39.141 | 57.238 |
| 8015007 | CA3SIO5 | 0.000E+00 | -50.679 | -73.867 | 106.335 |
| 8450004 | NEPHELINE | 7.475E-09 | -8.126 | -14.218 | 33.204 |
| 8015006 | GEHLENITE | 1.113E-29 | -28.954 | -56.822 | 116.125 |
| 2003000 | ALOH3(A) | 3.111E-04 | -3.507 | -10.380 | 27.045 |
| 2003001 | BOEHMITE | 1.972E-02 | -1.705 | -8.578 | 28.130 |
| 2077000 | CHALCEDONY | 3.259E-01 | -.487 | 3.523 | -4.615 |
| 2077001 | CRISTOBALITE | 3.776E-01 | -.423 | 3.587 | -5.500 |
| 5015001 | CALCITE | 7.691E-04 | -3.114 | 8.475 | 2.585 |
| 2003003 | GIBBSITE © | 1.267E-02 | -1.897 | -8.770 | 22.800 |
| 3003000 | Al2O3 | 5.836E-10 | -9.234 | -22.980 | .000 |
| 8450000 | MAGADIITE | 2.873E-11 | -10.542 | 14.300 | .000 |
| 3050000 | NATRON | 1.294E-13 | -12.888 | 1.311 | -15.745 |

```
Type VI - EXCLUDED SPECIES (not included in mole balance)
  ID      NAME        CALC MOL      LOG MOL   NEW LOGK    DH
   823  ADS2PSIo    5.514E-01      -.259          .000     .000
   813  ADS1PSIo    7.799E-02     -1.108          .000     .000
________________________________________________________________

         PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
        TYPE I and TYPE II (dissolved and adsorbed) species

 +H+1
+          15.0    PERCENT BOUND IN SPECIES #3301400   HCO3 -

+          32.5    PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+          41.2    PERCENT BOUND IN SPECIES #3309921   H ACETATE

+         >1000.    PERCENT BOUND IN SPECIES #8113302   =1SOH

+         >1000.    PERCENT BOUND IN SPECIES #8213302   =2SOH

 +NO3-1
+         100.0    PERCENT BOUND IN SPECIES #    492   NO3-1

 +Pb+2
+           2.2    PERCENT BOUND IN SPECIES #    600   Pb+2

+           6.5    PERCENT BOUND IN SPECIES #8216002   =2SOPbOH

+          11.1    PERCENT BOUND IN SPECIES #6009921   PBACETATE

+           1.5    PERCENT BOUND IN SPECIES #6009922   PBACETATE2

+           6.5    PERCENT BOUND IN SPECIES #8116002   =SOPbOH

+          71.7    PERCENT BOUND IN SPECIES #8216000   =2SOpb+

 +Na+1
+          98.1    PERCENT BOUND IN SPECIES #    500   Na+1

+           1.4    PERCENT BOUND IN SPECIES #8215000   =2SOna

 +ADS2PSIo
+         >1000.    PERCENT BOUND IN SPECIES #8213302   =2SOH

 +Ca+2
+          90.7    PERCENT BOUND IN SPECIES #    150   Ca+2
```

```
+          9.2    PERCENT BOUND IN SPECIES #1509920   CaACETATE


+ADS1PSIo
+        >1000.   PERCENT BOUND IN SPECIES #8113302   =1SOH


+Acetate
+         96.8    PERCENT BOUND IN SPECIES #    992   Acetate

+          2.7    PERCENT BOUND IN SPECIES #3309921   H ACETATE

+ADS2TYP1
+         54.2    PERCENT BOUND IN SPECIES #    821   ADS2TYP1

+         22.9    PERCENT BOUND IN SPECIES #8213300   =2SO-

+         22.9    PERCENT BOUND IN SPECIES #8213302   =2SOH

+ADS1TYP1
+         14.3    PERCENT BOUND IN SPECIES #    811   ADS1TYP1

+         42.8    PERCENT BOUND IN SPECIES #8113300   =1SO-

+         42.9    PERCENT BOUND IN SPECIES #8113302   =1SOH

+H4SiO4
+        100.0    PERCENT BOUND IN SPECIES #    770   H4SiO4

+CO3-2
+         47.9    PERCENT BOUND IN SPECIES #3301400   HCO3 -

+         51.9    PERCENT BOUND IN SPECIES #3301401   H2CO3 AQ

+H2O
+         71.0    PERCENT BOUND IN SPECIES #3300020   OH-

+          2.3    PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

+          2.1    PERCENT BOUND IN SPECIES # 303302   Al(OH)4 -

+          7.6    PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

+         16.2    PERCENT BOUND IN SPECIES #6003300   PbOH +
```

```
+Al+3
+          2.4    PERCENT BOUND IN SPECIES # 303300   AlOH +2

+          26.9    PERCENT BOUND IN SPECIES # 303301   Al(OH)2 +

+          12.1    PERCENT BOUND IN SPECIES # 303302   Al(OH)4 -

+          58.4    PERCENT BOUND IN SPECIES # 303303   Al(OH)3 AQ

____________________________ PART 5 of OUTPUT FILE _________________________
 DATE OF CALCULATIONS: 29-APR-96  TIME: 16:46:10
```

**Table E33** Equilibrated Mass Distribution at the Last Node after 7 Pore Volumes

| IDX | NAME | DISSOLVED | | SORBED | | PRECIPITATED | |
|---|---|---|---|---|---|---|---|
| | | MOL/KG | PERCENT | MOL/KG | PERCENT | MOL/KG | PERCENT |
| 330 | H+1 | 5.793E-04 | 88.9 | 7.244E-05 | 11.1 | 0.000E+00 | .0 |
| 492 | NO3-1 | 2.000E-03 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 600 | Pb+2 | 1.154E-06 | 15.3 | 6.409E-06 | 84.7 | 0.000E+00 | .0 |
| 500 | Na+1 | 9.860E-04 | 98.6 | 1.394E-05 | 1.4 | 0.000E+00 | .0 |
| 150 | Ca+2 | 5.170E-04 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 992 | Acetate | 1.000E-02 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 770 | H4SiO4 | 9.755E-05 | .0 | 0.000E+00 | .0 | 1.999E-01 | 100.0 |
| 140 | CO3-2 | 2.042E-04 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 2 | H2O | 2.927E-08 | 100.0 | 0.000E+00 | .0 | 0.000E+00 | .0 |
| 30 | Al+3 | 1.276E-09 | .0 | 0.000E+00 | .0 | .000E-01 | 100.0 |

```
   Charge Balance: SPECIATED
0     Sum of CATIONS =  1.968E-03 Sum of ANIONS   1.177E-02
0       PERCENT DIFFERENCE =   7.135E+01  (ANIONS - CATIONS)/(ANIONS +
CATIONS)
0    EQUILIBRIUM IONIC STRENGTH (m) =  7.341E-03
0    EQUILIBRIUM pH              =  6.276
```

```
 ******* DIFFUSE LAYER ADSORPTION MODEL ********

  **** Parameters For Adsorbent Number 1 ****
   Electrostatic Variables:  psi0 =  .065545    sig0 =  .016603
                       psib =  .000000    sigb =  .000000
                       psid =  .000000    sigd =  .000000
   Adsorbent Concentration (g/l):  15.740
   Specific Surface Area (sq. meters/g):   35.00

  **** Parameters For Adsorbent Number 2 ****
   Electrostatic Variables:  psi0 =  .015292    sig0 =  .003038
                       psib =  .000000    sigb =  .000000
                       psid =  .000000    sigd =  .000000
   Adsorbent Concentration (g/l):  11.870
   Specific Surface Area (sq. meters/g):  15.00
0    DATE ID NUMBER:          960429
     TIME ID NUMBER:       16461097
     ACCESSORY OUTPUT FILE: n
______________________________ PART 6 of OUTPUT FILE ______________________________
 DATE OF CALCULATIONS: 29-APR-96  TIME: 16:46:10

0Saturation indices and stoichiometry of all minerals
0   ID #    NAME      Sat. Index      Stoichiometry in [brackets]
  2003000 ALOH3(A)      -3.507   [  1.000]  30  [  3.000]   2  [ -3.000] 330
  5015000 ARAGONITE      -3.253   [  1.000] 150  [  1.000] 140
  2003001 BOEHMITE      -1.705   [ -3.000] 330  [  1.000]  30  [  2.000]   2
  5015001 CALCITE       -3.114   [  1.000] 150  [  1.000] 140
  2077000 CHALCEDONY      -.487   [ -2.000]   2  [  1.000] 770
  2077001 CRISTOBALITE   -.423   [ -2.000]   2  [  1.000] 770
  2003002 DIASPORE         .000   [ -3.000] 330  [  1.000]  30  [  2.000]   2
  2003003 GIBBSITE (C)  -1.897   [ -3.000] 330  [  1.000]  30  [  3.000]   2
  3003000 Al2O3         -9.234   [  2.000]  30  [  3.000]   2  [ -6.000] 330
  8450000 MAGADIITE    -10.542   [ -1.000] 330  [ -9.000]   2  [  1.000] 500
                       [  7.000] 770
  3050000 NATRON       -12.888   [  2.000] 500  [  1.000] 140  [ 10.000]   2
  2077002 QUARTZ         -.004   [ -2.000]   2  [  1.000] 770
  2077003 SIO2(A,GL)     -.992   [ -2.000]   2  [  1.000] 770
  2077004 SIO2(A,PT)    -1.300   [ -2.000]   2  [  1.000] 770
  5050001 THERMONATR   -14.323   [  2.000] 500  [  1.000] 140  [  1.000]   2
  5060000 CERRUSITE     -1.903   [  1.000] 600  [  1.000] 140
  2060000 MASSICOT      -7.288   [ -2.000] 330  [  1.000] 600  [  1.000]   2
  2060001 LITHARGE      -7.098   [ -2.000] 330  [  1.000] 600  [  1.000]   2
  2060002 PBO, .3H2O    -7.358   [ -2.000] 330  [  1.000] 600  [  1.330]   2
  5060001 PB2OCO3       -8.910   [ -2.000] 330  [  2.000] 600  [  1.000]   2
                       [  1.000] 140
```

```
5060002 PB3O2CO3     -14.808   [ -4.000] 330 [  3.000] 600 [  1.000] 140
                     [  2.000]   2
8260000 PBSIO3        -5.708   [ -1.000]   2 [ -2.000] 330 [  1.000] 600
                     [  1.000] 770
8060000 PB2SIO4      -12.525   [ -4.000] 330 [  2.000] 600 [  1.000] 770
2060004 PB(OH)2 (C)   -2.528   [ -2.000] 330 [  1.000] 600 [  2.000]   2
5060003 HYDCERRUSITE  -6.983   [ -2.000] 330 [  3.000] 600 [  2.000] 140
                     [  2.000]   2
2060005 PB2O(OH)2    -14.955   [ -4.000] 330 [  2.000] 600 [  3.000]   2
8450001 ANALCIME      -4.637   [  1.000] 500 [  1.000]  30 [  2.000] 770
                     [ -1.000]   2 [ -4.000] 330
8603000 HALLOYSITE    -3.268   [  2.000]  30 [  2.000] 770 [  1.000]   2
                     [ -6.000] 330
8603001 KAOLINITE       .000   [  2.000]  30 [  2.000] 770 [  1.000]   2
                     [ -6.000] 330
8415000 LEONHARDITE   -2.946   [ -1.000]   2 [-16.000] 330 [  2.000] 150
                     [  8.000] 770 [  4.000]  30
8450002 LOW ALBITE    -4.520   [  1.000] 500 [  1.000]  30 [  3.000] 770
                     [ -4.000] 330 [ -4.000]   2
8450003 ANALBITE      -5.434   [  1.000] 500 [  1.000]  30 [  3.000] 770
                     [ -4.000] 330 [ -4.000]   2

0  ID #    NAME      Sat. Index     Stoichiometry in [brackets]
8415001 ANORTHITE    -10.638   [  1.000] 150 [  2.000]  30 [  2.000] 770
                     [ -8.000] 330
8603002 PYROPHYLLITE   -.696   [  2.000]  30 [  4.000] 770 [ -4.000]   2
                     [ -6.000] 330
8415003 WAIRAKITE    -12.098   [  1.000] 150 [  2.000]  30 [  4.000] 770
                     [ -8.000] 330 [ -2.000]   2
2015000 LIME         -23.731   [ -2.000] 330 [  1.000] 150 [  1.000]   2
2015001 PORTLANDITE  -13.609   [ -2.000] 330 [  1.000] 150 [  2.000]   2
8215002 WOLLASTONITE  -7.940   [ -1.000]   2 [ -2.000] 330 [  1.000] 770
                     [  1.000] 150
8215003 P-WOLLSTANIT  -8.790   [ -1.000]   2 [ -2.000] 330 [  1.000] 770
                     [  1.000] 150
8015001 CA-OLIVINE   -23.527   [ -4.000] 330 [  1.000] 770 [  2.000] 150
8015002 LARNITE      -25.019   [ -4.000] 330 [  1.000] 770 [  2.000] 150
8015007 CA3SIO5      -50.679   [ -6.000] 330 [  1.000] 770 [  3.000] 150
                     [  1.000]   2
8450004 NEPHELINE     -8.126   [ -4.000] 330 [  1.000] 770 [  1.000]  30
                     [  1.000] 500
8015006 GEHLENITE    -28.954   [-10.000] 330 [  2.000]  30 [  1.000] 770
                     [  2.000] 150 [  3.000]   2
```

# Appendix F

## Program Listing of the COSTCHESP

```
                                 ****************************
C                                *                          *
C                                *       CHESP.INC          *
C                                *                          *
C                                *     for Version 2.01     *
C                                *  Release date  06/01/95  *
C                                *     for VAX  and PC      *
C                                ****************************
C
c
c
c             Explanation of variables and parameters in CHESP.INC
c             -------------------------------------------------------
c
c
c
c                                ***************************
c     CHESP variables occurring in type declaration statements are
c     defined below.  Those variables not appearing in a type
c     declaration statement are typed implicitly in accord with the
c     usual first letter in name rules.  Explanations for these
c     variables are given following the explicitly typed variables.
c
c
c
c*** REAL*8 EPS
c
c      EPS -      The convergence criteria expressed as a fraction of
c                 the input total dissolved concentration for each
c                 component.  EPS = 1e-3 means that for each component,
c                 the convergence criteria is one thousandths part of
c                 the input total.  Set by parameter statement in
c                 CHESP.INC.
c
c
c*** INTEGER NXDIM, NYDIM
c
c      NXDIM -    The maximum number of components and the dimension
c                 of several arrays.  The value used for NXDIM has
c                 a great impact on the size of the executable image.
```

```
c                Set by parameter statement in CHESP.INC.
c      NYDIM -   The maximum number of species and the dimension of
c                several arrays.  The value used for NXDIM has
c                a great impact on the size of the executable image.
c                Set by parameter statement in CHESP.INC.
c
c*** CHARACTER FLAG*5, DISPYN*1, XSTOP*1, UNITS*5, NAME*12, FIL123*12
c
c      FLAG -    Indicates the units of concentration; read from
c                input file.
c      DISPYN -  Yes/no flag indicating whether the status messages
c                are to be displayed on screen during execution.
c
c      XSTOP -   Stop execution flag set to N at beginning of
c                problem(s) and to Y after last problem is completed.
c                Also re-set as appropriate when an error occurs
c                depending the nature of the error (should the next
c                problem be attempted or not, etc.).
c
c      UNITS -   Storage variable to save the initial concentration
c                units for later use in converting each successive
c                total concentration value of a titration to molal.
c
c      NAME -    An array of NYDIM elements containing species names.
c                Read from the thermodynamic database files.
c
c      FIL123 -  Name of the output file to which equilibrated
c                totals are to be written in format suitable for
c                spreadsheet import for component id's in array
c                ID123 and for H+ and E- if present.
c
c
c*** INTEGER CORALK, ISWEEP, NPROB, IPROB, MPROB, N123, ID123,
c            IDTIME, IDDATE
c
c      CORALK -  Flag read from the input file indicating whether
c                the entry for component 140 is to be considered as
c                a measure of alkalinity or as total dissolved
c                inorganic carbon expressed as CO3-2 total
c                concentration.
c
c      ISWEEP -  Flag indicating whether this run is a sweep, i.e.,
c                a titration over the total concentration or
c                activity of some component (ISWEEP > 0).  A value
c                1 indicates the titration points are specified in
c                the input file as a starting value and increment.
c                A value of 2 indicates the titration points are
c                specified explicitly.
c
c      NPROB -   The total number number of points in the sweep or
c                titration including the first and last points.
c
c      IPROB -   The titration point number.  Ranges from 1 to NPROB.
c
c      MPROB -   The problem number of a multi-problem set.  Each
c                problem of such a set may itself be a sweep
c                (titration).
c
```

```
c      N123 -     The number of components (not counting H+ or E-)
c                 whose equilibrated mass distributions are to be
c                 written to file FIL123 for later import by a
c                 spreadsheet program.  Read from the input file.
c
c      ID123 -    An array of 3 elements that stores the id #'s of
c                 the N123 components to be written to FIL123.
c
c      IDTIME -   A number constructed from the time in subroutine
c                 TSTAMP and used as a portion of the run id number
c                 written in the main output file (MINOUT.OUT) and
c                 in FIL123.
c
c      IDDATE -   A number constructed from the date in subroutine
c                 TSTAMP and used as a portion of the run id number
c                 written in the main output file (MINOUT.OUT) and
c                 in FIL123.
c
c
c
c*** INTEGER*2 JMAX, JPTA, IMAX, IPTA
c
c      JMAX(i) -  Stores the number of non-zero elements of
c                 stoichiometry arrays A and B in species i.
c                 That is, the number of components in which species
c                 i has non-zero stoichiometry.
c
c      JPTA(i,j)- Stores the column number address of the jth
c                 component which has non-zero stoichiometry
c                 in species i.
c
c      IMAX(j) -  Stores the number of non-zero elements of
c                 stoichiometry arrays A and B in component j.
c                 That is, the number of species in which component
c                 j has non-zero stoichiometry.
c
c      IPTA(j,i)- Stores the row number address of the ith species
c                 which has non-zero stoichiometry in component j.
c
c
c
c**** REAL*8 A, B, AA, BB, C, CAP1, CAP2, DENS, DH, EE, FCC, FIONS, GC,
c            GK, GX, MU, MUHALF, NONCRB, PSI0, PSIB, PSID, R, RJ,
c            SOLCON, SSA, T, TEMP, TEMPK, TIS, VH, VHC, ALKFCT,
c            DHA, DHB, GAMMA, GFW, MAXGK, MINGK, SPCZ, X, Y, Z,
c            SIGO, SIGB, SIGD, UVALUE, CPPM, SOILKG
c
c      A -        An array of NYDIM rows and NXDIM columns containing
c                 the stoichiometry of component j in species i (A(i,j))
c                 as used in mass action expressions.  Read from the
c                 thermodynamic database files.
c      B -        An array of NYDIM rows and NXDIM columns containing
c                 the stoichiometry of component j in species i
c                 (B(i,j)) as used in mass balance expressions.  For
c                 most species, A(i,j) = B(i,j) but this is not
c                 necessarily true.
c      AA -       A variable in the "modified" Extended Debye-Huckel
c                 and the Davies equations.  Almost constant at
```

```
c                 AA = 0.51 except for small temperature effects.
c                 Calculated at the chosen temp in Subroutine PREP.
c      BB -       A variable in the "modified" Extended Debye-Huckel
c                 equation.  Almost constant constant at BB = 0.3 except
c                 for small temperature effects.  Calculated at the
c                 chosen temp in Subroutine PREP.
c      C -        An array of NYDIM elements containing the computed
c                 concentration in molal for all species.  Re-computed
c                 at each iteration.
c      CAP1 -     An array of 5 elememts containing the single
c                 capacitance term used in the Constant Capacitance
c                 adsorption model (CCM) or the inner layer capacitance
c                 of the Triple-Layer Model (TLM) for each of up to 5
c                 adsorbing surfaces.  Not used in the Diffuse-Layer
c                 Model (DLM).
c      CAP2 -     An array of 5 elements containing the outer layer
c                 capacitance of up to 5 adsorbing surfaces.  Pertains
c                 to the TLM only.
c      DENS -     The density of water; assigned 1.0.
c      DH -       An array of NYDIM elements containing the enthalpy
c                 of reaction for each species. Read from the
c                 thermodynamic database.
c      EE -       A constant in the electrostatic adsorption models.
c      FCC -      Faraday's constant.
c      FIONS -    Fixed ionic strength; read from input file.
c      GC -       An array of NYDIM elements containing the common log
c                 of the concentration c(i) of each species i.
c      GK -       An array of NYDIM elements containing the common log
c                 of the equilibrium constants.  Read from the
c                 thermodynamic database.
c      GX -       An array of NXDIM elements containing the common log
c                 of free component activities.
c      MU -       The computed ionic strength.
c      MUHALF -   The square root of the computed ionic strength.
c      NONCRB -   The computed non-carbonate alkalinity.
c      PSI0 -     An array of 5 elements containing the surface
c                 potential in the "zero layer" for each of up to 5
c                 adsorbing surfaces.  Pertains to the CCM, DLM, and
c                 TLM.
c      PSIB -     An array of 5 elements containing the surface
c                 potential in the "beta-layer" for each of up to 5
c                 adsorbing surfaces.  Pertains to the TLM only.
c      PSID -     An array of 5 elements containing the surface
c                 potential in the "d-layer" for each of up to 5
c                 adsorbing surfaces.  Pertains to the TLM only.
c      R -        The universal gas constant in kcal/(K mol).
c      RJ -       The universal gas constant in J/(K mol).
c      SOLCON -   An array of 5 elements containing the solid
c                 concentrations of up to 5 adsorbing surfaces in g/l.
c      SSA -      An array of 5 elements containing the specific
c                 surface area of up to 5 adsorbing surfaces in
c                 sq.meters/g.
c      T -        An array of NXDIM elements containing the analytical
c                 total dissolved input concentrations of each
c                 component.
c      TEMP -     Temperature in Celsius.
c      TEMPK -    Temperature in Kelvin.
c      TIS -      An upper limit for ionic strength calculated in
```

```
c                     Subroutine PREP.
c      VH -           A variable in the Van't Hoff equation.  Varies with
c                     temperature; calculated in Subroutine INPUT.
c      VHC -          A constant in the expression for VH.
c      ALKFCT -       An array of NYDIM elements containing the alkalinity
c                     factors of all species.  The alkalinity factor is zero
c                     for all solids.  For complexes it is equal to the
c                     number of equivalents of CO3-2 minus the number of
c                     equivalents of H+ produced upon dissociation of one
c                     mole of the complex.  Read from the thermodynamic
c                     database.
c      DHA -          An array of NYDIM elements containing the ion size
c                     parameters for use in the "modified" extended
c                     Debye-Huckel equation.
c      DHB -          An array of NYDIM elements containing solvent effects
c                     parameters for use in the "modified" extended
c                     Debye-Huckel equation.
c      GAMMA -        An array of NYDIM elements containing the common
c                     log of the activity coefficients for each species.
c      GFW -          An array of NYDIM elements containing the gram formula
c                     weight of each species.  Read from the thermodynamic
c                     database.
c      MAXGK -        An array of NYDIM elements containing the maximum
c                     reported common log of the equilibrium constant for
c                     each species.  Read from the thermodynamic database.
c                     Not used in calculations.
c      MINGK -        An array of NYDIM elements containing the minimum
c                     reported common log of the equilibrium constant for
c                     each species.  Read from the thermodynamic database.
c                     Not used in calculations.
c      SPCZ -         An array of NYDIM elements containing the charge of
c                     each species.  Read from the thermodynamic database.
c      X -            An array of NXDIM elements containing the computed
c                     activity of each free component species.  Re-computed
c                     at each iteration.
c      Y -            An array of NXDIM elements containing the computed
c                     mass imbalance of each component.  Re-computed at each
c                     iteration.  Upon return from Subroutine SIMQ, this
c                     array is used to store the computed change in
c                     component activities required to reduce the mass
c                     imbalance to zero.
c      Z -            A square two-dimensional array of NXDIM rows and
c                     columns containing the Jacobian elements, that is,
c                     the partial derivatives or gradients of Y with
c                     respect to the activity of each free component
c                     species.
c      SIGO -         An array of 5 elements containing the charge density
c                     in the "zero layer" pertaining to each of up to 5
c                     adsorbing surfaces in the electrostatic adsorption
c                     models (CCM,DLM,TLM).
c      SIGB -         An array of 5 elements containing the charge density
c                     in the "beta layer" pertaining to each of up to 5
c                     adsorbing surfaces in the electrostatic adsorption
c                     model (TLM only).
c      SIGD -         An array of 5 elements containing the charge density
c                     in the "d layer" pertaining to each of up to 5
c                     adsorbing surfaces in the electrostatic adsorption
c                     model (TLM only).
```

```
c
c      UVALUE -    An array of up to 24 elements used to store the
c                  total concentration or activity of successive
c                  titration points in a sweep.  Values are obtained
c                  from the input file or from the starting value and
c                  increment obtained from the input file.
c
c      CPPM -      The cumulative total concentration of all components
c                  expressed in ppm.  Used to convert ppm to molal,
c                  CPPM is computed in subroutine PREP and updated in
c                  subroutine NXTPRB as the total concentration of the
c                  sweep component is changed.
c
c     Variables not explicitly defined in type declarations but appearing
c     in common blocks:
c
c      ITMAX -     An upper limit on the number of iterations allowed.
c      ITER -      The current iteration number.
c      IADS -      Flag indicating the type of adsorption model to be
c                  used.  From input file.
c      NUMADS -    The number of adsorbing surfaces.  From input file.
c      NNN -       The total number of components (including H2O) in the
c                  problem.  Must be less than or equal to NXDIM.
c      IPRINT -    Flag indicating whether to allow oversaturated solids
c                  to precipitate and if so, the level of detail in the
c                  output file as each precipitates.  From input file.
c      IDEBUG -    Flag indicating whether to dump certain variable
c                  contents at each iteration for error analysis.
c                  From input file.
c      KOUNT -     A counter variable used for various purposes in
c                  Subroutine INPUT but most importantly, used to count
c                  the number of inserted species.  See IDYDUM below.
c      MAXSIZ -    A maximum exponent size used in Subroutine OUTPUT and
c                  perhaps in other routines.
c      ICHARG -    A flag indicating whether to terminate execution if
c                  charge imbalance exceeds 30%.  From input file.
c      NITER -     A flag indicating the value at which to set ITMAX
c                  (see above).  From input file.
c      ISOPT -     Flag indicating whether to compute ionic strength or
c                  fix it at the value specified by FIONS.  From input
c                  file.
c      IPRDCT -    Flag indicating whether to use an alternate method of
c                  computing the activity estimates for the next
c                  iteration.  Not accessible in Version 2.01 and not
c                  recommended.
c      IPHVRY -    A flag indicating whether to use a procedure to
c                  calculate the equilibrium pH of a solution containing
c                  an initial finite solid phase.  It ordinarily requires
c                  two runs to make this calculation and this built-in
c                  procedure is supposed to reduce this to one run.
c                  Unfortunately, it doesn't work.  If more info is
c                  required, see Technical Bulletin TB201a on CHESP
c                  available from CEAM.  This flag is read from the
c                  input file.
c      KKDAV -     Flag indicating whether to use the "modified" extended
c                  Debye-Huckel or the Davies equation for computing
c                  activity coefficients.  From input file.
c      KKTHR -     Flag indicating the desired level of detail pertaining
```

```
c                  to thermodynamic data in the output file.
c                  From input file.
c      LUNnn -     Logical unit assignments for I/O.  Most files are
c                  opened in CHESP.FOR so see that program for
c                  specifics.
c      MESSIN,
c      SCRNOUT -   More logical unit assignments.
c      M2 -        Array of 5 elements containing the address of the
c                  electrostatic component id number pertaining to the
c                  "d-layer" for up to 5 adsorbing surfaces in the TLM.
c      NN -        An array of 6 elements containing the total number of
c                  entities of each type in the problem.  For example,
c                  NN(1) = total number of species that are also
c                  components,  NN(2) = total number of aqueous
c                  complexes, NN(3) = total number of fixed species, etc.
c      IDX -       An array of NXDIM elements containing the three-digit
c                  component id numbers of all components in this
c                  problem.
c      IDY -       An array of NYDIM elements containing the the three
c                  and seven-digit id numbers of all species (including
c                  free components species).
c      IDYDUM -    A dummy array of 100 elements containing the id
c                  numbers of up to 100 inserted species.  This array is
c                  loaded from the input file and later passed to
c                  Subroutine IAP for checking against the solid species
c                  for duplication.  The number of entries in array
c                  IDYDUM is stored in KOUNT.
c
c ***********************************************************************
c
c                    P A R A M E T E R    S T A T E M E N T S
c
c
c------------------------------------------------------------------------
c     THE VAX AND PC IMPLEMENTATION OF THIS FILE ARE IDENTICAL
c     EXCEPT FOR THE PARAMETER STATEMENT SETTINGS OF NXDIM AND NYDIM.
c
c     Recommended settings are:
c
c      IBM PC (or compatible) -
c          with 512K RAM:         nxdim = 32, nydim = 400
c          with 640K RAM:         nxdim = 50, nydim = 600
c      VAX 11/785 -               nxdim = 50, nydim = 600
c
c     Settings for the VAX can be even larger if needed.
c
c
c     The version number is also assigned here in CHESP.INC via
c     a parameter statement.
c
C
c***********************************************************************
c
c                    P A R A M E T E R    S T A T E M E N T S
c
c
c------------------------------------------------------------------------
c     THE VAX AND PC IMPLEMENTATION OF THIS FILE ARE IDENTICAL
```

```
c     EXCEPT FOR THE PARAMETER STATEMENT SETTINGS OF NXDIM AND NYDIM.
c
c     Recommended settings are:
c
c      IBM PC (or compatible) -
c          with 512K RAM:         nxdim = 30, nydim = 400
c          with 640K RAM:         nxdim = 40, nydim = 500
c      VAX 11/785 -               nxdim = 50, nydim = 600
c
c     Settings for the VAX can be even larger if needed.
c
c
c
C -----------------------------------
C     List of variables for cost
c-----------------------------------
c     Poros        = porosity of the soil
c     ro dry       = density of the soil
c     kh           = permeability of the soil
C     D            = the diffusion-dispersion coefficient  = a*exp(b*c)
c     KHC          = osmosis coefficient varies for each component
c     KCH         = ion restriction coefficient varies for each component
c     DX           = d coef in x- direction varies for each component
c     DZ           = d coef in z- directionvaries for each component
c     DXTDZ        = dx/dz
c     RT           = universal gases coefficient
c     TT           = absolute temperature
c     MS           = molecular weight of the non conservative component
c     GS           = specific weight of the solvent
c     Dep          = depth of soil column
c     NDEPS        = number of depth steps of the soil column
c     NTS          = number of time steps
c     DELX         = x- step length
c     DELZ         = z- step length
c     delt         = time step inetrval
c     NXN          = number of nodes in x-directiom
c     NZN          = number of nodes in z-directiom of the clay liner
c     CI           = upper boundary concenteration
c     H0           = upper boundary head
c     CB           = backgraound concenteration in the pore fluid
c     CP           = precipitated concentration for non conservative
c     CS           = adsorbed concentration for non conservative
c     AKZ          = calculated Kd for first non conservative
c     AKP          = calculated Kd for second non conservative
c     PHT          = pH of each soil slice
c     WB           = weight of the soil column
c     WSL          = weight of soil slice
c     vv           = volume of the void
c     ITERT        = no. Of iterations in fluid field solution program
c     ITMAXT       = maximum number of iteration
c     RELAX        = realaxation factor in poison(fluid) subroutine
c
C**********************************************************
C     MAIN PROGRAM
C**********************************************************
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
```

```
      include 'CHESP.INC'


      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZt(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore
      OPEN(19,FILE='CC1.DAT')
      OPEN(16,FILE='CZ1.DAT')
      OPEN(17,FILE='CP1.DAT')
      OPEN(18,FILE='H1.DAT')
      open(15,file='in1')
C IMPOSE THE BOUNDARY CONDITIONS
      CALL INBOUND
 920  III=0
      DO 300 Nt=1,NTS
C CALCUALTE THE LAPLACIAN OF CONCENTRATIONS FOR THE EFFECT OF OSMOTIC  c
PRESSURE
      ITERT=ITERT+1
      IF(ITERT.GT.1) GOTO 820
      CALL LAPLAS
C CALCUALTE THE HYDRUALIC HEAD WITH THE POSSONS EQUATION
 820  CALL POISON
C  CALCULATE THE CONCENTRATIONS FOR CONSERVATIVE COMPONENTS
C     CHECK THE CRITERIA
      IF(ITERT.EQ.ITMAX) GOTO 501
      IF(III.EQ.1) GO TO 920
 501  CALL TRANS
C CALCUALTE THE CONCENTRATIONS FOR NON CONSERVATIVE COMPONENTS
      CALL EXPLIT
      DO 93 Is=1,NXN
      IF(IS.Gt.1) GO TO 55
      DO 91 Js=2,NZN
      C1=CCl(Is,Js)
      C2=cna(Is,Js)
      C3=CZ(Is,Js)
      C4=cpb(Is,Js)
      IF(C1*C2*C3*C4.EQ.0.) GO TO 93
 1920 CALL CHESP
      close(6)
      close(1)
      close(11)
C  CALL EXPLIT TO COLUCULATE THE CONCENTRATIONS OF NON CONSERVATIVE
C SOLVE TRANSPORT EQUATION TO OBTAIN INITIAL GUESSES OF TOTAL
C CONCENTRATIONS OF NON CONSERVATIVE COMPONENTS
      CPP(IS,JS)=(1.D0-RELAX)*CPb(IS,JS)+RELAX*CPb(IS,JS)
      CALL EXPLIT
      TOTAL=ABS(CPP(IS,JS)-cpb(is,js)/cpp(is,js))
      IF(TOTAL.1E.0000001) go to 192
      C1=CCl(Is,Js)
      C2=cna(Is,Js)
```

```
      C3=CZ(Is,Js)
      go to 1920
 192  CCL(Is,Js)=C1
      write(*,*)'total=',total
      write(*,*) nt, js,' transport' ,c1,c2,c3,C4
 193  cna(Is,Js)=C2
      CZ(Is,Js)=C3
      cpb(Is,Js)=C4
      CP1(Is,Js)=C1P
      CP2(Is,Js)=C2P
      CP3(Is,Js)=C3P
      CP4(Is,Js)=C4P
      CS1(Is,Js)=C1S
      CS2(Is,Js)=C2S
      CS3(Is,Js)=C3S
      CS4(Is,Js)=C4S
      akz(IS,JS)=((C2P+C2S)*POROS/RO)/C2
      akp(IS,JS)=((C4P+C4S)*POROS/RO)/C4
      PHT(is,js)=PH
  91   CONTINUE
      GO TO 93
  55  CCL(Is,Js)=CCL(1,Js)
      cna(Is,Js)=cna(1,Js)
      CZ(Is,Js)=CZ(1,Js)
      cpb(Is,Js)=cpb(1,Js)
      CP1(Is,Js)=CP1(1,JS)
      CP2(Is,Js)=CP2(1,JS)
      CP3(Is,Js)=CP3(1,JS)
      CP4(Is,Js)=CP4(1,JS)
      CS1(Is,Js)=CS1(1,JS)
      CS2(Is,Js)=CS2(1,JS)
      CS3(Is,Js)=CS3(1,JS)
      CS4(Is,Js)=CS4(1,JS)
  93   CONTINUE
      ITERT=0
  300 CONTINUE
      STOP
      END
C************************************************************
C     INPUT BOUNDARY CONDITION  SUNROUNTINE # 1
C     CHARACTERISTICS,CONSTANTS, GEOMETERY OF THEREGION, NUMBER OF
C     SPACE AND TIME STEPS ARE GIVEN
c***************************************************************
      SUBROUTINE INBOUND
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZt(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore
C     GIVEN MAXIMUM NUMBER OF itertATION
```

```
C
      itmaxt=300
C     GIVE OVER REALXATION FACTOR
      RELAX=1.8D0
C
C     SOIL CHARACTERISTICS(GR,CM,DAY)
C
      READ(15,*) NDEPS
      read (15,*)  delt
      read (15,*)  nts
      read (15,*)  cBcL
      read (15,*)  cBc
      read (15,*)  cBz
      read (15,*)  cBp
      read (15,*)  cIcL
      read (15,*)  cIc
      read (15,*)  cIz
      read (15,*)  cIp
      read (15,*)  H0
      read (15,*)  NLS
      read (15,*)  acL
      read (15,*)  ac
      read (15,*)  az
      read (15,*)  ap
      read (15,*)  bcl
      read (15,*)  bc
      read (15,*)  bz
      read (15,*)  bp
      read (15,*)  kh
      read (15,*)  WB,RO,POROS,WW,LEN,DEP,LENL,AREA
      read(15,*)OCL,OC,OZ,OP
      read(15,*)Npor,ms
C     GEOMETRY OF THE REGION
C     VOL=AREA*DEP
      WS=WB/(1+WW)
      WSL=WS/(NDEPS+1)
      SG =2.58D0
      VS= WS/GS
      VV=VOL-VS
      DXTDZ=0.d0
C
C     CONSTANTS
C
      Rt=82.0567D0*1034
      tT=273.D0+20.
      GS=1.D0
C
C
C     GEOMETRY OF SPACE AND TIME STEPS
C
      NLLS=NLS
C
C     SPACE AND TIME STEPS
C
      DELX=(LEN/2.D0)/NLS
      DELZ=DEP/NDEPS
C
c     NUMBER OF SPACE NODES
```

```
      NXN=NLS+1
      NXLN=NLLS+1
      NZN=NDEPS+1
      DEL2=(DELX/DELZ)**2
C
C     INITIAL AND BOUNDARY CONDITIONS
C
C     UPPER BOUNDARY CONDITIONS

      DO 20 I=1,NXN
      H(I,1)=H0
      AHN(I,1)=H(I,1)
      CCL(I,1)=CICL
      cna(I,1)=CIC
      CZ(I,1)=CIZ
      cpb(I,1)=CIP
   20 CONTINUE
C
C     LOWER BOUNDARY CODITIONS
C
      DO 30 I=1,NXN
      H(I,NZN)=0.0
   30 CONTINUE
C
C     INITIAL CONCENTERATION
C
      DO 50 I=1,NXN
      DO 50 J=2,NZN
      CCL(I,J)=CBCL
      cna(I,J)=CBC
      CZ(I,J)=CBZ
  50  cpb(I,J)=CBP

C     GIVING INITIAL VALUES TO HEADS

      NZNM1=NZN-1
      DO 70 I=1,NXN
      DO 70 J=2,NZNM1
      H(I,J)=150.D0
  70  CONTINUE
      RETURN
      END

C***********************************************************************
C     LAPLASIAN SUBROUTINE #2
C************************************************************************
      SUBROUTINE LAPLAS
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZt(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
```

```
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore

C     CALCULATING THE LAPLACIAN OF CONCENTERATION

      DO 80 J=2,NDEPS
      DO 80 I=1,NXN
      IF(I.EQ.NXN.OR.I.EQ.1) GOTO 76
      D2CX2=(CT(I+1,J)-2*CT(I,J)+CT(I-1,J))/(DELX**2)
      GOTO 77
   76 D2CX2=0.0
   77 D2CZ2=(CT(I,J+1)-2*CT(I,J)+CT(I,J-1))/(DELZ**2)
      DLAP(I,J)=D2CX2+D2CZ2
   80 CONTINUE
      RETURN
      END
C**********************************************************************
C     SUBROUNTINE #3
C     HYDRALIC HEAD  ARE CALCULATED BY USING THE GAUSS OVER RELAXATION
C     METOD
C************************************************************************
      SUBROUTINE POISON
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZT(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore


C     OBTAINING HEADS BY ITERATION
      DO 95 L=1,3
      DO 90 J=2,NDEPS
      DO 90 I=1,NXN

      IF(L.EQ.1) khc=OC
      IF(L.EQ.2) khc=OZ
      IF(L.EQ.3) khc=OP
      LAMBDA=(POROS*KHC)/(KH*MS)
C     LINE OF SYMMETRY BOUNDARY CONDITIONS

      IF(I.EQ.1) GOTO 85

C     RIGHT HAND BOUNDARY CONDITIONS

      IF(I.EQ.NXN) GOTO 87

C     STRAT itertATION

      AHN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((H(I+1,J)+H(I-1,J)
     $+DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP(I,j))/
```

```
     $(2.D0+2.D0*DEL2))
      GO TO 88
  85  AHN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((2.0D0*H(I+1,J)
     $+DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP(I,J))/
     $(2.D0+2.D0*DEL2))
      GO TO 88
  87  AHN(I,J)=(1.D0-RELAX)*H(I,J)+RELAX*((2.D0*H(I-1,J)
     $+DEL2*(H(I,J+1)+H(I,J-1))+LAMBDA*(DELX**2)*DLAP(I,J))/
     $(2.D0+2.D0*DEL2))
  88  CONTINUE
      TOL=ABS(AHN(I,J)-H(I,J))
      IF(TOL.GE.0.001D0) III=1
      H(I,J)=AHN(I,J)
  90  CONTINUE
  95  CONTINUE
      RETURN
      END

C************************************************************************
c       SUBROUTINE #4
        SUBROUTINE TRANS
C THIS SUBROUTINE CALCULATES CONCENTRATIONS OF CONSERVATIVE COMPONENTS
C AT NEW TIME  STEP USING EXPLICIT FINITE DIFFERENCE MERHOD
C************************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZT(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore
      khcc=ocl
      OSM=KCH*KHCc/(2.0D0*KH*MS)
C
      IF(NT.LT.NTS) GO TO 100
C     TIME=NTS*DELT/365.D0
c     WRITE(1,331)TIME
c331  FORMAT(5X,'THE TOTAL TIME=',F10.2,'YEARS')
C
C     DETERMINATION OF VELOCITIES AND CONCENTERATIONS
C
 100  DO 120 I=2,NLS
      DO 120 J=2,NDEPS
      DCXC=(CCL(I+1,J)-CCL(I-1,J))/(2.D0*DELX)
      DCZC=(CCL(I,J+1)-CCL(I,J-1))/(2.D0*DELZ)
      DHXC=(AHN(I+1,J)-AHN(I-1,J))/(2.D0*DELX)
      DHZC=(AHN(I,J+1)-AHN(I,J-1))/(2.D0*DELZ)
      VX=((-KH/POROS)*DHXC-KHCc*DCXC)
      VZ=((-KH/POROS)*DHZC-KHCc*DCZC)
      WRITE(1,332) VX, VZ
 332  FORMAT(5X,'VX=', F15.8,10X,'VZ=',F15.8)
```

```
C
C     BACKWARD FINITE DIFFERENCE
C
C     DCX=(CCL(I,J)-CCL(I-1,J)/(DELX)
C     DCZ=(CCL(I,J)-CCL(I,J-1))/(DELZ)
C
C     USE CENTRAL DIFFRENCE
C
      DCX=DCXC
      DCZ=DCZC
C
      D2C2X=(CCL(I+1,J)**2-2.D0*CCL(I,J)**2+CCL(I-1,J)**2)/(DELX**2)
      D2C2Z=(CCL(I,J+1)**2-2.D0*CCL(I,J)**2+CCL(I,J-1)**2)/(DELZ**2)
      DCXD=(CCL(I+1,J)-CCL(I-1,J))/(2.0*DELX)
      DCZD=(CCL(I,J+1)-CCL(I,J-1))/(2.0*DELZ)
      D2CX=(CCL(I+1,J)-2.D0*CCL(I,J)+CCL(I-1,J))/(DELX**2)
      D2CZ=(CCL(I,J+1)-2.D0*CCL(I,J)+CCL(I,J-1))/(DELZ**2)
      ADT=(1+RI)*(VX*DCX+VZ*DCZ)
      OSMT=OSM*(D2C2X+D2C2Z)
      DZc=ACL*EXP(Bcl*CCL(I,J))
      DX=DXTDZ*DZc
      DIFTX=bcl*DX*(DCXD**2)+DX*D2CX
      DIFTZ=bcl*DZc*(DCZD**2)+DZc*D2CZ
      CPLW=CCL(I,J)
      Cn(I,J)=CPLW+(DELT)*(-ADT-OSMT+DIFTX+DIFTZ)
  120 CONTINUE


      DO 121 I=2,NLS
       DO 121 J=2,NDEPS
         CCL(i,j) = Cn(i,j)
  121  CONTINUE

      DO 200 I=1,NXN
      CCL(I,NZN)=CCL(i,NZN-1)
  200 CONTINUE
      DO 250 J=2,NZN
      CCL(1,J)=CCL(2,J)
      CCL(NXN,J)=CCL(NXN-1,J)
  250 CONTINUE
      RETURN
      END
C**********************************************************************
C     SUBROUTINE #5
C     THIS SUBROUTINE CALCULATES CONCENTERATIONS AT ADVANCED TIME
C     STEP USING EXPLICIT FINITE DIFFERENCE MERHOD FOR NON_CONSERVATIVE
c     COMPONENS
C*********************************************************************
      SUBROUTINE EXPLIT
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZT(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
```

```
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore


      IF(Nt.LT.NTS) GO TO 100
C     TIME=NTS*DELT/365.D0

C     DETERMINATION OF VELOCITIES AND CONCENTERATIONS

 100  DO  33 L=1,3
      DO 1 I=1,NXN
      DO 1 J=1,NZN
      IF(L.NE.1)  GO TO 2
      Ct(I,J)=cna(I,J)/1.d0
      GO TO 1
  2   IF(L.NE.2) GO TO 3
      Ct(I,J)=CZ(I,J)/1.d0
      GO TO 1
  3   Ct(I,J)=cpb(I,J)/1000.d0
  1   CONTINUE

C SPECIFIED DIFFUSION COEFFICIENT FOR EACH COMPONENT

      IF(L.EQ.1) ta=AC
      IF(L.EQ.2) ta=AZ
      IF(L.EQ.3) ta=AP
      IF(L.EQ.1) tb=bC
      IF(L.EQ.2) tb=bZ

C SPECIFIED OSMOTIC COEFFICIENT FOR EACH COMPONENT

      IF(L.EQ.3) tb=bPC
      IF(L.EQ.1) khc=OC
      IF(L.EQ.2) khc=OZ
      IF(L.EQ.3) khc=OP

      KHC=KHC*3600*24
      KCH=(KHC*POROS)/(Rt*tT)
      RI=KCH/KH
      OSM=KCH*KHC/(2.0D0*KH*MS)
      DO 120 I=2,NLS
      DO 120 J=2,NDEPS
      DCXC=(Ct(I+1,J)-Ct(I-1,J))/(2.D0*DELX)
      DCZC=(Ct(I,J+1)-Ct(I,J-1))/(2.D0*DELZ)
      DHXC=(AHN(I+1,J)-AHN(I-1,J))/(2.D0*DELX)
      DHZC=(AHN(I,J+1)-AHN(I,J-1))/(2.D0*DELZ)
      VX=((-KH/POROS)*DHXC-KHC*DCXC)
      VZ=((-KH/POROS)*DHZC-KHC*DCZC)


c     WRITE(1,332) VX, VZ
 332  FORMAT(5X,'VX=', F15.8,10X,'VZ=',F15.8)

C WRITTEN BT=KD FOR EACH COMPONENET
C     BACKWARD FINITE DIFFERENCE
```

```
C       DCX=(Ct(I,J)-Ct(I-1,J)/(DELX)
C       DCZ=(Ct(I,J)-Ct(I,J-1))/(DELZ)

C       USE CENTRAL DIFFRENCE

        DCX=DCXC
        DCZ=DCZC

        D2C2X=(Ct(I+1,J)**2-2.D0*Ct(I,J)**2+Ct(I-1,J)**2)/(DELX**2)
        D2C2Z=(Ct(I,J+1)**2-2.D0*Ct(I,J)**2+Ct(I,J-1)**2)/(DELZ**2)
        DCXD=(Ct(I+1,J)-Ct(I-1,J))/(2.0*DELX)
        DCZD=(Ct(I,J+1)-Ct(I,J-1))/(2.0*DELZ)
        D2CX=(Ct(I+1,J)-2.D0*Ct(I,J)+Ct(I-1,J))/(DELX**2)
        D2CZ=(Ct(I,J+1)-2.D0*Ct(I,J)+Ct(I,J-1))/(DELZ**2)
        ADT=(1+RI)*(VX*DCX+VZ*DCZ)
        OSMT=OSM*(D2C2X+D2C2Z)
        Dzt(j)=ta*EXP(tb*Ct(I,J))
        DX=DXTDZ*DZt(j)
        DIFTX=tb*DX*(DCXD**2)+DX*D2CX
        DIFTZ=tb*DZt(j)*(DCZD**2)+DZt(j)*D2CZ
        CPLW=Ct(I,J)
        CN(I,J)=CPLW+(DELT)*(-ADT-OSMT+DIFTX+DIFTZ)
  120   CONTINUE

        DO 121 I=2,NLS
         DO 121 J=2,NDEPS
           Ct(i,j) = CN(i,j)
  121    CONTINUE

        DO 200 I=1,NXN
        Ct(I,NZN)=Ct(i,NZN-1)
  200   CONTINUE
        DO 250 J=2,NZN
        Ct(1,J)=Ct(2,J)
        Ct(NXN,J)=Ct(NXN-1,J)
  250   CONTINUE

        DO 4 I=1,NXN
        DO 4 J=1,NZN
        IF(L.NE.1)  GO TO 5
        cna(I,J)=Ct(I,J)*1.d0
        GO TO 4
    5   IF(L.NE.2) GO TO 6
        CZ(I,J)=Ct(I,J)*1.d0
        GO TO 4
    6   cpb(I,J)=Ct(I,J)*1000.d0
    4   CONTINUE

   33   CONTINUE
c       WRITE(*,*)((cpb(I,J),J=1,NZN),I=1,NXN)
        RETURN
        END
c******************************* subroutine # 6*****************
        SUBROUTINE OUT
c**************************************************************
        IMPLICIT REAL*8(A-H,O-Z)
        REAL*8 KH, KCH, KHC,MS,LEN,LENL,LAMBDA
        DIMENSION  ZZ(25),cpbt(9,50)
```

```
      COMMON /CHA/ct(9,50),H(9,50),pht(9,50),HH(9,50),AHN(9,50),
     *cna(9,50),akz(9,50),akp(9,50)
      COMMON /Cnew/ Cn(9,50),Ccl(9,50),DLAP(9,50),cZ(9,50),cpb(9,50)
      COMMON /CSOR/CS1(9,50),CS2(9,50),CS3(9,50),CS4(9,50),CPP(9,50)
      COMMON /CPRE/CP1(9,50),CP2(9,50),CP3(9,50),CP4(9,50),DZT(25)
      COMMON/var0/POROS,RO,KH,D,ta,tb,KHC,KCH,DX,DXTDZ,rt,tt,MS,GS
      COMMON/VAR1/ LEN,DEP,LENL,NLLS,NLS,NDEPS,NTS,DELX,DELZ,DELT
      COMMON/VAR2/ NXN,NXLN,NZN,H0,DEL2,LAMBDA,Nt,itert,NPOR
      COMMON/VAR3/ at,bt,OSM,itmaxt,RELAX,RI,AZ,AP,AC,ACL,bcl,bc,bz,bp
      COMMON/VAR4/CBCL,CBC,CBZ,CBP,CIC,CIZ,CIP,CICL,OCL,OC,OZ,OP
      COMMON/VAR5/flow1,flow2,flow3,flow4,AREA,VZ,VV,WS,WSL,pore
      TIME=NT*DELT

C CALCULATING THE MASS BALANCE

C TOTAL INTRODUCED CONCENTRATION FOR NON CONSERVATIVE CONTAMINANT

      flow4=VV* PORE*cpb(1,1)/1000.d0

c TOTAL LEACHED FOR EACH CONTAMINANT

      CLEACH4=VV*PORE*cpbt(1,NZN)/1000.d0

C TOTAL ADSORBED CONTAMINANT

      DO 110 JS=2,NZN
      CRET4= CRET4+((CP4(1,JS)+CS4(1,JS))*
     *PORE*VV)/1000.D0
c     CRET4= CRET4+CP4(1,JS)*POROS*WSL/(RO*1000.D0)+CS4(1,JS)*WSL*
c    *POROS*WSL/(RO*1000.D0)
 110  CONTINUE


C TOTAL MIGRATED CONTAMINAT

      DO 111 JS=2,NZN
      CPORE4= CPORE4+((CPB(1,JS)*POROS*WSL))/(RO*1000.D0)
C COMPARING INPUT AND OUTPUT CONTAMINANT
  111 CONTINUE
      CTOTAL4=(CRET4+CPORE4)+CLEACH4
      ZI=0.D0
      DO 13 JS=1,NZN
      ZZ(JS)=ZI+Delz*(JS-1)
  13  CONTINUE
      is=nxn/2
      WRITE(19,1001)TIME ,flow1,PORE
      WRITE(17,1001)TIME ,flow4*ms*1000,PORE,CTOTAL4*ms*1000
      DO 1 Js=1,NZN
      WRITE(19,1000)ZZ(JS),CCL(Is,Js)*35500,Cp1(Is,Js)*35500,Cs1(Is,Js)
     **35500
      WRITE(16,1000)ZZ(JS),cna(Is,Js)*23000,Cp2(Is,Js)*23000,Cs2(Is,Js)
     **23000
      WRITE(17,1000)ZZ(JS),Cz(Is,Js),CP3(Is,Js),Cs3(Is,Js),
     *cpb(Is,Js)*1000*ms,CP4(Is,Js)*1000*ms,Cs4(Is,Js)*1000*ms,
     *cpbt(is,js)*1000*ms
c     WRITE(18,1000)ZZ(Js),ahn(IS,Js),PHT(IS,Js),akp(IS,JS)
      WRITE(18,1000)ZZ(Js),dzt(Js),PHT(IS,Js),akp(IS,JS)
c     WRITE(18,1000)ZZ(Js),PHT(IS,Js),akz(IS,JS),akp(IS,JS)
```

```
 1000 FORMAT(1pe10.3,1X,30(1pe10.3,1X))
 1001 FORMAT('TIME IN DAY='1PE10.3,3X 'introduced concentration in mg=',
     * 1pe10.3,2X,'PORE=',1pe10.3,2X,'CTOTAL',1pe10.3/)
  1   CONTINUE
      RETURN
      END
*************************************** subrountine 7****************
       SUBROUTINE CHESP
c
c     Version 3.01   Release date: 09/30/91
c -------------------------------------------------------------------
c  IMPORTANT -  To modify for VAX compiler, use editor or word
c               processor to search for the characters "CHANGE ME"
c               (without the quotes).  These characters have been
c               inserted to delineate the FORTRAN code that is
c               different in the VAX and PC versions.
c -------------------------------------------------------------------
c
c
      include 'CHESP.INC'
      character filename*12, xerr*1, msg*1
      logical preexist
      include 'CONST.INC'

c  -- Set counter for accumulating the total number of errors
c     encountered.
      ierrtotl = 0
c
      call minval
c  -- Assign Logical unit numbers
      lun01 = 01
      lun02 = 02
      lun03 = 03
      lun04 = 04
      lun05 = 05
      lun07 = 07
      lun10 = 10
      lun11 = 11
      lun14 = 14
      ierrin = 13
c
c     ----------------------------------------------------------
c     CHANGE ME
c     This machine dependent section results from the fact that the
c     only logical unit in Ryan-McFarland FORTRAN that accommodates
c     FORTRAN carriage control for printing is unit 6.  Therefore,
c     on the PC unit 6 is used for the output file 'minout.out' and
c     screen output is re-assigned to unit 8.  However, VAX FORTRAN
c     accommodates FORTRAN carriage control on all units EXCEPT unit 6.
c     Therefore 'minout.out' is assigned to unit 8 and screen output
c     defaults to unit 6.
c
c     ATENTION!   ATTENTION!   ATTENTION!   ATTENTION!   ATTENTION!
c  -- FOR COMPILING ON THE VAX, COMMENT OUT THE NEXT THREE EXECUTABLE
c         LINES AND REMOVE COMMENT DELIMITERS FROM THE NEXT TWO LINES.
c  -- FOR COMPILING ON THE PC, REMOVE COMMENT DELIMITERS FROM THE NEXT
c         THREE EXECUTABLE LINES AND COMMENT OUT THE NEXT TWO LINES.
      lunout =  06
```

```
      scrnout = 08
      open (unit=scrnout,file='con')
c      lunout =  08
c      scrnout = 06
c     ---------------------------------------------------------------
c
c  -- OPEN ALL DATABASE FILES.
c     Before each OPEN, call ENQUIRE to check whether the file
c     exists.  Set flag indicating error (xerr), whether the file
c     is supposed to pre-exist (preexist), and whether or not
c     ENQUIRE is to print an error message concerning
c     disposition (msg).
c
      xerr = 'N'
      msg = 'Y'
c
c  -- Open the main thermodynamic database file.
      filename = 'THERMO.UNF'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=lun02,file='THERMO.UNF',status='OLD',
     *  form='unformatted')
c
c  -- Open the component database file.
      filename = 'COMP.DBS'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=lun03,file='COMP.DBS',status='OLD')
c
c  -- Open the solids database file.
      filename = 'TYPE6.UNF'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=lun04,file='TYPE6.unf',status='OLD',
     *  form='unformatted')
c
c  -- Open the alkalinity factor for non-carbonates file.
      filename = 'ALK.DBS'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=lun10,file='ALK.DBS',status='OLD')
c
c  -- Open the database of metal/composite organic matter file.
      filename = 'COMPLIG.DBS'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=lun14,file='complig.dbs',status='old')
c
c  -- Open the temperature dependent log K file.
      filename = 'ANALYT.DBS'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
```

```
      open (unit=lun07,file='ANALYT.DBS',status='OLD')
c
c  -- Open the error message file.
      filename = 'ERROR.DBS'
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
      if (xerr.eq.'Y') go to 999
      open (unit=ierrin,file='error.dbs',status='old')
c

c  -- Display opening screen and obtain I/O filenames.
CDWD
      call display (1)
CDWD
      if (xstop.eq.'Y') go to 999
c
c
c  -- CALL MAIN DRIVER
      call maind

 110  continue
c
 999  return
      end
c(8)*************************************************************
      SUBROUTINE ENQUIRE (FILENAME,PREEXIST,XERR,SCRNOUT,MESSG)
c***************************************************************
c  -- The purpose of this subroutine is to inquire whether
c     the file named FILENAME exists and return the logical
c     variable FILEXIST as .TRUE. or .FALSE. accordingly.
c     The logical variable PREEXIST indicates whether the
c     file is supposed to already exist.  The character
c     variable MESSG indicates whether ENQUIRE is to write an
c     error message on the screen if a file that is supposed
c     to already exist does not or vica versa.  The character
c     variable XERR indicates whether the disposition of the
c     file is as it should be (XERR = 'N' for "no error") or
c     not as it should be (XERR = 'Y' for "error").
c
      CHARACTER FILENAME*12, XERR*1, MESSG*1
      LOGICAL FILEXIST,PREEXIST
      INTEGER SCRNOUT
C
C
      INQUIRE (FILE=FILENAME,EXIST=FILEXIST)
      IF (PREEXIST) THEN
        IF (.NOT.FILEXIST) THEN
          IF (MESSG.EQ.'Y') WRITE (SCRNOUT,1000) FILENAME
          XERR = 'Y'
          GO TO 999
        END IF
      ELSE IF (.NOT.PREEXIST) THEN
        IF (FILEXIST) THEN
          IF (MESSG.EQ.'Y') WRITE (SCRNOUT,1010) FILENAME
          XERR = 'Y'
        END IF
      END IF
C
```

```
  999 RETURN
C
 1000 FORMAT(' THE REQUIRED FILE ',a12,' IS NOT PRESENT IN THIS SUB-',
     *        'DIRECTORY.',
     *      /,' CONSULT THE INSTALLATION INSTRUCTIONS (READ.ME).    ')
 1010 FORMAT(' THE FILE ',a12,' ALREADY EXISTS IN THIS SUB-DIRECTORY.',
     *        ' RENAME IT TO SOME',
     *      /,' OTHER NAME OR MOVE IT TO A DIFFERENT DIRECTORY AND',
     *        ' TRY AGAIN.')
      END
c(9)*******************************************************************
      SUBROUTINE   MINVAL
C*********************************************************************
C     + + + COMMON BLOCKS + + +
C     numeric constants
      INCLUDE 'CONST.INC'
C
C     + + + LOCAL VARIABLES + + +
      INTEGER*4     R2PREC,D2PREC,TI
      REAL*4        R1,R2,R3,R4,  TR
      REAL*8        D1,D2,D3,D4
C
C     + + + FUNCTIONS + + +
      REAL*4   RNOP
      REAL*8   DNOP
C     + + + INTRINSICS + + +
      INTRINSIC  INT,LOG10,DBLE
C
C     + + + EQUIVALENCE STATEMENTS + + +
      EQUIVALENCE (TR,TI)
C
C     + + + OUTPUT FORMATS + + +
 2000 FORMAT(' UNKNOWN DOUBLE PRECISION FORMAT, using default double pre
     .cision values!')
 2010 FORMAT(' UNKNOWN MACHINE TYPE, using default precision values!')
C
C     + + + STATEMENT FUNCTION DEFINITIONS + + +
C     No OPperation, used to keep Ryan/McFarland optimization honest
      RNOP(R1) = R1
      DNOP(D1) = D1
C
C     + + + END SPECIFICATIONS + + +
C
C     Calculate machine dependent numeric constants
C
C     Determine the number of decimal digits of REAL precision number and
C     the smallest REAL greater than 1.0.
C     First find the number of significant binary digits, then convert
C     it to the number of significant decimal digits.  Any machine used
C     today is going to have more than 7 binary digits of precision
C     (actually, we're cheating, because 1 is added to R2PREC after
C     it is tested.  This usually results in 7 decimal digits of
C     precision, which is usually the case, whereas strictly
C     speaking only 6 decimal digits are guaranteed, and 6 is
C     usually the result if R2PREC is initialized to 6).
      R2PREC = 7
      R1 = 1.0
      R2 = 0.0078125
```

```
 100  CONTINUE
      R3 = R1 + R2
C     this 'nop' keeps Ryan/McFarland optimization honest.  Without it,
C     the precision of an 80 bit floating point register is computed
C     (instead of a 4-byte real) when R/M optimization is turned on.
C     You can comment out the call to NOP if you observe that by
C     doing so DECCHR doesn't provide extra digits of precision.
      R4 = RNOP(R3)
      IF (R1 .NE. R3) THEN
         RP1MIN = R3
         R2PREC = R2PREC + 1
         R2 = R2 / 2.0
         GO TO 100
      END IF
C
      RPREC = INT(LOG10(2.0**R2PREC))
C
C     Determine the number of decimal digits of the typical DOUBLE C
C     precision
C     number and the smallest DOUBLE greater than 1.0D0.
      D2PREC = 7
      D1 = 1.0D0
      D2 = 0.0078125D0
 200  CONTINUE
      D3 = D1 + D2
C     this 'nop' keeps Ryan/McFarland optimization honest.  Without it,
C     the precision of an 80 bit floating point register is computed
C     (instead of a 4-byte real) when R/M optimization is turned on.
C     You can comment out the call to NOP if you observe that by
C     doing so DECCHR doesn't provide extra digits of precision.
      D4 = DNOP(D3)
      IF (D1 .NE. D3) THEN
         DP1MIN = D3
         D2PREC = D2PREC + 1
         D2 = D2 / 2.0D0
         GO TO 200
      END IF
C
      DPREC = INT(LOG10(2.0D0**D2PREC))
C
      TR = 1.0
      IF (TI .EQ. 1065353216) THEN
C       this should be the case for the Sun or Ryan/McFarland
        R1    = 1.0E-19
C        R0MIN = 1.17549435E-19 * R1
        R0MIN = 1.1754945E-19 * R1
        R1    = 1.0E+19
        R0MAX = 3.40282347E+19 * R1
        D1    = 1.0D-28
        D0MIN = (2.22507385850720219D-28 * D1**10)
        D1    = 1.0D+28
        D0MAX = (1.7976931348623157D0 * D1**11)
      ELSE IF (TI .EQ. 16512) THEN
C       this should be the case for the VAX
        R1    = 1.0E-20
        R0MIN = 2.9387359E-19 * R1
        R1    = 1.0E+18
        R0MAX = 1.7014117E+20 * R1
```

```
        IF (DPREC .EQ. 17) THEN
C          this should be the case for the default /NOG_FLOAT compiler C
            option
           D1   = 1.0D-20
           D0MIN = 2.938735877055719D-19 * D1
           D1   = 1.0E+19
           D0MAX = 1.7014118346046923D+19 * D1
        ELSE IF (DPREC .EQ. 16) THEN
C          this should be the case for the /G_FLOAT option
           D3 = 1.0D-21
           D4 = 1.0D-20
           D0MIN = (5.562684646268008D-20)*(D4**5)*(D3**9)
           D3 = 1.0D+21
           D4 = 1.0D+20
           D0MAX = (8.988465674311578D+21) * (D3**6) * (D4**8)
        ELSE
C          assume D_FLOAT real*8 type
           WRITE(*,2000)
           D1   = 1.0D-20
           D0MIN = 2.938735877055719D-19 * D1
           D1   = 1.0E+19
           D0MAX = 1.7014118346046923D+19 * D1
        END IF
      ELSE
        WRITE(*,2010)
        R1    = 1.0E-19
        R0MIN = 1.17549435E-19 * R1
        R1    = 1.0E+18
        R0MAX = 1.7014117E+20 * R1
        D1    = 1.0D-20
        D0MIN = 2.938735877055719D-19 * D1
        D1    = 1.0E+19
        D0MAX = 1.7014118346046923D+19 * D1
      ENDIF
C
      RETURN
      END
c(10)******************************************************
      Subroutine DISPLAY (msgno)
c *******************************************************
c  -- The purpose of this routine is to display the program title and
c     CEAM address, obtain I/O filenames, and display execution status
c     information and error messages on the screen while CHESP
c     executes.
c
c     The screen is divided into an upper region (the TITLE AREA),
c     middle region (the STATUS AREA) and lower region (the ERROR
c     AREA).  The variable "msgno" represents the message number and
c     is passed to DISPLAY by the calling program to indicate the
c     status text to be displayed.  In addition to text status
c     information, iteration, sweep number, and problem number
c     information may be displayed.  Also, information on the current
c     list of TYPE IV solids may be displayed.
c
c  -- The flag "prtstat" indicates whether to display the status
c     information for iteration, sweep, and problem numbers.
c  -- The flag "prtsld" indicates whether to display the status
c     information for TYPE IV solids.
```

```
c  -- The variables "string1, string2, ..." and the array "string(i)"
c     are used to temporarily store the ANSI escape sequence for
c     cursor position.
c  -- The variable "stringc" is used to temporarily store the ANSI
c     escape sequence for changing the foreground and background
c     screen colors.
c  -- The parameters "errcode" and "ierr" are available to DISPLAY
c     through named common blocks (CHESP.INC).  These are written
c     out as the error message code heading th ERROR AREA.  The ERROR
c     AREA is caused to remain long enough for the user to read by
c     calling Subroutine DELAY for some few seconds.  This may also be
c     done for other messages.
c
      include 'CHESP.INC'
CDWD
      integer*4  msgno
      INTEGER*2  IDLAY
CDWD
      character prtstat*1, string1*8, string2*8, string3*8, string4*8,
     *          string5*8, stringc*8, strings*8, prtsld*1, blank*12,
     *          oufil*12, infil*12, xerr*1, messg*1
      logical preexist
      dimension strings(20)
c
c  -- Set to display status information unless directed otherwise.
      prtstat = 'y'
      prtsld = 'y'
CDWD
      IDLAY = 0
CDWD
c
c  -- Branch on message number "msgno".
c
c
      if (msgno.eq.1) then
c  -- TITLE AREA - Display CHESP version number, Laboratory address.
c
c  -- Set the overall background color to white (47) and the
c     foreground to anything.
c
c  -- Clear the screen to turn the screen white.
c
c  -- Set lines 3 through 5 to start in column 10.  For example,
c     string1 is set to begin printing on line 3 at column 10.  To
c     implement this, one need only write string1 to the display
c     device.  It will be interpreted as a command to position the
c     cursor, not as a string to be displayed.
cd      string1 = '[3;10H'
cd      string2 = '[4;10H'
cd      string3 = '[5;10H'
cd      string4 = '[6;10H'
cd      string5 = '[7;10H'
c
c  -- Set the foreground display to white (37) and the background to
c     blue (44).
        stringc = '[44;37m'
c
c  -- Implement these settings and write in the TITLE AREA.
```

```
c
c  -- Set background BLACK, foreground GREEN.
        stringc = '[40;32m'
c
c
c  -- OBTAIN INPUT AND OUTPUT FILENAMES
c
c  -- Check for the presence of a file named MININ.DAT.  If there
c     is such a file, assume it is the intended input file and
c     open it as such.  Open MINOUT.OUT as the output file.  If
c     there is no file named MININ.DAT, obtain both the input and
c     the output filenames from the user.
c
      infil = 'MININ.DAT'
      preexist =  .TRUE.
      xerr = 'N'
      messg = 'N'
      call enquire (infil,preexist,xerr,scrnout,messg)
c
c  -- If ENQUIRE found MININ.DAT, OPEN same as input file and OPEN
c     as output a file named MINOUT.OUT
      if (xerr.eq.'N') then
         oufil = 'MINOUT.OUT'
         open (unit=lun01,file=infil,status='OLD')
         open (unit=lunout,file=oufil,status='unknown')
         go to 106
      end if
c
c  -- In the absence of a file named MININ.DAT, obtain I/O
c     filenames from the user.
c
c  -- OBTAIN INPUT FILENAME
c
c  -- Set attribute to high intensity, position cursor at line 10,
c     column 1 and write input file prompt.
c
c      string1 = '[1m'
 5700 format (a4)
 5705 format (a8,'              <- Type input data file name (use X t',
     *            'o exit), then press <Enter>. ')
c
c  -- Re-position cursor at beginning of line 9.  This is because
c     the READ statement in INFILE will advance the cursor to the
c     beginning of the next line (line 10) which is where it needs
c     to be.
      string1 = '[9;1H'
 5710 format (a6)
c
c  -- Call INFILE to obtain the input filename.  INFILE will return
c     the filename in infil.  If xerr is returned as 'Y', the
c     specified file was not found so put up a TRY AGAIN prompt.
c     If xerr is returned as 'X', the user has elected to exit,
c     so return.
c
      call infile (infil,xerr)
105   if (xerr.eq.'Y') then
c  --    Move cursor to line 10 and write TRY AGAIN prompt.
         string1 = '[10;1H'
```

```
 5715 format (a8,'             <- Try again.  (File ',a12,' entered by',
     *           ' user does not exist.)')
c  --    Re-position cursor to line 9 so that the READ in INFILE
c        will leave it in the right place.
         string1 = '[9;1H'
         xerr = 'N'
         call infile (infil,xerr)
         go to 105
      else if (xerr.eq.'X') then
c  --    If 'X' is entered instead of a filename, exit gracefully,
c        clearing the screen first.
         xstop = 'Y'
         go to 999
      end if
c
c
c  -- OBTAIN OUTPUT FILENAME (only if MININ.DAT is not the input
c     filename and subsequently, MINOUT.OUT is the output file).
c
      if (infil.ne.'MININ.DAT') then
c  --    Position cursor at line 10 and write output file prompt.
         string1 = '[10;1H'
 5720 format (a8,'             <- Type output listing file name, the',
     *           'n press <Enter>.              ')
c  --    Re-position cursor at line 9 so that the READ in OUFILE
c        will leave it in the correct position.
 706     string1 = '[9;1H'
c  --    OUFILE opens the specified output file and returns the output
c        filename in oufil.
         call oufile (oufil)
         if (oufil.eq.infil) then
            string1 = '[10;1H'
 5735 format (a8,'             <- Try again.  Output file name cannot',
     *           ' be same as input file name.')
            go to 706
         else if (oufil.eq.' ') then
            go to 706
         end if
c  --    Open output file "oufil" on unit lunout
         open (unit=lunout,file=oufil,status='unknown')
      end if
c
c  -- Restore normal screen attributes, re-set black background,
c     green foreground.
      string1 = '[0m'
      string2 = '[32;40m'
 5725 format (a4,a8)
c
c  -- Write I/O file names for user information on line 10.
 106  string1 = '[10;1H'
 5730 format (a8,' INPUT: ',a12,'          <--  FILES  -->      ',
     *           '          OUTPUT: ',a12)
c
c
c  -- Set to not display the iteration number and solids status.
        prtstat = 'n'
        prtsld = 'n'
c
```

```
c
      else if (msgno.eq.3) then
c  -- STATUS AREA - "CHESP READING INPUT DATA"
c  -- Set to begin display in column 19 of line 12 and set background
c     color to black, foreground to green.
        string1 = '[12;19H'
        stringc = '[40;32m'
c
c  -- Implement these settings and write in the STATUS AREA.
c
c
      else if (msgno.eq.4) then
c  -- STATUS AREA - "CALCULATING SATURATION INDICES"
c  -- Set to begin display in column 19 of line 12 and set background
c     color to black, foreground to green.
        string1 = '[12;19H'
        stringc = '[40;32m'
c
c  -- Implement these settings and write in the STATUS AREA.
c
c
      else if (msgno.eq.5) then
c  -- ERROR AREA - "     --- COMPUTATIONS ABORTED ---", "... ERROR..."
c
c  -- Set background color to white (47) and foreground to anything.
        stringc = '[47;32m'
c  -- Set to begin next display at lines 10 through 22 beginning in
c     column 1.  The purpose of this is to "clear" the STATUS AREA
c     by writing over it with the background color (white).
        strings(1) = '[10;1H'
        strings(2) = '[11;1H'
        strings(3) = '[12;1H'
        strings(4) = '[13;1H'
        strings(5) = '[14;1H'
        strings(6) = '[15;1H'
        strings(7) = '[16;1H'
        strings(8) = '[17;1H'
        strings(9) = '[18;1H'
        strings(10) = '[19;1H'
        strings(11) = '[20;1H'
        strings(12) = '[21;1H'
        strings(13) = '[22;1H'
c
c  -- Implement these settings and write in the STATUS AREA.
        do 300 i = 1, 13
  300   continue
c
c  -- Set background color to red (41) and foreground to white (37).
        stringc = '[41;37m'
c
c  -- Set to begin display in column 27 for lines 20 and 21.
        string1 = '[20;27H'
        string2 = '[21;27H'
c
c  -- Implement these settings and write in the ERROR AREA.
c
c
      else if (msgno.eq.6) then
```

```
c  -- STATUS AREA - "EQUILIBRATING AQUEOUS SOLUTION"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     color to black, foreground to green.
        string1 = '[12;19H'
        stringc = '[40;32m'
c
c  -- Implement these settings and write in the STATUS AREA.
c
c
      else if (msgno.eq.14) then
c  -- STATUS AREA - "THE MINERAL xxxxxxxx HAS DISSOLVED"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     color to black, foreground to green.
        string1 = '[12;19H'
        stringc = '[40;32m'
c
c  -- Implement these settings and write in the STATUS AREA.
c
c
      else if (msgno.eq.15) then
c  -- STATUS AREA - "THE MINERAL xxxxxxxx HAS PRECIPITATED"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     color to black, foreground to green.
        string1 = '[12;19H'
        stringc = '[40;32m'
c
c  -- Implement these settings and write in the STATUS AREA.
c
c
      else if (msgno.eq.18.and.ierrtotl.eq.0) then
c  -- STATUS AREA - "CHESP EXECUTION COMPLETED NORMALLY"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     and foreground colors to normal display attributes.
        string1 = '[12;19H'
        stringc = '[0m'
c
c  -- Clear screen
c
c  -- Write final message in the STATUS AREA.
c
c  -- Set to not display the iteration number and solids status.
        prtstat = 'n'
        prtsld = 'n'
c
c
      else if (msgno.eq.18.and.ierrtotl.eq.1) then
c  -- STATUS AREA - "CHESP EXECUTION COMPLETED WITH 1 ERROR"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     and foreground colors to normal display attributes.
        string1 = '[12;19H'
        string2 = '[13;19H'
        stringc = '[0m'
c
```

```
c
c  -- Write final message in the STATUS AREA.
c
c  -- Set to not display the iteration number and solids status.
        prtstat = 'n'
        prtsld = 'n'
c
      else if (msgno.eq.18.and.ierrtotl.gt.1) then
c  -- STATUS AREA - "CHESP EXECUTION COMPLETED WITH (>1) ERRORS"
c
c  -- Set to begin display in column 19 of line 12 and set background
c     and foreground colors to normal display attributes.
        string1 = '[12;19H'
        string2 = '[13;19H'
        stringc = '[0m'
c
c
c  -- Write final message in the STATUS AREA.
c
c  -- Set to not display the iteration number and solids status.
        prtstat = 'n'
        prtsld = 'n'
c
      end if
c
c
c  -- Display the status information regarding iteration, sweep, and
c     problem number.
      if (prtstat.eq.'y') then
c
c  -- For "msgno" not equal to 5 (which is an error message), display
c     the iteration number, etc., in the STATUS AREA.
        if (msgno.ne.5) then
          string2 = '[12;2H'
          string3 = '[13;2H'
          string4 = '[14;2H'
c
c
c  -- For "msgno" equal to 5 only, display the iteration number, etc.,
c     in the  ERROR AREA.
        else
          prtsld = 'n'
          string1 = '[18;10H'
          string2 = '[20;10H'
          string3 = '[21;10H'
          string4 = '[22;10H'
c
c  -- Hold the error screen for an additional 7 sec so that it may be
c     easily read.
CDWD
          IDLAY=5
          call delay (IDLAY)
CDWD
        end if
      end if
c
c
c
```

```
c
c  -- Display the current list of TYPE IV Finite Solids.  The list
c     may change from one call to this routine to the next with
c     new solids being added or existing solids disappearing from
c     the list.  Space is provided for only 17 such solids. If there
c     are more than 17 (not likely), no attempt is made to write more
c     after the 17th is displayed.
      if (prtsld.eq.'y'.and.msgno.eq.14
     *   .or.prtsld.eq.'y'.and.msgno.eq.15) then
         string1 = '[12;65H'
         strings(1) = '[13;65H'
         strings(2) = '[14;65H'
         strings(3) = '[15;65H'
         strings(4) = '[16;65H'
         strings(5) = '[17;65H'
         strings(6) = '[18;65H'
         strings(7) = '[19;65H'
         strings(8) = '[20;65H'
         strings(9) = '[21;65H'
         strings(10) = '[22;65H'
         strings(11) = '[15;49H'
         strings(12) = '[16;49H'
         strings(13) = '[17;49H'
         strings(14) = '[18;49H'
         strings(15) = '[19;49H'
         strings(16) = '[20;49H'
         strings(17) = '[21;49H'
         strings(18) = '[22;49H'
c
c  -- Compute array index bounds for the TYPE IV species; nn(4) gives
c     the number of such species.
         i0 = nn(1) + nn(2) + nn(3) + 1
         ii = i0 + nn(4) - 1
         j = 1
         if (nn(4).gt.0) then
c
c  -- Display the names of up to the first 12 in the TYPE IV list.
           do 500 i = i0, ii
c
             if (j.le.17) then
               j = j + 1
             end if
  500      continue
c
           stringc = '[47;32m'
           blank = '            '
c
c  -- If there are no TYPE IV species, they will have disappeared
c     from the list one by one until there is only one left.  When
c     it too has dissolved, simply blank it's name by writing blanks
c     with the background color.
         else
           stringc = '[47;32m'
           strings(1) = '[13;65H'
           blank = '            '
         end if
      end if
c
```

```
c
c
c
999   RETURN
c
  900 format (a8)
 1001 format(a7,'                                                    ',
     *             '             ',
     *      /a7,'                    CHESP Version 3.11          ',
     *             '             ',
     *      /a7,'            Geotechnical research Centre (GRC) ',
     *             '             ',
     *      /a7,' McGill University, Montreal, Canada ',
     *              'PQ.   30613 ',
     *      /a7,'                                                    ',
     *             '             ')
 1003 format(a8,'         CHESP READING INPUT DATA         ')
 1004 format(a8,'       CALCULATING SATURATION INDICES        ')
 1005 format(a8,'        ---  COMPUTATION ABORTED  ---        ',
     *      /a8,'SEE OUPUT FILE FOR COMPLETE ERROR DIAGNOSTIC ')
 1006 format(a8,'       EQUILIBRATING AQUEOUS SOLUTION        ')
 1008 format(a8,'                                              ',
     *          '                                  ')
 1014 format(a8,'   THE MINERAL ',a12,' HAS DISSOLVED    ')
 1015 format(a8,'  THE MINERAL ',a12,' HAS PRECIPITATED  ')
 1018 format(a8,'    CHESP EXECUTION COMPLETED NORMALLY    ')
 1019 format(a8,' CHESP EXECUTION COMPLETED WITH ',i2,' ERROR',
     *          '  ',
     *      /a8,'SEE OUPUT FILE FOR COMPLETE ERROR DIAGNOSTIC ')
 1020 format(a8,' CHESP EXECUTION COMPLETED WITH ',i2,' ERRORS',
     *          ' ',
     *      /a8,'SEE OUPUT FILE FOR COMPLETE ERROR DIAGNOSTICS')
  616 format(a8,'               ***  ERROR NUMBER ',a7,i2,'  *** ',
     *          '              ')
  620 format(a7,' ITERATION: ',i3,' ')
  625 format(a7,' SWEEP:     ',i3,' ')
  630 format(a7,' PROBLEM:   ',i3,' ')
  621 format(a8,' ITERATION: ',i3,' ')
  626 format(a8,' SWEEP:     ',i3,' ')
  631 format(a8,' PROBLEM:   ',i3,' ')
  635 format(a8,'    SOLIDS:    ')
  640 format(a8,' ',a12,'  ')
c
      END
c(11)*******************************************************************
      subroutine maind
c***********************************************************************
c *******************************************************************
c
c THIS IS THE MAIN DRIVER FOR CHESP. THE PROGRAM IS SET UP TO
c EXECUTE MULTIPLE DATA SETS STORED IN THE SAME FILE. THIS FORMAT
c ALLOWS ALL DATA SETS IN THE FILE TO BE EXECUTED EVEN IF AN
c ERROR OCCURS IN ONE OF THE FILES.
c
c *******************************************************************
c
      include 'CHESP.INC'
c
```

```
c -- THE INCLUDE FILE HAS A PARAMETER STATEMENT THAT SETS BOTH
c    NXDIM AND NYDIM.  (THEIR VALUES DEPEND UPON THE MEMORY
c    CAPACITY OF THE COMPUTER.)  THE INCLUDE STATEMENT ABOVE
c    MUST COME BEFORE THE DIMENSION STATEMENT FOR GK1 SINCE
c    NYDIM IS USED FOR AN ADJUSTABLE ARRAY DIMENSION. 10-14-87 JDA
c
      dimension gk2(nydim)
c
      real*8 gk2
      integer idxx
      character sweep*10, probl ml*1, lastime*1, action*12, state*5
c
      problml = 'y'
      xstop = 'n'
      mprob = 0
      ierr =  0
c
  100 continue
        if (ierr.gt.0.and.ierr.le.7) go to 999
        if (ierr.gt.7) problml = 'y'
        lastime ='n'
c
c
c  -- Call INPUT to initially read the input file for this problem
c     and to read in the appropriate data from database files.  At
c     the conclusion of the current problem, call INPUT again to
c     read the next problem in a multi-problem file, or, failing to
c     find a next problem, transfer control back to program CHESP
c     with XSTOP = 'Y' to stop execution.
      if (problml.eq.'y') then
        iprob = 1
        mprob = mprob + 1
        k1 = 0
        call init
        call input (idxx, sweep)
        if (ierr.ne.0) go to 999
        if (xstop.eq.'y') go to 999
c
c  -- If this is other than the initial problem in a series of
c     problems involving multiple runs at various fixed pH's
c     (but NOT a multi-problem file, rather a single-problem file
c     with a titration operation specified), then call NXTPRB to
c     generate the problem for the next run, or if the previous run
c     was the last run, transfer control back to program CHESP
c     with XSTOP = 'y' to stop execution.
      else
        call nxtprb (idxx, sweep)
        if (xstop.eq.'y') then
           problml = 'y'
           xstop = 'n'
           go to 100
        end if
      end if
c
      if (iprob.eq.1) then
        call prep
        call guess
      end if
```

```
      if (ierr.ne.0) go to 100
      if (isopt.ne.0.and.iprob.eq.1) call actvty
  140 continue
c
c STORE TEMPERATURE CORRECTED LOGK FOR USE EACH ITERATION
c IN SOLID SELECTION LOOP
c
      if (isopt.ne.0) go to 160
      i3 = nn(1)+nn(2)
      do 150 i = 1, i3
         if (iter.eq.0.and.iprob.eq.1) then
            gk2(i) = gk(i)
         else
            gk(i) = gk2(i)
         endif
  150 continue
  160 continue
c
      call solid
      if (ierr.ne.0) go to 100
c
      if (isopt.eq.0) then
         call kcorr2
      end if
c
      call solve
      if (ierr.ne.0) go to 100
c
      call solidx (action,k1)
c
c  -- SOLIDX returns a value of zero for k if no solid precipitated
c     or dissolved.  Thus, if the returned value of k is other than
c     zero, the solution must be re-equilibrated.
      k1 = k1+1
      if (action.ne.'finished    ') go to 140
      lastime = 'y'
      call outcmp
      call outspc (lastime)
      call outpc (lastime)
      state = 'both '
      call iap (state)
      if (isweep.gt.0) probl ml = 'n'
      go to 100
  999 return
c
      end

c(12)*********************************************************************
      subroutine infile (filename,xerr)
c*************************************************************************
c  -- The purpose of this routine is to read the input filename
c     entered by the user in response to the input filename
c     prompt displayed on the screen by Subroutine DISPLAY and
c     OPEN that file is a valid filename is specified.
c     This routine calls ENQUIRE to check on the existence of
c     of the file prior to OPEN.  A code xerr is returned to
c     the calling sub-program (DISPLAY) to indicate whether
c     a good filename was entered or not or if the user
```

```
c     chooses to exit (idicated by entering X).
c
      include 'CHESP.INC'
c
      character xerr*1, filename*12, filenam2*12, msg*1
      logical preexist
      xerr = 'N'
      msg = 'N'
      lun05 = 5
      read (lun05,1100) filename
      if (filename.eq.'x'.or.filename.eq.'X') then
c   --   Return xerr = 'X' to indicate the user's desire to exit
         xerr = 'X'
         go to 999
      end if
      preexist =  .TRUE.
      call enquire (filename,preexist,xerr,scrnout,msg)
c  -- Return xerr = 'Y' to indicate that a bad filename was
c     entered and a "TRY AGAIN" prompt should be issued by DISPLAY.
      if (xerr.eq.'Y') go to 999
c
      open (unit=lun01,file=filename,status='OLD')
c
c
  999 return
 1100 format (a12)
      end
C(13)******************************************************************
      subroutine oufile (filename)
c******************************************************************
c  -- The purpose of this routine is to read the output filename
c     entered by the user in response to the oyput filename
c     prompt displayed on the screen by Subroutine DISPLAY and
c     OPEN that file.  the filename is passed back to the
c     calling subprogram.
c
      include 'CHESP.INC'
c
      character filename*12
c
      lun05 = 5
      read (lun05,1100) filename
      return
 1100 format (a12)
      end
c(14)*******************************************************************
      subroutine delay (isec)
c******************************************************************
c  -- The purpose of this subroutine is to provide a means of
c     delaying execution of the calling program for "isec"
c     seconds.  The method used is to make an initial call
c     to GETTIM, convert the hours, minutes, seconds returned
c     to total seconds, then to make repeated calls to that same
c     routine and, after a similar conversion, to difference the
c     two total seconds.  Stop calling GETTIM and return to the
c     calling program when the absolute value of the difference
c     exceeds the requested delay time, isec.
c
```

```
c  -- The VAX and PC versions of this routine are different. This
c     is the PC version.
c
      integer*2  hr, mn, sc, hd, isec, tsec1, tsec2, tdiff
c
      call gettim(hr,mn,sc,hd)
      tsec1 = hr*3600 + mn*60 + sc
c
   10 call gettim(hr,mn,sc,hd)
      tsec2 = hr*3600 + mn*60 + sc
      tdiff = abs(tsec1-tsec2)
      isec = abs(isec)
      if (tdiff.lt.isec) go to 10
c
      return
      end
c(15)*******************************************************************
      subroutine input (idxx, sweep)
c*********************************************************************
c SUBROUTINE INPUT REQUIRES 4 INPUT FILES
c  FILE LUN01. CONTAINS THE RUN SPECIFIC INFORMATION(WATER ANALYSIS)
c  FILE LUN02. CONTAINS THERMODYNAMIC DATA FOR ALL SPECIE TYPES EXCEPT
c              TYPE 6 SOLIDS
c  FILE LUN03. CONTAINS A LIST OF ALL ACCEPTED COMPONENTS AND THE
c            NECESSARY AUXILLARY THERMODYNAMIC DATA
c  FILE LUN04. CONTAINS THE THERMODYNAMIC DATA FOR ALL TYPE 6 SOLIDS
c
c
c  SUBROUTINE INPUT PERFORMS THE FOLLOWING FUNCTIONS
c            1. READS SAMPLE DESCRIPTION AND COMPONENT INFORMATION FR
c               FILE LUN01. THIS SECTION OF FILE LUN01. ENDS WITH A BLA
c            2. READS FILE LUN03. AND FINDS A MATCH BETWEEN ALL COMPON
c               IN THE INPUT STREAM
c            3. READS FILE LUN02. AND STORES ALL SPECIES WHICH HAVE AL
c               NECESSARY COMPONENTS IN THE SAMPLE INPUT(FILE 11.)
c            4. READS FILE LUN01. FOR ALL TYPE,LOGK,OR DH CHANGES TO T
c               EXISTING THERMODYNAMIC DATA STORED FROM FILE LUN02.
c            5. IF THE SPECIE ID IS A TYPE 6 SOLID THEN THE INFORMATI
c               READ IN DURING OPERATION (4)ABOVE IS STORED IN DUMMY
c               UNTIL THE TYPE 6 SOLIDS FILE IS READ. THIS REQUIRES R
c               THE TYPE 6 SOLIDS FILE ONLY ONCE.
c            6. THE INFORMATION FOR INSERTED SPECIES NOT IN THE DATA
c               IS READ FROM FILE LUN01.
c
c THE THERMODYNAMIC DATA FOR TYPE 6 SOLIDS WAS STORED IN A SEPARATE F
c ELIMINATE THE NEED TO INCREASE THE SIZE OF THE A AND B MATRICIES.TH
c MINEQL CODE OF JOHN WESTALL STORED THE STOICHIOMETRY FOR ALL SPECIE
c THE A AND B MATRICIES.THIS PROCEDURE REQUIRED MODIFICATION BECAUSE
c LARGE NUMBER OF SOLIDS IN THE WATEQ3 AND WATEQ4 DATA BANKS.
c
c !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
c %%INPUT              CORRECTION HISTORY
c !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
c  DATE                     CORRECTION
c 10-10-87    CHANGED FORMAT STATEMENTS 500, 502, 503, 504 TO USE
c             E10.3 AND F7.2 FOR READING CONCENTRATIONS AND ACTIVITIES
c             AND EQUILIBRIUM CONSTANTS AND ENTHALPIES.
c
```

```
c             CHANGED TO STOP WRITING MODIFICATION HISTORY TO OUTPUT
c             FILE.
c !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
c
      include 'CHESP.INC'
c
      dimension idt(12),at(12),gkdum(100),ifnd(100),ityp(100),
     *          dhdum(100),bt(3),ibt(3),cdum(100)
c
      character spcnam*12, acteq*21 ,adsmodel*20, sweep*10, insh2o*1,
     *          rgt*1, match*1
      character*75 desc,carry
      real*8 alkft,conc,dht,gkt,gxt,mingkt,maxgkt,spcdh,spcdha,spcdhb,
     *       spcgfw,spz,tt,atmp1,atmp2,atmp3,atmp4
      real*8 at,bt,cdum,dhdum,gkdum,startval,valinc
c
      real lines
      integer isurf, jsurf, idxx, ierparm, nlines
c
      include 'CONST.INC'
      call display (3)
c
      sweep = '          '
      idxx = 0
c  -- Initialize flag indicating whether H2O has been inserted as a
c     component to no ('n').
      insh2o = 'n'
c
      do 100 j = 1, 100
         idydum(j) = 0
  100 continue
c
c     INPUT PROBLEM DATA
c READ SAMPLE DESCRIPTION,TEMPERATURE AND UNITS
c
      read (lun01,9000,end=110) desc
      go to 120
 110  call display (18)
      xstop = 'y'
      go to 999
c
  120 read (lun01,9000) carry
c
      write (lunout,5700) 1
      call tstamp
c
      write (lunout,9130) desc
      write (lunout,9140) carry
c
c
      read (lun01,9010) temp,flag,fions
c
      tempk = temp+273.16d0
      units = flag
c
c  -- Compute the temperature dependent term for the Van't Hoff
c     correction used in FUNCTION VHOFF.
      vh = (298.16d0-tempk)/(298.16d0*tempk*vhc*r)
```

```
c
c  -- Read the sequence of integers in the input file.  These are
c     various program flags.
      read (lun01,9210) icoralk,idebug,icharg,iprint,niter,iparm,isopt
     *   ,iprdct,kkdav,kkthr,isweep,n123,ntyp123
c
c  -- So far, 4 lines have been read from the input file.
      ierparm = 4
c
c  -- Write the interpretation of the flags to the output file.
      write (lunout,9250) temp,flag
      if (isopt.eq.0) then
         write (lunout,9260)
      else
         write (lunout,9270) fions
      endif
      if (icoralk.eq.0) then
         write (lunout,9280)
      elseif (icoralk.eq.1) then
         write (lunout,9290)
      endif
      if (icharg.eq.0) then
         write (lunout,9310)
      else
         write (lunout,9300)
      endif
      if (iprint.eq.0) then
         write (lunout,9320)
      else
         write (lunout,9330) iprint
      endif
      if (niter.eq.0) then
         itmax = 40
      elseif (niter.eq.1) then
         itmax = 10
      elseif (niter.eq.2) then
         itmax = 100
      elseif (niter.eq.3) then
         itmax = 200
      elseif (niter.eq.4) then
         itmax = 500
      endif
      write (lunout,9340) itmax
      if (kkdav.eq.0) then
         acteq = 'Debye-Huckel equation'
      else
         acteq = 'Davies equation      '
      endif
      write (lunout,9350) acteq
      if (kkthr.eq.0) then
         write (lunout,9360)
      else if (kkthr.eq.1) then
         write (lunout,9365)
      else if (kkthr.eq.2) then
         write (lunout,9370)
      endif
c
c  -- The isweep flag indicates whether this is a sweep run (isweep=1)
```

```
c     or not (isweep=0).  Proceed to read sweep parameters if it is.
      if (isweep.eq.1) then
        read (lun01,9211) sweep, idxx, nprob
        ierparm = ierparm + 1
        if (sweep.eq.'activity  '.or.sweep.eq.'ACTIVITY  ') then
          sweep = 'ACTIVITY  '
          read (lun01,9212) valinc
          ierparm = ierparm + 1
        else if (sweep.eq.'total conc'.or.sweep.eq.'TOTAL CONC') then
          sweep = 'TOTAL CONC'
          read (lun01,9214) valinc
          ierparm = ierparm + 1
        end if
      else if (isweep.eq.2) then
        read (lun01,9211) sweep, idxx, nprob
        ierparm = ierparm + 1
        if (sweep.eq.'activity  '.or.sweep.eq.'ACTIVITY  ') then
          sweep = 'ACTIVITY  '
          read (lun01,9213) (uvalue(i),i=2,nprob)
          lines = float((nprob-1))/6.0
          nlines = lines
          if ((lines-float(nlines)).gt.0.0) nlines = nlines+1
          ierparm = ierparm + nlines
        else if (sweep.eq.'total conc'.or.sweep.eq.'TOTAL CONC') then
          sweep = 'TOTAL CONC'
          read (lun01,9215) (uvalue(i),i=2,nprob)
          lines = float((nprob-1))/6.0
          nlines = lines
          if ((lines-float(nlines)).gt.0.0) nlines = nlines+1
          ierparm = ierparm + nlines
        end if
      end if
c
c  -- The n123 flag indicates the number of components for special
c     spreadsheet-type output (n123=0 if none).  If n123>0, proceed
c     to read the relevant parameters from the input file.
      if (n123.ne.0) then
        read (lun01,9800) fil123, (id123(i),i=1, n123)
        ierparm = ierparm + 1
        open (unit=lun11,file=fil123,status='unknown')
      end if
c
c  -- Read next line from input file.  This line pertains to whether
c     adsorption is to be modeled, the number of adsorbing surfaces,
c     and a number identifying the adsorption model.
      read (lun01,9220) iads,numads,iabq
c modification1
      IF((C4-c4s)/c4.le.001) idas=0.0d0
      ierparm = ierparm+1
      if (iads.gt.0) then
         if (iabq.eq.1) then
            adsmodel = 'Activity Kd          '
         elseif (iabq.eq.2) then
            adsmodel = 'Activity Langmuir    '
         elseif (iabq.eq.3) then
            adsmodel = 'Activity Freundlich '
         elseif (iabq.eq.4) then
            adsmodel = 'Ion - Exchange       '
```

```
         elseif (iabq.eq.5) then
            adsmodel = 'Constant Capacitance'
         elseif (iabq.eq.6) then
            adsmodel = 'Triple Layer        '
         elseif (iabq.eq.7) then
            adsmodel = 'Diffuse Layer       '
         endif
         write (lunout,9380) adsmodel
         write (lunout,9390) numads
      endif
      write (lunout,9400)
c
c -- If the number of adsorbing surfaces (numads)  > 0, then the next
c    "numads" lines each has parameters relevant to one surface.
      if (numads.gt.0) then
         do 130 i = 1, numads
            read (lun01,9230) atmp1, atmp2, atmp3, atmp4, isurf
            ierparm = ierparm+1
            jsurf = isurf - 80
            solcon(jsurf) = atmp1
            ssa(jsurf) = atmp2
            cap1(jsurf) = atmp3
            cap2(jsurf) = atmp4
            write (lunout,9240) solcon(jsurf), ssa(jsurf), cap1(jsurf),
     *                          cap2(jsurf), isurf
c
c -- Interpret the surface specific parameters in reference to
c    the selected adsorption model and check that all parameters
c    relative to that model have been input.
            if (iads.gt.1) then
               if (solcon(jsurf).lt.DOMIN.or.ssa(jsurf).lt.DOMIN) then
                  write (lunout,9700) ierparm
                  ierr = 4
                  call error
                  go to 999
               end if
               if (iads.eq.2.or.iads.eq.3) then
                  if (dabs(cap1(jsurf)).lt.DOMIN) then
                     write (lunout,9700) ierparm
                     ierr = 4
                     call error
                     go to 999
                  end if
               endif
               if (iads.eq.3) then
                  if (dabs(cap2(jsurf)).lt.DOMIN) then
                    write (lunout,9700) ierparm
                    ierr = 4
                    call error
                    go to 999
                  end if
               endif
            endif
c
  130    continue
      endif
c
c  -- Read the component id number, total dissolved concentration,
```

```
c     log free activity guess, and flag indicating whether CHESP
c     is allowed to adjust the guess prior to beginning the iterations.
c     This adjustment is not the same as estimating the new log
c     activity with each succeeding iteration-- that will certainly
c     be done.  The guess that is the subject of a possible
c     re-adjustment here is the INITIAL guess before iterations begin.
c     A better guess here means a faster and more certain convergence.
      j = 0
  140 read (lun01,9020) idxt,tt,gxt,rgt
      if (idxt.eq.0) go to 150
c
c  -- If this is a sweep run, check whether this is the sweep component.
      if (isweep.gt.0) then
        if (idxt.eq.idxx) then
          if (sweep.eq.'TOTAL CONC') then
             startval = tt
          end if
        end if
      end if
c
      write (lunout,9030) idxt,tt,gxt,rgt
      j = j+1
      idx(j) = idxt
      gx(j) = gxt
      t(j) = tt
c  -- Any value other than no (n or N) (including no value at all) is
c     interpreted as yes (y) for the flag indicating whether its it OK
c     to adjust the log free activity guess in subroutines GUESS and
c     GUESS1 prior to beginning the iterations.
      if (rgt.eq.'N') rgt = 'n'
      if (rgt.eq.'n') then
        reguess(j) = 'n'
      else
        reguess(j) = 'y'
      end if
c  -- For components not accompanied by an activity guess at all,
c     make an initial guess of free activity = total conc.  Note
c     that this is not the adjustment referred to above.
      if (dabs(gxt).lt.DOMIN) then
         x(j) = 1.0d0
      else
         x(j) = 10.0d0**gxt
      endif
c
c--  Go back to read the next component in the input file.
      go to 140
c Modification starts from here
 150  ic=j
      do 1900 i= 1, ic
      if (idx(i).eq.id123(1)) then
      t(i)=C1
      endif
      if (idx(i).eq.id123(2)) then
      t(i)=C2
      endif
      if (idx(i).eq.id123(3)) then
      t(i)=C3
      endif
```

```
      if (idx(i).eq.id123(4)) then
      t(i)=C4
      endif
      if (idx(i).eq.id123(5)) then
      t(i)=C5
      endif
c     write(*,*)c1,id123(1),'cl',c2,id123(2),'zn',c3,id123(3),'pb'
c    *,' concenteration'
 1900 continue
c end of modification
c  150 continue
c
c  -- Insert H2O as a component and reset insh2o to yes ('y').
c
      ii = j
      do 190 i = 1, ii
         if (idx(i).eq.2) go to 200
  190 continue
      ii = ii+1
      insh2o = 'y'
      idx(ii) = 2
      gx(ii) = 0.d0
      t(ii) = 0.d0
      x(ii) = 1.d0
      write (lunout,9160)
  200 continue
      j = ii
      if (j.gt.nxdim) then
        ierr = 1
        call error
        go to 999
      end if
      nnn = j
c
c     INITIALIZE NN
c
      do 210 l = 1, 6
         nn(l) = 0
  210 continue
c
c     INITIALIZE A,B
c
      do 220 i = 1, nydim
         do 220 j = 1, nxdim
            b(i,j) = 0.0d0
            a(i,j) = 0.0
  220 continue
c
c MAKE SURE ALL INPUT SPECIES ARE VALID COMPONENTS
c
      jj = nnn
      numfnd = 0
c
      do 250 i = 1, jj
         rewind lun03
c
c -- CHANGED UPPER BOUND ON LOOP 221 FROM 73 TO 200 ON 10-12-87 JDA
c
```

```
         do 230 l = 1, 200
            read (lun03,9090,end=260) idyt,spcnam,spz,spcdha,spcdhb,
     *         spcgfw
            if (idyt.eq.idx(i)) then
               numfnd = numfnd+1
               name(i) = spcnam
               spcz(i) = spz
               dha(i) = spcdha
               dhb(i) = spcdhb
               gfw(i) = spcgfw
c
c INCLUDE COMPONENTS AS SPECIES
c
               idy(i) = idx(i)
               a(i,i) = 1.0
               gk(i) = 0.0d0
               dh(i) = 0.d0
               maxgk(i) = 0.0
               mingk(i) = 0.0
               go to 240
            endif
  230    continue
  240    continue
  250 continue
  260   if (numfnd.ne.jj) then
          ierparm = ierparm+numfnd+1
          write (lunout,9710) idx(i),ierparm
          ierr = 6
          call error
          go to 999
        end if
      if (insh2o.eq.'y') then
        ierparm = ierparm+jj
      else
        ierparm = ierparm+jj+1
      end if
c
      nn(1) = nnn
c
c INPUT THERMODYNAMIC DATA FOR Composite ligand species
c
      i = nn(1)
      nn(2) = 0
      rewind lun14
      i0 = i
  271 read(lun14,9080,end=301)idyt,spcnam,spcdh,gkt,maxgkt,mingkt,spz,
     *      spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),idt(j),j=1,ncmp)
c
c
         if (idyt.eq.0) go to 301
c
c
c CHECK TO INSURE ALL COMPONENTS INCLUDED
c
         do 281 j = 1, ncmp
            if (iadx(idt(j)).eq.0) go to 271
  281    continue
         i = i+1
```

```
          if (i.gt.nydim) then
            ierr = 2
            call error
            go to 999
          end if
c
c    ASSIGN PARAMETERS FOR COMPLEX (I)
c
          idy(i) = idyt
          gk(i) = gkt
          dha(i) = spcdha
          dhb(i) = spcdhb
          gfw(i) = spcgfw
          spcz(i) = spz
          dh(i) = spcdh
          name(i) = spcnam
          maxgk(i) = maxgkt
          mingk(i) = mingkt
          alkfct(i) = alkft
c
          do 291 m = 1, ncmp
             a(i,iadx(idt(m))) = at(m)
  291     continue
c
c  -- Provide special operations for species that represent
c     complexes with composite ligands.
c  -- First find out if the species read in is a complex involving
c     a composite ligand.  If so, set up the "b" matrix elements
c     for mass balance stoichiometries.
c  -- The mass balance stoichiometry for each component in the
c     reaction is equal to the mass action stoichiometry of that
c     component.
          id1 = idclf*10000
          id2 = idcll*10000 + 9999
          if (idyt .ge. id1 .and. idyt .le. id2) then
c11-08a NOTE: The stoichiometry elements in the database are actually
c         for mass balance, though they are read into array a.  Therefore,
c         they are loaded into array b in the usual place below, i.e.,
c         b = a.
c       We are assuming one composite ligand component per run.
c       Sigma is approximately the same for all components for a given
c       composite ligand.  However, provision is made for the more
c       general case of a sigma specific to each reaction which is
c       stored in the reaction entry in those spaces ordinarily used for
c       enthalpy (dh).  The variable nrxcl counts the number of reactions
c       involving the complex ligand.
            nrxcl = nrxcl + 1
c  -- Store the 7-digit id of the reaction in array idrxcl.
            idrxcl(nrxcl) = idyt
            gkcl(nrxcl) = gkt
c  -- The value entered for enthalpy of reaction (dh) in the database
c     is actually sigma for this entry and the value of dh is unknown
c     so make it equal zero.
            sigma = dh(i)
            dh(i) = 0.0d0
            do 292 m = 1, ncmp
              if (idt(m).ge.idclf.and.idt(m).le.idcll) then
                jxlig = iadx(idt(m))
```

```
             else if (idt(m).ne.002) then
               if (nidxcl.eq.0) then
                 nidxcl = 1
                 idxcl(nidxcl) = idt(m)
               else
                 match = 'N'
                 do 293 n = 1, nidxcl
                   if (idt(m).eq.idxcl(n)) match = 'Y'
  293            continue
                 if (match.eq.'N') then
                   nidxcl = nidxcl + 1
                   idxcl(nidxcl) = idt(m)
                 end if
               end if
               do 294 n = 1, nidxcl
                if (idt(m).eq.idxcl(n)) stoica(nrxcl,n) = at(m)
  294          continue
             end if
  292      continue
         end if
c
c  READ DATA FOR NEXT SPECIES
c
         go to 271
c
c  -- Set up pointer array for composite species.
c     jmax(i) stores the number of non-zero elements of array "stoica"
c     for species i.  jpta(i,j) stores the column number address of
c     the jth component which has non-zero stoichiometry in species i.
 301  do 302 icl = 1, nrxcl
        jmaxcl(icl) = 0
        do 303 jcl = 1, nidxcl
          if (abs(stoica(icl,jcl)).gt.0.0) then
           jmaxcl(icl) = jmaxcl(icl) + 1
           jptacl(icl,jmaxcl(icl)) = jcl
          endif
 303    continue
 302  continue
c
c
c
         nn(2) = i-i0
c INPUT THERMODYNAMIC DATA FOR ALL SPECIES EXCEPT TYPE 6 SOLIDS
c
      i = nn(1) + nn(2)
      rewind lun02
      do 310 l = 2, 6
         i0 = i
  270    read (lun02) idyt,spcnam,spcdh,gkt,maxgkt,mingkt,spz,
     *      spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),idt(j),j=1,ncmp)
c
c READ NEXT GROUP OF THERMODYNAMIC DATA: NOTE DEFAULT GROUPS
c FOR THERMODYNAMIC DATA MUST BE SEPARATED BY TWO BLANK LINES
c IN THE THERMODYNAMIC DATA FILE ALSO THERE MUST BE TWO
c BLANK LINES AT THE END OF THE FILE OR YOU WILL HIT  AN
c END OF FILE CONDITION
c
         if (idyt.eq.0) go to 300
```

```
c
c IF IPRINT=0 DO NOT STORE DATA FOR TYPE 5 FROM FILE LUN02
c
        if (iprint.eq.0.and.l.eq.5) go to 270
c
c CHECK TO INSURE ALL COMPONENTS INCLUDED
c
        do 280 j = 1, ncmp
           if (iadx(idt(j)).eq.0) go to 270
  280   continue
        i = i+1
        if (i.gt.nydim) then
          ierr = 2
          call error
          go to 999
        end if
c
c   ASSIGN PARAMETERS FOR COMPLEX (I)
c
        idy(i) = idyt
        gk(i) = gkt
        dha(i) = spcdha
        dhb(i) = spcdhb
        gfw(i) = spcgfw
        spcz(i) = spz
        dh(i) = spcdh
        name(i) = spcnam
        maxgk(i) = maxgkt
        mingk(i) = mingkt
        alkfct(i) = alkft
c
        do 290 m = 1, ncmp
           a(i,iadx(idt(m))) = at(m)
  290   continue
c
c
c  READ DATA FOR NEXT SPECIES
c
        go to 270
c
  300   nn(l) = nn(l) + i-i0
  310 continue
c
c     READ SPECIES MODIFICATION & TYPE SPECIFICATIONS
      fxdph = 'n'
      fxdph = 'n'
c
      entry intype
      k = 0
  320 read (lun01,9060) ltype,ntype
      ierparm = ierparm + 1
      if (ltype.eq.0) go to 360
      write (lunout,9070) ltype,ntype
      if (ltype.gt.6) then
c  -- The error parameter will contain the line number in the input
c     file where the LTYPE greater than six occurs.
        write (lunout,9700) ierparm
        ierr = 5
```

```
          call error
          go to 999
        end if
        do 350 n = 1, ntype
           conc = 0.0d0
           if (ltype.eq.4) then
              read (lun01,9040) idyt,gkt,dht,conc
              ierparm = ierparm+1
              write (lunout,9050) idyt,gkt,dht,conc
           else
              read (lun01,9045) idyt,gkt,dht
              ierparm = ierparm+1
              write (lunout,9055) idyt,gkt,dht
              if (idyt.eq.001) then
                 fxdpe = 'y'
                 systempe = gkt
              end if
              if (idyt.eq.330) then
                 fxdph = 'y'
                 systemph = gkt
              end if
           endif
c
           if (ltype.eq.3.and.isweep.gt.0) then
             if (sweep.eq.'ACTIVITY') then
               if (idyt.eq.idxx) then
                 startval = gkt
               end if
             end if
           end if
c
c     SEARCH
c
           ii = 0
           do 340 l = 1, 6
              if (nn(l).eq.0) go to 340
              i0 = ii+1
              ii = ii+nn(l)
              do 330 i = i0, ii
                 if (idy(i).ne.idyt) go to 330
                 if (dabs(gkt).gt.DOMIN) gk(i) = gkt
                 if (dabs(dht).gt.DOMIN) dh(i) = dht
                 if (dabs(conc).gt.DOMIN) c(i) = conc
c  -- If the type modification is to fix the activity of some
c     component other than H2O or E-, that is, to make that component
c     TYPE 3, then call Subroutine DUPCMP to first duplicate it as a
c     TYPE 1 component.  Upon return from DUPCMP, call Subroutine
c     SWITCH to MOVE one of the two identical entries to TYPE 3.
c     In this way, the TYPE 1 identity of the component is retained.
                 if(idyt.le.999.and.idyt.gt.2.and.ltype.eq.3) then
                   idnew = idyt
                   call dupcmp (idnew,i)
                 end if
                 call switch (l,ltype,i)
                 go to 350
  330         continue
  340      continue
c
```

```
c SEARCH UNSUCCESSFUL: STORE DATA FOR ONE LOOP THROUGH TYPE 6 FILE
c
         k = k+1
         dhdum(k) = dht
         idydum(k) = idyt
         gkdum(k) = gkt
         cdum(k) = conc
         ityp(k) = ltype
         ifnd(k) = 0
  350 continue
      go to 320
c
c LOOP THROUGH TYPE 6 SOLIDS FILE ONLY ONCE
c
  360 ii = k
      if (ii.eq.0) go to 430
      kount = 0
      rewind lun04
  370 read (lun04) idytnw,spcnam,spcdh,gkt,maxgkt,mingkt,spz,
     *   spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),idt(j),j=1,ncmp)
c
c IF ENTIRE FILE READ PRINT THE SPECIES WHICH DID NOT
c MATCH THEN TERMINATE EXECUTION
c
      if (idytnw.eq.0) then
         do 380 j = 1, ii
            if (ifnd(j).eq.1) go to 380
            write (lunout,9720) idydum(j)
            ierr = 3
            call error
            go to 999
  380    continue
      endif
c
c LOOP THROUGH ALL STORED SPECIES
c
      do 410 i = 1, ii
         if (idytnw.ne.idydum(i)) go to 410
c
c CHECK TO INSURE ALL COMPONENTS PRESENT
c
         do 390 m = 1, ncmp
            if (iadx(idt(m)).ne.0) go to 390
            write (lunout,9180) idytnw,idt(m)
            ifnd(i) = 1
            go to 420
  390    continue
         i0 = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)+1
         idy(i0) = idytnw
         gk(i0) = gkdum(i)
         if (dabs(gk(i0)).lt.DOMIN) gk(i0) = gkt
         dha(i0) = spcdha
         dhb(i0) = spcdhb
         gfw(i0) = spcgfw
         spcz(i0) = spz
         dh(i0) = dhdum(i)
         if (dabs(dh(i0)).lt.DOMIN) dh(i0) = spcdh
         if (cdum(i).gt.DOMIN) c(i0) = cdum(i)
```

```
         name(i0) = spcnam
         maxgk(i0) = maxgkt
         mingk(i0) = mingkt
         alkfct(i0) = alkft
         do 400 m = 1, ncmp
            a(i0,iadx(idt(m))) = at(m)
  400    continue
         ifnd(i) = 1
         nn(6) = nn(6)+1
         l = 6
         ltype = ityp(i)
         call switch (l,ltype,i0)
         go to 420
  410 continue
      go to 370
c
c NOW INCREASE COUNTER OF FOUND SPECIES AND CHECK TO
c SEE IF ALL WERE FOUND
c
  420 kount = kount+1
      if (kount.eq.ii) then
         rewind lun04
         go to 430
      endif
      go to 370
c
c    SETUP B MATRIX
c
  430 continue
c
      i0 = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      do 440 i = 1, i0
        do 440 j = 1, nnn
            b(i,j) = a(i,j)
            if (idy(i).ge.idl.and.idy(i).le.id2) then
            a(i,j) = 0.0
           end if
  440 continue
c////////////////////////////////////////////////////////
c      i0 = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
c      do 440 i = 1, i0
c        do 440 j = 1, nnn
c            b(i,j) = a(i,j)
c  440 continue
ccllllllllllllllllllllllllllllllllllllllllllllllllllllllll
c      do 339 i = 1, i0
c         if (idy(i).eq.1452110) then
c         write (lunout,*) idy(i)
c        do 338 j = 1, nnn
c            write (lunout,*) idx(j),'  A= ', a(i,j),' B= ',b(i,j)
c  338    continue
c         end if
c  339 continue
cllllllllllllllllllllllllllllllllllllllllllllllllllllllll
c      do 441 i = 1, i0
c         if (idy(i).ge.2400000.and.idy(i).le.2499999) then
c           ii = iady(330)
cc         if (idy(i).ge.2570000) kk = iadx(330)
```

```
c           do 442 j = 1, nnn
c             if (a(i,j).ne.0.0) then
c              if (idx(j).ge.240.and.idx(j).le.249) then
c                  jj = j
c               else if (idx(j).ne.330.and.idx(j).ne.002) then
c                  ii = iady(idx(j))
c               end if
c             end if
c 442       continue
c           b(i,jj) = abs(spcz(ii))
cc          if (idy(i).ge.2570000) b(i,kk) = -b(i,jj)
c         end if
c 441  continue
c///////////////////////////////////////////////////////////
c      do 443 i = 1, i0
c         if (idy(i).eq.1452110) then
c         write (lunout,*) idy(i)
c        do 444 j = 1, nnn
c            write (lunout,*) idx(j),'  A= ', a(i,j),' B= ',b(i,j)
c  444    continue
c         end if
c  443 continue
c  CHECK FOR INSERTION OF SPECIES NOT IN DATA BASE
c
      kount = 0
  450 continue
      read (lun01,9060) ltype,ntype
      ierparm = ierparm + 1
c
c TERMINATE INPUT STREAM
c
      if (ltype.eq.0) go to 510
      if (ltype.gt.6) then
c  -- The error parameter will contain the line number in the input
c     file where the LTYPE greater than six occurs.
        write (lunout,9700) ierparm
        ierr = 5
        call error
        go to 999
      end if
      write (lunout,9070) ltype,ntype
      do 500 n = 1, ntype
c
c 5/12/83 KRUPKA CHANGED NUMBER OF MAX COMPONENTS IN REACTION
c          FOR NEW SPECIES OR SOLID FROM 9 TO 12; ALSO
c          CHANGED  DIM OF ARRAY 'AT' AND 'IDT' AND FORMAT 570
c
         read (lun01,9190) idyt,spcnam,spcdh,gkt,maxgkt,mingkt,spz,
     *      spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),idt(j),j=1,12),
     *      nbcmp,(bt(j),ibt(j),j=1,3)
         write (lunout,9200) idyt,spcnam,spcdh,gkt,maxgkt,mingkt,spz,
     *      spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),idt(j),j=1,12),
     *      nbcmp,(bt(j),ibt(j),j=1,3)
c
c A BLANK CARD INITIATES CHECK FOR INSERTED SPECIES
c ***NOTE: IT TAKES 2 BLANK CARDS IN A ROW TO TERMINATE INPUT STREAM
c
c
```

```
c CHECK TO INSURE ALL COMPONENTS OF INSERTED SPECIE ARE PRESENT
c
        do 460 j = 1, ncmp
           if (iadx(idt(j)).ne.0) go to 460
           write (lunout,9100) idyt
           go to 500
  460   continue
c
c SEARCH MEMORY FOR DUPLICATE ID NUMBERS
c NOTE: THIS SEARCH DOES NOT INCLUDE TYPE 6 SOLIDS
c THE ID NUMBERS NOT FOUND IN MEMORY WILL BE
c STORED AND COMPARED AGAINST THE TYPE 6 SOLIDS
c FILE WHEN TYPE 6 SOLIDS ARE READ IN SUBROUTINE IAP
c
        ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
        do 470 m = 1, ii
           if (idy(m).ne.idyt) go to 470
           write (lunout,9110) idyt
           go to 500
  470   continue
c
c NOW STORE ID NUMBERS FOR LATER SEARCH IN SUBROUTINE IAP
c
        kount = kount+1
        idydum(kount) = idyt
c
c INSERT SPECIE FROM INPUT SAMPLE FILE
c
        i = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)+1
        if (i.gt.nydim) then
          ierr = 2
          call error
          go to 999
        end if
        idy(i) = idyt
        gk(i) = gkt
        dha(i) = spcdha
        dhb(i) = spcdhb
        gfw(i) = spcgfw
        spcz(i) = spz
        dh(i) = spcdh
        name(i) = spcnam
        maxgk(i) = maxgkt
        mingk(i) = mingkt
        alkfct(i) = alkft
c
        do 480 j = 1, ncmp
           jp = iadx(idt(j))
           a(i,jp) = at(j)
           b(i,jp) = at(j)
  480   continue
c
c NOW CORRECT B MATRIX
c
        if (nbcmp.gt.0) then
           do 490 j = 1, nbcmp
              b(i,iadx(ibt(j))) = bt(j)
  490      continue
```

```
         endif
c
         l = 6
         nn(6) = nn(6)+1
c
c NOW SWITCH TYPES IF NECESSARY
c
         call switch (l,ltype,i)
  500 continue
      go to 450
c
  510 continue
c
c CHANGE S(0) AND H2O TO TYPE 3
c
      i = iady(2)
      l = 1
      ltype = 3
      call switch (l,ltype,i)
c
c
c OUTPUT DATA AFTER ALL INSERTIONS AND TYPE CHANGES
c
      if (isweep.eq.1) then
        do 128 i = 1, nprob
          uvalue(i) = startval + (i-1) * valinc
  128   continue
      else if (isweep.eq.2) then
        uvalue(1) = startval
      end if
      if (isweep.gt.0) then
        write (lunout,5750) 1
        call tstamp
        write (lunout, 9400)
        write (lunout, 9401)
        write (lunout, 9216) nprob
        if (sweep.eq.'ACTIVITY  ') then
          if (idxx.eq.330) then
            write (lunout, 9217)
          else if (idxx.eq.001) then
            write (lunout, 9218)
          else
            write (lunout, 9219) idxx
          end if
          write (lunout, 9222) (uvalue(i),i=1,nprob)
        else
          write (lunout, 9221) idxx
          write (lunout, 9223) (uvalue(i),i=1,nprob)
        end if
        write (lunout, 9224)
        write (lunout, 9401)
        write (lunout, 9400)
      end if
      call oincmp
      if (kkthr.eq.0) call oinspc
c
c     close(1)
c       open (unit=lun01,file='minin.dat',status='unknown')
```

```
  999 return
c
 9000 format (a75)
 9010 format (f5.2,1x,a5,1x,f6.3,1x,f7.4)
 9020 format (i7,1x,e10.3,1x,f7.2,1x,a1)
 9030 format (' ',i7,1x,1pe10.3,1x,0pf7.2,1x,a1)
 9040 format (i7,2(2x,f9.4),2x,e10.3)
 9050 format (' ',i7,2(2x,f9.4),2x,1pe10.3)
 9045 format (i7,2(2x,f9.4))
 9055 format (' ',i7,2(2x,f9.4))
 9060 format (i3,1x,i3)
 9070 format (' ',i3,1x,i3)
 9080 format (i7,1x,a12,2f10.4,2f8.3,3f5.2,f9.4/f5.2,1x,i1,3x,5(f7.3,
     *   1x,i3,3x))
 9090 format (i3,1x,a8,f4.1,4x,f5.2,f5.2,8x,f11.5)
 9100 format ('0','Not all of the required components for species: ',
     *   i7,' are present.  SPECIES IGNORED')
 9110 format ('0','There is a species in the thermodynamic database',
     *             ' with this same id: ',i7,
     *           /,' SPECIES IGNORED')
 9130 format ('0',a75)
 9140 format (' ',a75)
 9160 format ('0',' H2O has been inserted as a COMPONENT')
 9180 format ('0','Species ',i7,' WITH TYPE CHANGE WAS A',
     *   ' TYPE 6 SOLID AND COMPONENT ',i3,' WAS NOT INPUT',
     *   ' :SPECIE IGNORED')
 9190 format (i7,1x,a12,2f10.4,2f8.3,3f5.2,f9.4/f5.2,i2,1x,6(f7.3,1x,
     *   i3,1x)/6(f7.3,1x,i3,1x)/i1,3(f7.3,1x,i3,1x))
 9200 format (' ',i7,1x,a12,2f10.4,2f8.3,3f5.2,f9.4/f5.2,i2,1x,6(f7.3
     *   ,1x,i3,1x)/6(f7.3,1x,i3,1x)/i1,3(f7.3,1x,i3,1x))
 9210 format (13(i1,1x))
 9211 format (a10,1x,i3,1x,i2)
 9212 format (f6.2)
 9213 format (6(1x,f6.2))
 9214 format (e10.3)
 9215 format (6(1x,e10.3))
 9216 format (' ----------- THE INPUT DATA WILL BE USED IN A SERIES ',
     *         'OF ',i2,' SWEEPS ------------',
     *        /'   The input parameters for each sweep will',
     *         ' be identical to this initial',
     *        /'   listing except that:')
 9217 format ('   --  The fixed equilibrium pH in successive sweeps',
     *         ' will be: ')
 9218 format ('   --  The fixed equilibrium pe in successive sweeps',
     *         ' will be: ')
 9219 format ('   --  The fixed equilibrium log activity of ',
     *         ' component number ',i3,' in',
     *        /'       successive sweeps will be: ')
 9221 format ('   --  The total dissolved concentration of ',
     *         ' component number ',i3,' in',
     *        /'       successive sweeps will be: ',e10.3)
 9224 format ('   --  After the first sweep, the initial',
     *         ' component activity guesses',
     *       /,'       for each successive sweep are the equilibrium' ,
     *         ' activities computed at the',
     *       /,'       end of the sweep which precedes it.')
 9222 format (6x,6(1x,f6.2),3(/,6x,6(1x,f6.2)))
 9223 format (6x,6(1x,1pe10.3),3(/,6x,6(1x,1pe10.3)))
```

```
 9220 format (i1,3x,i1,3x,i1)
 9230 format (e9.3,1x,f7.2,1x,f5.3,1x,f5.3,1X,I2)
 9240 format (' ',1pe9.3,1x,0pf7.2,1x,f5.3,1x,f5.3,1X,I2)
 9250 format (/,' ------------------------------------------------'
     *   ,'-------------------------------',/
     *   '  Temperature (Celsius): ',f6.2,/
     *   '  Units of concentration: ',a5)
 9260 format ('  Ionic strength to be computed.')
 9270 format ('  Ionic strength: ',f6.3,' molal; FIXED')
 9280 format ('  If specified, carbonate concentration',
     *   ' represents total inorganic carbon.')
 9290 format ('  Carbonate concentration represents carbonate',
     *   ' alkalinity.')
 9300 format ('  Do not automatically terminate if charge imbalance',
     *   ' exceeds 30% ')
 9310 format ('  Automatically terminate if charge imbalance',
     *   ' exceeds 30% ')
 9320 format ('  Precipitation is allowed only for those solids',
     *   ' specified as ALLOWED',/,'    in the input file (if any).')
 9330 format ('  Precipitation is allowed for all solids in the',
     *   ' thermodynamic database and'/,
     *   '    the print option for solids is set to: ',i1)
 9340 format ('  The maximum number of iterations is: ',i3)
 9350 format ('  The method used to compute activity',
     *   ' coefficients is: ',a21)
 9360 format ('  Full output file')
 9365 format ('  Intermediate output file ')
 9370 format ('  Abbreviated output file')
 9380 format ('  Adsorption model: ',a20)
 9390 format ('  Number of adsorbing surfaces: ',i1)
 9400 format (/' --------------------------------------------------',
     *   '----------------------------')
 9401 format (/' !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!',
     *   '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!')
 9800 format (a12,6(1x,i7))
 9700 format (/,' An error has occurred at line ',i3,' of the input',
     *          ' file.')
 9710 format (/,' The component id ',i3,' listed on line ',i3,' of',
     *          ' the input file',
     *        /,' is not a valid CHESP component.')
 9720 format (/,' Species id ',i7,' listed in the input file was',
     *          ' not found in any',
     *        /,' CHESP database file.')
 5750 format ('1',//,' ________________________________________',
     *        '________________________________________',
     *      /,'______________________________ PART ',i1,' of',
     *        ' OUTPUT FILE ___________________________')
 5700 format (//,' ________________________________________',
     *        '________________________________________',
     *      /,'______________________________ PART ',i1,' of',
     *        ' OUTPUT FILE ___________________________')
c
      end
c(16)*******************************************************************
      subroutine nxtprb (idxx, sweep)
c***********************************************************************
c
c  -- The purpose of this routine is to generate the next problem
```

```
c     from the initial problem specification read from the input
c     file and stored on unit 12.  This routine is called from
c     subroutine MAIND after a speciation problem is solved but
c     before the next in a series of identical problems begins.
c     The series of problems are presented to CHESP as a
c     single-problem input file with the specifications for changing
c     the pH, eh, or total concentrations of some component,
c     embedded within it.
c
c     NXTPRB is called only for problems that are to be run at
c     a series of fixed activities or total concentrations of some
c     component.
c
      include 'CHESP.INC'
c
      real*8 spz
      integer idxx
      character sweep*10, uflag*5
      include 'CONST.INC'
c
      if (iprob.eq.nprob) then
        xstop = 'y'
        go to 999
      end if
c
      iter = 0
c
      iprob = iprob + 1
c  -- Find address of sweep component in component space.
      j = iadx(idxx)
c
c  -- Find address of sweep component in species space.  Ordinarily,
c     Function IADY might be used for this but since modifying to
c     retain component 330 as a TYPE 1 species, that component will
c     have two addresses in species space.  The first is the TYPE 1
c     address and the second is the TYPE 3 fixed species address.
c     IADY always returns the first address (which will also be the
c     only address if the component is not fixed).  Here, we always
c     want the second address so a modified form of IADY is used
c     here to provide same.
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      if (ii.lt.1) go to 110
      do 100 i = 1, ii
         if (idy(i).eq.idxx) iii = i
  100 continue
      i = iii
      go to 120
  110 continue
      i = 0
  120 continue
      if (sweep.eq.'ACTIVITY  ') then
        gx(j) = (-1) * uvalue(iprob)
        x(j) = 10.0d0**gx(j)
        gk(i) = uvalue(iprob)
      else if (sweep.eq.'TOTAL CONC') then
        t(j) = uvalue(iprob)
c
        uflag = units
```

```
        if (uflag.eq.'MEQ/L') then
          i = iady(idx(j))
          spz = abs(spcz(i))
          t(j) = t(j)*gfw(i)/dmax1(1.0d0,spz)
          uflag = 'MG/L '
        endif
c
        if (uflag.eq.'MG/L ') then
          t(j) = t(j)/dens
          uflag = 'PPM  '
        endif
c
c  -- For conversion of other units to molal, an approximation is
c     used that involves the sum of all component concentrations
c     in ppm.  This sum is computed initially in subroutine PREP
c     and must now be adjusted before using it in the ppm to molal
c     conversion equation because the concentration of the sweep
c     component hase changed.  Subtract the former concentration of
c     sweep component and add the new concentration of same.
        cppm = cppm - uvalue(iprob-1)
        cppm = cppm + t(j)
c
        if (uflag.eq.'PPM  ') then
          i = iady(idx(j))
          if (gfw(i).lt.DOMIN) go to 500
          t(j) = t(j)*(1.0d0/(1.0d0-1.0d-6*cppm))/(1.0d3*gfw(i))
          uflag = 'MOL  '
        endif
  500   continue
      end if
c
      write (lunout,5750) 1
      call tstamp
      write (lunout, 9400)
      write (lunout, 9401)
      write (lunout,2000)  iprob, nprob
      if (sweep.eq.'ACTIVITY   ') then
        if (idxx.eq.330) then
          write (lunout,2010) uvalue(iprob)
        else if (idxx.eq.001) then
          write (lunout,2020) uvalue(iprob)
        else
          write (lunout,2030) name(i), uvalue(iprob)
        end if
      else if (sweep.eq.'TOTAL CONC') then
        write (lunout,2040) name(i), t(j)
      end if
      write (lunout,2050)
      write (lunout, 9401)
      write (lunout, 9400)
c
  999 return
 9400 format (/' ---------------------------------------------------',
     *   '---------------------------')
 9401 format (/' !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!',
     *   '!!!!!!!!!!!!!!!!!!!!!!!!!!!!')
 2000 format (' *** This is the beginning of SWEEP NUMBER ',i2,
     *        ' in the series of ',i2,' ***',
```

```
     *       /' --------------------------------------------------',
     *        '----------------------------',
     *       /' --------------------------------------------------',
     *        '----------------------------',
     *      //' The input for this sweep is identical to the initial',
     *       ' sweep except:')
 2010 format ('   1)  The fixed pH is:  ',f6.2)
 2020 format ('   1)  The fixed Eh is:  ',f6.2)
 2030 format ('   1)  The fixed log activity of the component ' ,a12,
     *         ' is:  ',f6.2)
 2040 format ('   1)  The total concentration of the component ',a12,
     *         ' is:  ',1pe10.3)
 2050 format ('   2)  The log activity guesses for all components',
     *         ' are as computed at',
     *      /,'        the point of FIRST convergence in the previous',
     *         ' problem.')
5750  format ('1',//,' ________________________________________',
     *         '______________________________________',
     *      /,' ______________________________ PART ',i1,' of',
     *         ' OUTPUT FILE ___________________________')
      end
c(17)*****************************************************************
      subroutine prep
c*****************************************************************
c *****************************************************************
c
c THIS ROUTINE IS CALLED IMMEDIATELY BEFORE THE ITERATIVE LOOP
c IN MAIN.
c
c ITS BASIC FUNCTIONS ARE:
c          1.CORRECT LOGK VALUES FOR TEMPERATURE
c
c          2.CALCULATE DEBYE-HUCKEL CONSTANTS(A&B)
c            AS A FUNCTION OF TEMPERATURE
c
c          3.CONVERT ALL UNITS TO MOLALITY
c
c          4.CALCULATE AN INITIAL CATION-ANION BALANCE
c
c *****************************************************************
c
      include 'CHESP.INC'
c
      real*8 bob1,bob2,bob3,bob4
      real*8 at,bt,cc1,cc2,cc3,ct,diff,dt,e0,et,ft,gt,s1,s2,s3,spz,
     *   vhoff
c
      include 'CONST.INC'
c CORRECT ALL LOGK'S FOR TEMPERATURE
c
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      i0 = nn(1)+1
      do 100 i = i0, ii
         gk(i) = vhoff(gk(i),dh(i))
  100 continue
c
c NOW READ IN THE ANALYTICAL EXPRESSIONS FOR
c LOG K WITH TEMPERATURE.
```

```
c
      k1 = 0
  110 read (lun07,9070) idt,at,bt,ct,dt,et,ft,gt
      if (idt.eq.0) k1 = k1+1
      if (k1.eq.2) then
         rewind lun07
         go to 120
      endif
c
      n = iady(idt)
      if (n.eq.0) go to 110
      gk(n) = at+bt*tempk+ct/tempk+dt*dlog10(tempk)+et*(tempk*tempk)+
     *   ft/(tempk*tempk)+gt/dsqrt(tempk)
      go to 110
  120 continue
c
c THE NEXT SECTION OF CODE WHICH COMPUTES THE DEBYE-HUCKEL
c CONSTANTS AS A FUNCTION OF TEMPERATURE WAS TAKEN DIRECTLY
c FROM WATEQ2(BALL ET AL. 1979). THE MATHEMATICS IS DOCUMENTED
c IN TRUESDELL AND JONES(1974).
c
      s1 = 374.11d0-temp
      s2 = s1**(1.0d0/3.0d0)
      bob1 = (1.0d0+0.1342489d0*s2-3.946263d-03*s1)
      bob2 = (3.1975d0-0.3151548d0*s2-1.203374d-3*s1)
      bob3 = (7.48908d-13*s1**4.0d0)
      bob4 = bob2+bob3
      s3 = dsqrt(bob1/bob4)
      if (tempk.lt.373.16d0) then
         ccl = 87.74d0-temp*(temp*(1.41d-6*temp-9.398d-4)+0.4008d0)
      else
         ccl = 5321d0/tempk+233.76d0-tempk*(tempk*(8.29d-7*tempk-
     *      1.417d-3)+.9297d0)
      endif
c
c INITIALIZE ADSORPTION CONSTANTS WHICH DEPEND UPON CCl
c
      e0 = 8.876d-09
      ee = dsqrt(8.0d0*ccl*e0*rj*tempk)
c
      ccl = dsqrt(ccl*tempk)
      aa = 18246d2*s3/ccl**3.0d0
      bb = 50.29d0*s3/ccl
c
c
c CONVERT ALL UNITS TO MOLALITY
c
      ii = nnn
      if (flag.eq.'MEQ/L') then
         do 130 j = 1, ii
            if (idx(j).ge.811.and.idx(j).le.859) go to 130
            if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 130
            i = iady(idx(j))
            spz = abs(spcz(i))
            t(j) = t(j)*gfw(i)/dmax1(1.0d0,spz)
  130    continue
         flag = 'MG/L '
      endif
```

```
c
      if (flag.eq.'MG/L ') then
         do 140 j = 1, ii
            if (idx(j).ge.811.and.idx(j).le.859) go to 140
            if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 140
            t(j) = t(j)/dens
  140    continue
         flag = 'PPM  '
      endif
c
      ccl = 0.0d0
      do 150 j = 1, nnn
         if (idx(j).ge.811.and.idx(j).le.859) go to 150
         if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 150
         ccl = ccl+t(j)
  150 continue
c
c
      if (flag.eq.'PPM  ') then
         do 160 j = 1, ii
            if (idx(j).ge.811.and.idx(j).le.859) go to 160
            if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 160
            i = iady(idx(j))
            if (gfw(i).lt.DOMIN) go to 160
            t(j) = t(j)*(1.0d0/(1.0d0-1.0d-6*ccl))/(1.0d3*gfw(i))
  160    continue
         flag = 'MOL  '
      endif
      cppm = ccl
c
      ii = nn(1)+nn(2)+1
      i3 = nn(1)+nn(2)+nn(3)
      if (i3.lt.ii) go to 200
      do 190 i = ii, i3
         do 180 j = 1, nnn
            if (idx(j).ne.idy(i)) go to 180
            if (dabs(gx(j)).lt.DOMIN) then
               gx(j) = -gk(i)
               x(j) = 10.0d0**gx(j)
            endif
  180    continue
  190 continue
  200 continue
c
c
c SUM THE CONCENTRATIONS OF ALL SPECIES FOR ACTIVITY
c OF WATER CALCULATIONS
c
      ccl = 0.0d0
      do 210 j = 1, nnn
         if (idx(j).le.2) go to 210
         if (idx(j).ge.811.and.idx(j).le.859) go to 210
         if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 210
c
c     CHANGED TO CHECK FOR THE ADDITION OF WATER OR e -)
c
         cc3 = t(j)
         ccl = ccl+cc3
```

```
  210 continue
c
c NOW ADD ACTIVITIES OF TYPE 3 AQUEOUS SPECIES
c
      i0 = nn(1)+nn(2)+1
      ii = nn(1)+nn(2)+nn(3)
      if (ii.lt.i0) go to 240
      do 230 i = i0, ii
         do 220 j = 1, nnn
            if (idy(i).ne.idx(j)) go to 220
            if (idx(j).le.2) go to 220
            if (idx(j).ge.811.and.idx(j).le.859) go to 220
            if (idx(j).ge.idclf.and.idx(j).le.idcll) go to 220
            cc3 = 10.0d0**(-gk(i))
            cc1 = cc1+cc3
  220    continue
  230 continue
  240 continue
c
c ***** NEED ERROR CHECK HERE *******
c
      indh2o = iady(2)
      if (cc1.gt.58.823d0) cc1 = 58.823d0
      gk(indh2o) = -dlog10(1.0d0-0.017d0*cc1)
c
c CALCULATE AND PRINT INITIAL CATION-ANION BALANCE
c
      cc1 = 0.0d0
      cc2 = 0.0d0
      tis = 0.0d0
c
      do 250 j = 1, nnn
         i = iady(idx(j))
         if (spcz(i).gt.0.0d0) then
            cc1 = cc1+spcz(i)*t(j)
         else
            cc2 = cc2-spcz(i)*t(j)
         endif
c         if (t(j).gt.0.0d0) then
           tis = tis+t(j)*spcz(i)*spcz(i)
c         end if
  250 continue
      tis = tis*0.5d0
c
      diff = 0.0d0
      cc3 = cc1+cc2
      if (dabs(cc3).gt.DOMIN) diff = DABS((cc2-cc1)/(cc2+cc1))
      diff = diff*100.0d0
c
      write (lunout,9060)
      write (lunout,9030) cc1,cc2
      write (lunout,9040) diff
c
      if (diff.gt.30.0d0.and.icharg.eq.0) then
        ierr = 8
        call error
        go to 999
      end if
```

```
c
 999  return
c
c
 9030 format ('0',7x,'Sum of CATIONS= ',1pe10.3,' Sum of ANIONS = ',
     *   1pe10.3)
 9040 format ('0',7x,'PERCENT DIFFERENCE = ',1pe10.3,2x,
     *   '(ANIONS - CATIONS)/(ANIONS + CATIONS)')
 9060 format (/,'0',5x,'Charge Balance: UNSPECIATED')
 9070 format (i7,1x,7(e10.3,1x))
c
      end
c(18)*******************************************************************
      subroutine guess
c**********************************************************************
c  -- The purpose of this subroutine is to make better activity
c     guesses for certain components--  those for which an equation of
c     some sort is provided below and for which the flag reguess(j)
c     is not equal to no ('n').
c
      include 'CHESP.INC'
c
      real*8 k1, k2, k3, k4, k5, k6, k7, k8, k9, k10,
     *       total, actH, actE, coefa, coefb, coefc
      character crredl*1, crred2*1, seredl*1, sered2*1
      include 'CONST.INC'
c
      crredl = 'n'
      crred2 = 'n'
      seredl = 'n'
      sered2 = 'n'
      if (fxdph.eq.'y') then
         actH = 10.0d0**(-systemph)
      else
         if (iadx(330).ne.0) then
           actH = 10.0d0**gx(iadx(330))
         else
           go to 999
         end if
      end if
      if (fxdpe.eq.'y') then
         actE = 10.0d0**(-systempe)
      else
         if (iadx(001).ne.0) actE = 10.0d0**gx(iadx(001))
      end if
c
c
      call guessl (actH,actE)
c
c
c  -- Type III species that involve acid/base CHESPistry only, i.e,
c     no requirement that the electron be defined as a component.
      i1 = nn(1)+nn(2)+1
      i2 = nn(1)+nn(2)+nn(3)
      do 20 i = i1,i2
c
c  -- Compute new guess for CO3-2
        if (idy(i).eq.3301403) then
```

```
            j1 = iadx(140)
            k1 = 10.0d0**gk(iady(3301403))
            if (reguess(j1).eq.'n') go to 20
            x(j1) = 1.0d0/(k1*(actH**2))
            gx(j1) = dlog10 (x(j1))
            reguess(j1) = 'r'
          end if
c
c
   20 continue
c
c
c
c  -- Type III species that involve acid/base AND redox CHESPistry.
c     The electron must be defined as a component.
      if (iadx(001).ne.0.and.iadx(330).ne.0) then
c
        i1 = nn(1)+nn(2)+1
        i2 = nn(1)+nn(2)+nn(3)
        do 30 i = i1,i2
c
c  -- Compute new guess for SO4-2
        if (idy(i).eq.7307320) then
          j1 = iadx(730)
          j2 = iadx(732)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(730)
            j2 = iadx(732)
          end if
          k1 = 10.d0**gk(iady(7307320))
          k2 = 10.d0**gk(iady(3307320))
          k3 = 10.d0**gk(iady(3307300))
c
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total / (1.0 + k1*(actH**9)*(actE**8)
     *              + k3*k1*(actH**10)*(actE**8) + k2*actH)
            gx(j2) = dlog10 (x(j2))
            reguess(j2) = 'r'
c
            if (reguess(j1).ne.'n') then
              x(j1) = k1*x(j2)*actH**9*actE**8
              gx(j1) = dlog10(x(j1))
              reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Compute new guess for Fe+3
        if (idy(i).eq.2802810) then
          j1 = iadx(280)
          j2 = iadx(281)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(280)
            j2 = iadx(281)
          end if
```

```
          k1 = 10.d0**gk(iady(2802810))
          k2 = 10.d0**gk(iady(2803300))
          k3 = 10.d0**gk(iady(2803302))
          k4 = 10.d0**gk(iady(2813300))
          k5 = 10.d0**gk(iady(2813301))
          k6 = 10.d0**gk(iady(2813302))
          k7 = 10.d0**gk(iady(2813303))
c
         total = t(j1) + t(j2)
         if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
           x(j2) = total / (1.0 + k1*actE + k2*k1*actE/actH
     *           + k3*k1*actE/actH**2 + k4/actH + k5/actH**2
     *           + k6/actH**3 + k7/actH**4)
           reguess(j2) = 'r'
           gx(j2) = dlog10 (x(j2))
c
           if (reguess(j1).ne.'n') then
              x(j1) = k1*x(j2)*actE
              gx(j1) = dlog10(x(j1))
              reguess(j1) = 'r'
           end if
         end if
        end if
c
c  -- Compute new guess for Mn+3
        if (idy(i).eq.4704710) then
          j1 = iadx(470)
          j2 = iadx(471)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(470)
            j2 = iadx(471)
          end if
          k1 = 10.d0**gk(iady(4704710))
          k2 = 10.d0**gk(iady(4703300))
          k3 = 10.d0**gk(iady(4703301))
          k4 = 10.d0**gk(iady(4700020))
          k5 = 10.d0**gk(iady(4700021))
c
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
             x(j2) = total / (1.0 + k1*actE + k2*k1*actE/actH
     *            + k3*k1*actE/actH**3 + k4*k1/((actH**8)*(actE**4))
     *            + k5*k1/((actH**8)*(actE**3)))
            reguess(j2) = 'r'
            gx(j2) = dlog10 (x(j2))
c
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actE
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c
c  -- Compute new guess for H3AsO4
        if (idy(i).eq.0600610) then
```

```
          j1 = iadx(060)
          j2 = iadx(061)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(060)
            j2 = iadx(061)
          end if
          k1 = 10.d0**gk(iady(0600610))
          k2 = 10.d0**gk(iady(3300600))
          k3 = 10.d0**gk(iady(3300601))
          k4 = 10.d0**gk(iady(3300602))
          k5 = 10.d0**gk(iady(3300603))
          k6 = 10.d0**gk(iady(3300611))
          k7 = 10.d0**gk(iady(3300612))
          k8 = 10.d0**gk(iady(3300613))
c
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
           x(j2) = total / (1.0 + k1*(actE**2)*(actH**2)
     *              + k2*k1*(actE**2)*actH + k3*k1*(actE**2)
     *              + k4*k1*(actE**2)/actH
     *              + k5*k1*(actE**2)*(actH**3)
     *              + k6/actH + k7/(actH**2) + k8/(actH**3))
            reguess(j2) = 'r'
            gx(j2) = dlog10 (x(j2))
c
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actH**2*actE**2
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Compute new guess for Cr(OH)2+ if couple Cr+2/Cr(OH)2+
        if (idy(i).eq.2102110) then
          crred1 = 'y'
          k1 = 10.d0**gk(iady(2102110))
          k2 = 10.d0**gk(iady(2113300))
          k3 = 10.d0**gk(iady(2113301))
          k4 = 10.d0**gk(iady(2113302))
          k5 = 10.d0**gk(iady(2113303))
          k6 = 10.d0**gk(iady(2113304))
c
          j1 = iadx(210)
          j2 = iadx(211)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(210)
            j2 = iadx(211)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total / (1.0 + k1*(actH**2)*actE + k2*(actH**2)
     *             + k3*actH + k4/actH + k5/(actH**2) + k6/(actH**2))
            gx(j2) = dlog10 (x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
```

```
               x(j1) = k1*x(j2)*actH**2*actE
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Compute new guess for Cr(OH)2+ if couple Cr(OH)2+/CrO4-2
          if (idy(i).eq.2112120) then
          crred2 = 'y'
          k2 = 10.d0**gk(iady(2113300))
          k3 = 10.d0**gk(iady(2113301))
          k4 = 10.d0**gk(iady(2113302))
          k5 = 10.d0**gk(iady(2113303))
          k6 = 10.d0**gk(iady(2113304))
          k7 = 10.d0**gk(iady(2112120))
          k8 = 10.d0**gk(iady(2123300))
          k9 = 10.d0**gk(iady(2123301))
          k10= 10.d0**gk(iady(2123302))
          j1 = iadx(212)
          j2 = iadx(211)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(212)
            j2 = iadx(211)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total / (1.0 + 1.0/(k7*(actH**6)*(actE**3))
     *             + k2*(actH**2) + k3*actH + k4/actH
     *             + k5/(actH**2) + k6/(actH**2)
     *             + k8/(k7*(actH**5)*(actE**3))
     *             + k9/(k7*(actH**4)*(actE**3))
     *             + k10/(k7*(actH**4)*(actE**3)))
            gx(j2) = dlog10 (x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = x(j2)/(k7*actH**6*actE**3)
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Mercury
        if (idy(i).eq.3603610) then
          k1 = 10.d0**gk(iady(3603610))
          k2 = 10.d0**gk(iady(3600000))
          k3 = 10.d0**gk(iady(3613300))
          k4 = 10.d0**gk(iady(3613302))
          k5 = 10.d0**gk(iady(3613303))
c
          j1 = iadx(360)
          j2 = iadx(361)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(360)
            j2 = iadx(361)
```

```
          end if
          coefa = 2*k1*(actH**4)*(actE**2)
          coefb = 1.0 + k2*dsqrt(k1)*(actH**2)*(actE**2) + k3*(actH**2)
     *              + k4*actH + k5/actH
          coefc = (-1)*(2*t(j1) + t(j2))
          if (coefc.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = (-coefb + dsqrt((coefb**2)-4.0d0*coefa*coefc))
     *              /(2.0d0*coefa)
            if (x(j2).lt.DOMIN) x(j2) = -coefc/coefb
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)**2*actH**4*actE**2
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Copper
        if (idy(i).eq.2302310) then
          k1 = 10.d0**gk(iady(2302310))
          k2 = 10.d0**gk(iady(2313300))
          k3 = 10.d0**gk(iady(2313301))
          k4 = 10.d0**gk(iady(2313302))
          k5 = 10.d0**gk(iady(2313303))
          k6 = 10.d0**gk(iady(2313304))
c
          j1 = iadx(230)
          j2 = iadx(231)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(230)
            j2 = iadx(231)
          end if
          coefa = k6/(actH**2)
          coefb = 1.0 + k1*actE + k2/actH + k3*(actH**2)
     *              + k4/(actH**3) + k5/(actH**4)
          coefc = (-1)*(t(j1) + t(j2))
          if (coefc.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = (-coefb + dsqrt((coefb**2)-4.0d0*coefa*coefc))
     *              /(2.0d0*coefa)
            if (x(j2).lt.DOMIN) x(j2) = -coefc/coefb
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actE
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Selenium
        if (idy(i).eq.7607610) then
          seredl = 'y'
          k1 = 10.d0**gk(iady(7607610))
          k2 = 10.d0**gk(iady(3307600))
```

```
          k3 = 10.d0**gk(iady(3307601))
          k4 = 10.d0**gk(iady(3307610))
          k5 = 10.d0**gk(iady(3307611))
c
          j1 = iadx(760)
          j2 = iadx(761)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(760)
            j2 = iadx(761)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
             x(j2) = total /(1.0d0+ k1*(actH**6)*(actE**6)
     *            + k2*(actH**7)*(actE**6) + k3*(actH**5)*(actE**6)
     *            + k4*actH + k5/actH)
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actH**6*actE**6
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
        if (idy(i).eq.7617620) then
          sered2 = 'y'
          k4 = 10.d0**gk(iady(3307610))
          k5 = 10.d0**gk(iady(3307611))
          k6 = 10.d0**gk(iady(7617620))
          k7 = 10.d0**gk(iady(3307620))
c
          j1 = iadx(762)
          j2 = iadx(761)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(762)
            j2 = iadx(761)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total /(1.0d0+ 1.0d0/(k6*(actH**3)*(actE**2))
     *           + k4*actH + k5/actH + k7/(k6*(actH**2)*(actE**2)))
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = x(j2)/(k6*actH**3*actE**2)
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Antimony
        if (idy(i).eq.7407410) then
          k1 = 10.d0**gk(iady(7407410))
          k2 = 10.d0**gk(iady(7403302))
```

```
          k3 = 10.d0**gk(iady(7400020))
          k4 = 10.d0**gk(iady(7403301))
          k5 = 10.d0**gk(iady(7403300))
          k6 = 10.d0**gk(iady(7400021))
          k7 = 10.d0**gk(iady(7413300))
          k8 = 10.d0**gk(iady(7410021))
          j1 = iadx(740)
          j2 = iadx(741)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(740)
            j2 = iadx(741)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total/(1.0d0 + k1*(actH**3)*(actE**2)
     *          + k2*k1*(actH**4)*(actE**2)
     *          + k3*k1*(actH**2)*(actE**2) + k4*k1*(actH**2)*(actE**2)
     *          + k5*k1*(actH**4)*(actE**2) + k6*k1*(actH**3)*(actE**2)
     *          + k7*(actH**2) + k8)
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actH**3*actE**2
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
        end if
c
c  -- Thallium
        if (idy(i).eq.8708710) then
          k1 = 10.d0**gk(iady(8708710))
          k2 = 10.d0**gk(iady(8703300))
          k3 = 10.d0**gk(iady(8713300))
          k4 = 10.d0**gk(iady(8713301))
          k5 = 10.d0**gk(iady(8713302))
          k6 = 10.d0**gk(iady(8713303))
          j1 = iadx(870)
          j2 = iadx(871)
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(870)
            j2 = iadx(871)
          end if
          total = t(j1) + t(j2)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
             x(j2) = total/(1.0d0 + k1*(actH**3)*(actE**2)
     *          + k2*k1*(actH**2)*(actE**2)
     *          + k3*(actH**3) + k4*(actH**2) + k5*actH + k6/actH)
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
            if (reguess(j1).ne.'n') then
               x(j1) = k1*x(j2)*actH**3*actE**2
               gx(j1) = dlog10(x(j1))
               reguess(j1) = 'r'
            end if
          end if
```

```
        end if
   30   continue
c
c   -- If both redox couples of chrome are imposed, recalculate
c      the Cr(OH)2+ activity guess using both.
        if (crred1.eq.'y'.and.crred2.eq.'y') then
          j1 = iadx(210)
          j2 = iadx(211)
          j3 = iadx(212)
          k1 = 10.d0**gk(iady(2102110))
          k2 = 10.d0**gk(iady(2113300))
          k3 = 10.d0**gk(iady(2113301))
          k4 = 10.d0**gk(iady(2113302))
          k5 = 10.d0**gk(iady(2113303))
          k6 = 10.d0**gk(iady(2113304))
          k7 = 10.d0**gk(iady(2112120))
          k8 = 10.d0**gk(iady(2123300))
          k9 = 10.d0**gk(iady(2123301))
          k10= 10.d0**gk(iady(2123302))
          if (j1.gt.j2) then
            call excol (j1,j2)
            j1 = iadx(210)
            j2 = iadx(211)
          end if
          if (j3.gt.j2) then
            call excol (j3,j2)
            j3 = iadx(212)
            j2 = iadx(211)
          end if
          total = t(j1) + t(j2) + t(j3)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
             x(j2) = total / (1.0 + k1*(actH**2)*actE
     *             + k2*(actH**2) + k3*actH + k4/actH
     *             + k5/(actH**2) + k6/(actH**2)
     *             + 1.0/(k7*(actH**6)*(actE**3))
     *             + k8/(k7*(actH**5)*(actE**3))
     *             + k9/(k7*(actH**4)*(actE**3))
     *             + k10/(k7*(actH**4)*(actE**3)))
            gx(j2) = dlog10 (x(j2))
            reguess(j2) = 'r'
          end if
        end if
c
c   -- Selenium
        if (sered1.eq.'y'.and.sered2.eq.'y') then
          k1 = 10.d0**gk(iady(7607610))
          k2 = 10.d0**gk(iady(3307600))
          k3 = 10.d0**gk(iady(3307601))
          k4 = 10.d0**gk(iady(3307610))
          k5 = 10.d0**gk(iady(3307611))
          k6 = 10.d0**gk(iady(7617620))
          k7 = 10.d0**gk(iady(3307620))
c
          j1 = iadx(760)
          j2 = iadx(761)
          j3 = iadx(762)
          if (j1.gt.j2) then
            call excol (j1,j2)
```

```
            j1 = iadx(760)
            j2 = iadx(761)
          end if
          if (j3.gt.j2) then
            call excol (j3,j2)
            j3 = iadx(762)
            j2 = iadx(761)
          end if
          total = t(j1) + t(j2) + t(j3)
          if (total.gt.DOMIN.and.reguess(j2).ne.'n') then
            x(j2) = total /(1.0d0 + k1*(actH**6)*(actE**6)
     *            + 1.0d0/(k6*(actH**3)*(actE**2))
     *            + k2*(actH**7)*(actE**6) + k3*(actH**5)*(actE**6)
     *            + k4*actH + k5/actH * k7/(k6*(actH**2)*(actE**2)))
            gx(j2) = dlog10(x(j2))
            reguess(j2) = 'r'
          end if
        end if
c
      end if
c
      icount = 0
      do 100 j = 1, nnn
        if (reguess(j).eq.'r') then
          icount = icount + 1
          if (icount.eq.1) write (lunout,1000)
          i = iady(idx(j))
          write (lunout,1010) name(i),gx(j)
        end if
  100 continue
      if (icount.gt.0) write (lunout,1020)
c
  999 return
c
 1000 format (///,t16,'-----------------------------------------',
     *                '--------------',
     *        /,t15,'|',2x,'IMPROVED ACTIVITY GUESSES PRIOR TO',
     *                      ' FIRST ITERATION:',1x,'|')
 1010 format (1x,t15,'|',7x,a12,t35,'Log activity guess:',2x,f7.2,
     *           t70,'|')
 1020 format (1x,t15,'|',t70,'|',/,t16,'----------------------------',
     *                '----------------------------')
      end
c(19)******************************************************************
      subroutine actvty
c**********************************************************************
c ******************************************************************
c
c ACTVTY
c
c THIS SUBROUTINE CALCULATES
c     1. ACTIVITY COEFFICIENTS FOR ALL SPECIES BY BOTH
c        THE DAVIES AND DEBYE-HUCKEL EQUATIONS
c     2. THE IONIC STRENGTH(XMU)
c     3. THE IONIC STRENGTH CORRECTION FOR THE EQUILIBRIUM
c        CONSTANTS BY CALLING KCORR
c
c **************************************************************
```

```
c
      include 'CHESP.INC'
      real*8 cc2,tmp,v,sqrxmu
c
      include 'CONST.INC'
      i0 = nn(1)+nn(2)
      ii = i0+nn(3)
      i3 = ii+nn(4)+nn(5)+nn(6)
      cc2 = 0.D0
c
c COMPUTE CONCENTRATIONS USING NEW X'S OLD K'S
c
      if (isopt.eq.1) then
         xmu = fions
         sqrxmu = dsqrt(xmu)
         go to 130
      endif
c
c COMPLEXES
c
        id1 = idclf*10000
        id2 = idcl1*10000 + 9999
        do 110 i = 1, i0
          if (idy(i).ge.id1.and.idy(i).le.id2) go to 110
          v = gk(i)
          do 100 k = 1, jmax(i)
             n = jpta(i,k)
             v = v+a(i,n)*gx(n)
  100     continue
c
          gc(i) = v
          c(i) = 10.0d0**gc(i)
c
  110  continue
c
c
c SUM THE CONCENTRATION OF ALL SPECIES FOR ACTIVITY
c COEFFICIENT CALCULATIONS
c
      do 120 i = 1, i0
c
c -- MODIFIED TO EXCLUDE ALL ADSORBENT COMPONENTS AND REACTION PRODUC
c
         if (idy(i).ge.811.and.idy(i).le.859) go to 120
         if (idy(i).le.2) go to 120
         if (idy(i).ge.8110000.and.idy(i).le.8599999) go to 120
         if (c(i).ge.0.0d0) then
           cc2 = cc2+c(i)*spcz(i)*spcz(i)
         end if
  120 continue
c
      xmu = cc2/2.0d0
      sqrxmu = dsqrt(xmu)
c
c FELMY 1982 ORIGINALLY SET LIMIT OF IONIC
c  STRENGTH TO 4.0 MOLAL
c
      if (xmu.gt.4.0d0) then
```

```
          xmu = tis
          sqrxmu = dsqrt(xmu)
       endif
c
  130 continue
c
c FIRST CALCULATE ACTIVITY COEFFICENTS WITH THE
c DAVIES EQUATION
c
      tmp = (sqrxmu/(1.0d0+sqrxmu)-0.24d0*xmu)
c
      do 140 i = 1, i3
c
c -- MODIFIED TO EXCLUDE ALL ADSORBENT COMPONENTS AND REACTION PRODUC
c
         if (idy(i).ge.811.and.idy(i).le.859) go to 140
         if (idy(i).eq.2) go to 140
         if (idy(i).ge.8110000.and.idy(i).le.8599999) go to 140
         if (abs(spcz(i)).lt.R0MIN) then
            gamma(i) = 0.0d0
         else
            gamma(i) = -aa*spcz(i)*spcz(i)*tmp
         endif
  140 continue
c
c NOW INITIALIZE ACTIVITY COEFFICIENTS FOR NEUTRAL COMPLEXES
c
      do 150 i = 1, i0
c
c -- MODIFIED TO EXCLUDE ALL ADSORBENT COMPONENTS AND REACTION PRODUC
c
         if (idy(i).ge.811.and.idy(i).le.859) go to 150
         if (idy(i).eq.2) go to 150
         if (idy(i).ge.8110000.and.idy(i).le.8599999) go to 150
         if (abs(spcz(i)).lt.D0MIN) gamma(i) = 0.1d0*xmu
  150 continue
      if (kkdav.eq.1) go to 170
c
c NOW USE THE DEBYE HUCKEL IF DHA IS NOT EQUAL TO 0
c
      do 160 i = 1, i3
c
c -- MODIFIED TO EXCLUDE ALL ADSORBENT COMPONENTS AND REACTION PRODUC
c
         if (idy(i).ge.811.and.idy(i).le.859) go to 160
         if (idy(i).eq.2) go to 160
         if (idy(i).ge.8110000.and.idy(i).le.8599999) go to 160
         if (abs(dha(i)).lt.R0MIN) go to 160
         gamma(i) = -aa*spcz(i)*spcz(i)*sqrxmu/(1.0d0+bb*dha(i)*
     *      sqrxmu)+dhb(i)*xmu
  160 continue
c
  170 continue
c
c NOW CORRECT LOGK FOR IONIC STRENGTH
c
      i0 = i0-1
      call kcorr
```

```
c
c DEBUG ROUTINE IN ACTVTY
c
      if (idebug.eq.1) then
         write (lunout,9000)
         write (lunout,9010) xmu
         write (lunout,9020) iter
         write (lunout,9030)
         ijj3 = nn(1)+nn(2)+nn(3)
         do 180 ijj = 1, ijj3
            write (lunout,9040) ijj,idx(ijj),x(ijj),idy(ijj),gamma(ijj)
     *         ,c(ijj),y(ijj)
  180    continue
      endif
      return
c
 9000 format ('0','DEBUG PRINT IN SUBROUTINE ACTVTY')
 9010 format ('0',10x,' XMU = ',f15.10)
 9020 format ('0',5x,'ITER = ',i5)
 9030 format ('0',5x,' I ',3x,'  IDX  ',3x,'     X     ',3x,'  IDY  ',
     *   3x,'   GAMMA  ',3x,'     C     ',3x,'     Y     ')
 9040 format (5x,i3,3x,i7,3x,1pe10.3,3x,i7,3x,0pf10.5,3x,1pe10.3,3x,
     *   e10.3)
c
      end
c(20)*******************************************************************
      subroutine solid
c
c ****************************************************
c
c THIS SUBROUTINE MODIFIES THE A,B,T AND GK MATRICES
c FOR THE PRESENCE OF FIXED SOLIDS. THE SUBROUTINE IS
c IDENTICAL TO SUBROUTINE SOLID IN MINEQL(WESTALL ET
c AL 1976) EXCEPT FOR CHANGES IN COMMONBLOCK.
c
c ****************************************************
c
      include 'CHESP.INC'
c
      include 'CONST.INC'
      ll = nn(3) + nn(4)
      if (ll.eq.0) go to 170
      i0 = nn(1)+nn(2)+nn(3)+nn(4)+1
      j0 = nnn+1
c
c --- BEGIN MAIN LOOP
c
      do 150 l = 1, ll
         i0 = i0-1
         j0 = j0-1
c
c FIND JEXC FOR I0
c
         do 100 j = 1, j0
            jj=j0-(j-1)
            if (abs(a(i0,jj)).gt.0.001) go to 110
            if (abs(b(i0,jj)).gt.0.001) go to 110
  100    continue
```

```
         ierr = 11
         call error
         go to 999
  110    jexc = j0-(j-1)
c
         if (j0.le.1) then
            ierr = 12
            call error
            go to 999
         endif
         call excol (jexc,j0)
         nxs = j0-1
         ncs = i0-1
c
c MODIFY A,B,T
c
         do 120 i = 1, ncs
            do 125 j = 1, nxs
               if (dabs(b(i0,j)).gt.DOMIN.and.dabs(b(i,j0)).gt.DOMIN)
     *         then
                 b(i,j) = b(i,j)-b(i0,j)*b(i,j0)/b(i0,j0)
               end if
               if (abs(a(i0,j)).gt.DOMIN.and.abs(a(i,j0)).gt.DOMIN)
     *         then
                 a(i,j) = a(i,j)-a(i0,j)*a(i,j0)/a(i0,j0)
               end if
  125       continue
  120    continue
         do 130 j = 1, nxs
            t(j) = t(j)-b(i0,j)*t(j0)/b(i0,j0)
  130    continue
         do 140 i = 1, ncs
            gk(i) = gk(i)-a(i,j0)*gk(i0)/a(i0,j0)
  140    continue
c
c
c --- END OF MAIN LOOP
c
  150 continue
c
c  -- Re-create the pointer arrays.
  170 call pointer
c
  999 return
c
      end
c(21)*******************************************************************
      subroutine kcorr
c*******************************************************************
c
c *******************************************************************
c
c KCORR
c
c THIS SUBROUTINE CORRECTS THE EQUILIBRIUM CONSTANTS FOR
c IONIC STRENGTH
c
c *******************************************************************
```

```
c
      include 'CHESP.INC'
c
c -- THE INCLUDE FILE HAS A PARAMETER STATEMENT THAT SETS BOTH
c    NXDIM AND NYDIM.  (THEIR VALUES DEPEND UPON THE MEMORY
c    CAPACITY OF THE COMPUTER.)  THE INCLUDE STATEMENT ABOVE
c    MUST COME BEFORE THE DIMENSION STATEMENT FOR GK2 SINCE
c    NYDIM IS USED FOR AN ADJUSTABLE ARRAY DIMENSION. 10-14-87 JDA
c
      dimension gk1(nydim)
c
      real*8 gk1
c
      i3 = nn(1)+nn(2)
      if (isopt.eq.0) then
        do 100 i = 1, i3
           gk(i) = gk1(i)
  100   continue
      end if
c
c  CORRECT FOR GAMMA OF SPECIES I
c
      do 120 i = 1, i3
         gk(i) = gk(i)-gamma(i)
  120 continue
c
c
      return
c
c AFTER ALTERING K'S FOR PRECIPITATION OR DISSOLUTION
c RESET GK1 ARRAY
c
      entry kcorr2
      i3 = nn(1)+nn(2)
      do 140 i = 1, i3
         gk1(i) = gk(i)
  140 continue
c
c
      return
      end
c(22)*******************************************************************
      subroutine solve
c**********************************************************************
c ********************************************************
c
c THIS SUBROUTINE SOLVES AQUEOUS SPECIATION PROBLEM
c WHICH HAS BEEN MODIFIED FOR SOLIDS IN SUBROUTINE SOLID.
c ********************************************************
c
c
      include 'CHESP.INC'
c
      dimension test(nxdim)
c
      real*8 v,v2,v5,vmax,cnvtest,test,residual,gclig
      character*1 holdis, convrged*1
      include 'CONST.INC'
```

```
c
      holdis = 'n'
      if (iads.gt.1) call adsid
c
      nc = nn(1)+nn(2)
      nx = nnn-nn(3)-nn(4)
      if (nx.lt.1) then
        ierr = 12
        call error
        go to 999
      end if
      if (iter.eq.0) k2 = 0
c
c  -- Time stamp the output file
      write (lunout,5750) 3
      call tstamp
      write (lunout,9000)
      write (lunout,9010)
      k2 = k2+1
      ipass = 0
  100 continue
      do 150 i = 1, nx
        if (dabs(x(i)).lt.DOMIN) then
          ierr = 10
          call error
          go to 999
        end if
        do 155 j = 1, nx
          z(i,j) = 0.0d0
  155   continue
  150 continue
c
c COMPLEXES
c
      id1 = idclf*10000
      id2 = idcll*10000 + 9999
      do 120 i = 1, nc
         v = gk(i)
         do 110 k = 1, jmax(i)
            n = jpta(i,k)
            v = v+a(i,n)*gx(n)
  110    continue
c
         if (v.lt.-100.0d0) then
           gc(i) = -100.0d0
         else
           gc(i) = v
         end if
         c(i) = 10.0d0**gc(i)
  120 continue
c
      do 125 i = 1, nc
        if (idy(i).ge.id1 .and. idy(i).le.id2) then
           call composit (i,gclig)
           gc(i) = gclig
           c(i) = 10.d0**gclig
        end if
  125 continue
```

```
c
      if (icoralk.ne.0.and.k2.eq.1) call alkcor
c
c -- MODIFIED FOR DIFFUSE LAYER MODEL JDA 10-31-87
c
      if (iads.gt.1) call adinit
c
c
c COMPUTE Z and mass imbalance Y
c
c
      do 160 j = 1, nx
         v = 0.0d0
         do 161 ii = 1, imax(j)
            n = ipta(j,ii)
            v5 = c(n)*b(n,j)
            do 162 kk = 1, jmax(n)
              k = jpta(n,kk)
              z(j,k) = z(j,k) + a(n,k) * v5 / x(k)
  162       continue
            v = v + v5
  161    continue
         y(j) = v - t(j)
  160 continue
c
      if (iads.eq.3) call adscaly
      if (iads.gt.1) call adsjac
c
c CONVERGENCE TEST
c
      convrged = 'y'
      do 210 j = 1, nx
         vmax = dabs(t(j))
         do 170 i = 1, 5
            if (solcon(i).lt.DOMIN) go to 170
            if (j.eq.m2(i).and.iads.eq.3) go to 190
  170    continue
         do 180 k = 1, imax(j)
            n = ipta(j,k)
            v2 = dabs(b(n,j)*c(n))
            if (v2.lt.vmax) go to 180
            vmax = v2
  180    continue
         go to 200
  190    if (vmax.le.1.0d-10) vmax = 1.0d-10
  200    if (vmax.lt.DOMIN) go to 210
         test(j) = dabs(y(j))/vmax
c  --  Require at least 2 iterations no matter what.
         if (test(j).gt.eps.or.iter.le.2) convrged = 'n'
         test(j) = eps*vmax
  210 continue
c
      if (convrged.eq.'y') then
       if (holdis.eq.'y') then
         isopt = 0
         holdis = 'n'
         ipass = 0
         go to 220
```

```
       end if
        go to 999
      end if
c
  220 iter = iter+1
c
c OUTPUT ITERATION INFORMATION
c
      iworst = 0
      cnvtest = 0.0d0
      do 230 j = 1, nx
         if (dabs(y(j))-test(j).gt.cnvtest) then
            iworst = j
            residual = dabs(y(j))-test(j)
         endif
  230 continue
      if (iworst.gt.0) then
         i = iady(idx(iworst))
         write (lunout,9020) iter-1,name(i),t(iworst),y(iworst),
     *      gx(iworst), residual
      endif
c
      if (iter.gt.itmax) then
        ierr = 13
        call error
        go to 999
      end if
c
c ITERATE
c
c NOW COMPUTE ACTIVITY COEFFICIENTS AND NEW X(J)
c
      call simq (z,y,nx,nxdim,ierr)
      if (ierr.ne.0) go to 999
      call newx
      if (iter.gt.1.and.isopt.eq.0) call actvty
      ipass = ipass + 1
      if (ipass.gt.12.and.isopt.eq.0) then
        isopt = 1
        holdis = 'y'
      end if
      go to 100
 999  return
 9000 format ('0'/,
     *   ' PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:')
 9010 format ('0',5x,'ITER',2x,'    NAME    ',2x,' TOTAL MOL ',2x,
     *   ' DIFF FXN ',2x,'LOG ACTVTY',2x,'  RESIDUAL')
 9020 format (5x,i3,3x,a12,2x,1pe11.3,2x,1pe10.3,2x,0pf10.5,2x,
     *        1pe11.3)
 5750 format ('1',//,' ________________________________________',
     *      '________________________________________',
     *     /,'______________________________ PART ',i1,' of',
     *        ' OUTPUT FILE ___________________________')
c
      end
c(23)************************************************************
      subroutine solidx (action,kl)
c*****************************************************************
```

```
c
c ********************************************************
c
c THIS SUBROUTINE UMMODIFIES THE A,B,T,GX,AND X MATRICES
c FOLLOWING SUBROUTINE SOLVE. THE SUBROUTINE ALSO
c SELECTS THE TYPE 4 AND 5 SOLIDS WHICH WILL DISSOLVE
c OR PRECIPITATE THIS ITERATION. THIS SUBROUTINE IS
c IDENTICAL TO SUBROUTINE SOLIDX IN MINEQL(WESTALL ET
c AL 1976) EXCEPT FOR CHANGES IN COMMON BLOCK.
c ********************************************************
c
c  -- The input variable kl is equal to zero the first call
c     to this routine.  kl is incremented in MAIND for each
c     successive trip through the equilibration loop; i.e.,
c     for each successive call to SOLIDX.  kl serves as a
c     flag signaling SOLIDX to count the number of initial
c     solids present at a specified finite amount (type 4)
c     and together with the solids print option, to determine
c     when and what to write to the output file.
c
c  -- The output variable kk is set to zero upon entry to this
c     routine and is set equal to -1 if a solid is determined to
c     have dissolved or to +1 if a solid has precipitated.  That
c     result is passed back to the calling routine (MAIND)
c     signaling whether to make another trip through the
c     equilibration loop (necessary if kk is other than 0).
c
      include 'CHESP.INC'
c
c -- THE INCLUDE FILE HAS A PARAMETER STATEMENT THAT SETS BOTH
c    NXDIM AND NYDIM.  (THEIR VALUES DEPEND UPON THE MEMORY
c    CAPACITY OF THE COMPUTER.)  THE INCLUDE STATEMENT ABOVE
c    MUST COME BEFORE THE DIMENSION STATEMENT FOR ARRAYS "CONC"
c    AND "SELECT" SINCE NYDIM IS USED FOR AN ADJUSTABLE ARRAY
c    DIMENSION. 10-15-87 JDA
c
      dimension conc(nydim),select(nydim)
      dimension itype4(20)
c
      real*8 conc,select,spcn,v,vi,vmax,vmin
      character lastime*1, action*12, state*5
      include 'CONST.INC'
c
      action = 'finished    '
c
      if (nn(3)+nn(4).eq.0) go to 190
      ll = nn(3)+nn(4)
      ii = nn(1)+nn(2)
      i0 = nn(1)+nn(2)+1
      j0 = nnn-nn(3)-nn(4)+1
      jj = nnn
      if (kl.eq.0) then
         i4 = nn(1)+nn(2)+nn(3)+nn(4)
         i3 = nn(1)+nn(2)+nn(3)+1
c
c NOW INITIALIZE ARRAYS FOR INITIAL SOLID MASS
c
         ntype4 = 0
```

```
         if (i4.ge.i3) then
            do 100 i = i3, i4
               if (c(i).gt.DOMIN) then
                  ntype4 = ntype4+1
                  conc(i) = c(i)
                  itype4(ntype4) = idy(i)
               endif
  100       continue
         endif
      endif
c
c
      ni = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      do 110 i = 1, ni
         select(i) = 0.0d0
  110 continue
c
c  Mass balance minus solids
c
      do 120 j = j0, jj
         y(j) = -t(j)
         do 120 i = 1, ii
            y(j) = y(j) + dble(b(i,j))*c(i)
  120 continue
c
c AMOUNT OF SOLIDS
c
      do 180 l = 1, ll
         c(i0) = -y(j0)/dble(b(i0,j0))
c
c PROVISION FOR C=0
c
         if (dabs(c(i0)).lt.DOMIN) then
            gc(i0) = 0.0d0
         else
            gc(i0) = dlog10(DABS(c(i0)))
         endif
c
c
         do 130 k = j0, jj
            y(k) = y(k)+dble(b(i0,k))*c(i0)
  130    continue
c
c UNMODIFY A,B,T,GX,X
c
         nxs = j0-1
         ncs = i0-1
         v = gk(i0)
         do 140 j = 1, nxs
             v = v+dble(a(i0,j))*gx(j)
  140    continue
           gx(j0) = -v/dble(a(i0,j0))
           x(j0) = 10.0d0**(gx(j0))
         do 150 i = 1, ncs
            do 152 j = 1, nxs
               if (dabs(b(i0,j)).gt.DOMIN.and.dabs(b(i,j0)).gt.DOMIN)
     *         then
                 b(i,j) = b(i,j)+b(i0,j)*b(i,j0)/b(i0,j0)
```

```
                end if
                if (abs(a(i0,j)).gt.DOMIN.and.abs(a(i,j0)).gt.DOMIN)
     *          then
                  a(i,j) = a(i,j)+a(i0,j)*a(i,j0)/a(i0,j0)
                end if
c  --  Note:  The above operations are to undo modifications done in
c             Subroutine SOLID.  Successive passes thru the SOLID/
c             SOLIDX loop causes numerical dispersion. That is, numbers
c             that should really be treated as zero are on the order of
c             1e-17 or so.  This doesn't hurt anything except that
c             the pointer arrays in which we would like to record
c             only the locations of non-zero elements are made
c             to include these "almost zero" non-zero elements.  So,
c             given 0.001 as the absolute value of the smallest
c             legitimate input stoichiometry, we require that to again
c             be the case after the "unmodifying" step above.  This
c             prevents accumulating errors that lead to dispersion.
                if (abs(b(i,j)).lt.0.001) b(i,j) = 0.0d0
                if (abs(a(i,j)).lt.0.001) a(i,j) = 0.0
  152         continue
  150      continue
           do 160 j = 1, nxs
              t(j) = t(j)+dble(b(i0,j))*t(j0)/dble(b(i0,j0))
  160      continue
           do 170 i = 1, ncs
              gk(i) = gk(i)+dble(a(i,j0))*gk(i0)/dble(a(i0,j0))
  170      continue
c
c NOW ADD THE INITIAL MASS OF A TYPE4 SOLID
c
           c(i0) = c(i0)+conc(i0)
           i0 = i0+1
           j0 = j0+1
  180 continue
  190 continue
c
c  SOLUBILITY PRODUCTS
c
      if (nn(5)+nn(6).eq.0) go to 220
      i0 = nn(1)+nn(2)+nn(3)+nn(4)+1
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      jj = nnn
      do 210 i = i0, ii
         v = gk(i)
         spcn = 0.0d0
         do 200 j = 1, jj
            v = v + a(i,j) * gx(j)
            if (idx(j).ne.002) spcn = spcn + abs(a(i,j))
  200    continue
         gc(i) = v
c
         if (DABS(v).lt.38.D0) then
            c(i) = 10.0d0**v
         else
            c(i) = 0.0d0
         endif
c
         if (spcn.lt.DOMIN) then
```

```
            select(i) = gc(i)
         else
            select(i) = gc(i)/spcn
         endif
  210 continue
  220 continue
c
      if (idebug.eq.4) then
         write (lunout,9000)
         write (lunout,9010)
         do 230 i = 1, ii
            write (lunout,9020) i,idx(i),x(i),idy(i),c(i),gk(i),y(i)
  230    continue
      endif
c
c   CHECK FOR DISSOLUTION
c
      if (nn(4).eq.0) go to 290
      imin = 0
      vmin = 0.0d0
      i0 = nn(1)+nn(2)+nn(3)+1
      ii = nn(1)+nn(2)+nn(3)+nn(4)
      do 240 i = i0, ii
         if (c(i).ge.vmin) go to 240
         vmin = c(i)
         imin = i
  240 continue
      if (imin.eq.0) go to 290
c
      if (iprint.eq.3) go to 250
      if (iprint.eq.2.or.iprint.eq.0.and.k1.eq.0) go to 250
      go to 260
  250 continue
      call outcmp
      lastime = 'n'
      call outspc (lastime)
      call outpc (lastime)
      state = 'under'
      call iap (state)
  260 continue
c
      write (lunout,9030) iter,name(imin)
c
      if (ntype4.ne.0) then
         do 280 i = 1, ntype4
            if (itype4(i).eq.idy(imin)) then
               do 270 j = 1, nnn
                 t(j) = t(j) + b(imin,j)*conc(imin)
  270          continue
               conc(imin) = 0.0d0
               ntype4 = ntype4-1
            endif
  280    continue
      endif
c
         conc(imin) = 0.0d0
c
c NOW EXCHANGE ROWS IN THE CONC ARRAY
```

```
c
          vi = conc(ii)
          conc(ii) = conc(imin)
          conc(imin) = vi
c
          call exrow (imin,ii)
          nn(5) = nn(5)+1
          nn(4) = nn(4)-1
          idwrite = ii
          call display (14)
          action = 'dissolved   '
          return
  290 continue
c
c CHECK FOR PRECIPITATION
c
      if (nn(5).eq.0) go to 330
      vmax = 0.0d0
      imaxx = 0
      i0 = nn(1)+nn(2)+nn(3)+nn(4)+1
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)
      do 300 i = i0, ii
         if (select(i).lt.vmax) go to 300
         vmax = select(i)
         imaxx = i
  300 continue
      if (imaxx.eq.0) go to 330
c
      if (iprint.eq.3) go to 310
      if (iprint.eq.2.or.iprint.eq.0.and.k1.eq.0) go to 310
      go to 320
  310 continue
      call outcmp
      lastime = 'n'
      call outspc (lastime)
      call outpc (lastime)
      state = 'over '
      call iap (state)
  320 continue
c
      call tstamp
      write (lunout,9050) iter,name(imaxx)
c
      call exrow (imaxx,i0)
      nn(4) = nn(4)+1
      nn(5) = nn(5)-1
      idwrite = i0
      call display (15)
      action = 'precipitated'
  330 continue
      return
c
 9000 format ('0','DEBUG PRINT IN SUBROUTINE SOLIDX')
 9010 format ('0',' I ',2x,'  IDX  ',2x,'     X    ',2x,'  IDY  ',2x,
     *  '     C    ',2x,'    GK    ',2x,'     Y     ')
 9020 format (' ',i3,2x,i7,2x,1pe10.3,2x,i7,2x,e10.3,2x,0pf9.4,2x,
     *  1pe10.2)
 9030 format ('0','  ITERATIONS= ',i3,':  SOLID ',a12,' DISSOLVES')
```

```
 9040 format (' ','VMIN = ',1pe10.3,' IMIN = ',i7)
 9050 format ('0','  ITERATIONS= ',i3,':  SOLID ',a12,' PRECIPITATES'
     *   )
 9060 format (' ','VMAX = ',1pe10.3,' IMAX = ',i7)
c
      end
c*********************  subroutine  # 24  ******************************
      subroutine tstamp
c**********************************************************************
c  -- The VAX and PC versions of this routine are different. This
c     is the PC version.
c
      include 'CHESP.INC'
      integer*2 yr, mo, dy, hr, mn, sc, hd
      character  month*3
      dimension month(12)
      data (month(i),i=1,12) /'JAN','FEB','MAR','APR','MAY','JUN','JUL',
     *      'AUG','SEP','OCT','NOV','DEC'/
c
      lunout = 06
c
      call getdat(yr,mo,dy)
      yr = yr - 1900
      iddate = yr*10000 + mo*100 + dy
      call gettim(hr,mn,sc,hd)
      idtime = hr*1000000 + mn*10000 + sc*100 + hd
      write (lunout,5000) version, dy, month(mo), yr, hr, mn, sc
5000  FORMAT(2X,' PC CHESP ',a5,3X,'DATE OF',
     *       ' CALCULATIONS:',1X,i2,'-',a3,'-',i2,2X,
     *        'TIME:',1X,i2,':',i2,':',i2,/)
c
      RETURN
      END
c****************  subroutine # 25   *****************************
      subroutine error
c*********************************************************************
c ***************************************************************
c
c     Reads/writes the error diagnostics for CHESP errors.
c
c ***************************************************************
c
      include 'CHESP.INC'
c
      character lastime*1, msg*78
      integer*4  jerr, nlines
c
      ierrtotl = ierrtotl + 1
c
  5   read (ierrin,500,end=999) errcode, jerr, nlines
      if (jerr.ne.ierr) then
        do 10 i = 1, nlines
          read (ierrin,1000) msg
 10     continue
        go to 5
      else
        write (lunout,2000) errcode,ierr
        do 20 i = 1, nlines
```

```
          read (ierrin,1000) msg
          write (lunout,4000) msg
 20     continue
      end if
c
      if (ierr.ge.8) then
        write (lunout,3000)
        call outcmp
        lastime = 'n'
        call outspc (lastime)
      end if
      rewind ierrin
c
      call display (5)
 999  return
c
 500  format (a7,i2,1x,i2)
1000  format (a78)
2000  format (/,' ***** ERROR CODE:  ',a7,i2,'  **  ERROR  **  ERROR',
     *         '  **  ERROR  **  ERROR  ****')
4000  format (1x,78a)
3000  format (/,' The following information for each component may be',
     *           ' useful for further error',
     *         /,' analysis.  THE VALUES LISTED DO NOT',
     *           ' CORRESPOND TO THE EQUILIBRIUM SOLUTION.')
c
      end
c*************************   subroutine  # 26 *************************
      subroutine init
c***********************************************************************
      include 'CHESP.INC'
c
      ierr = 0
      itmax = 40
      dens = 1.0d0
      xmu = 0.0d0
      vhc = 2.302585d0
      r = 0.00198719d0
      rj = 8.314d0
      fcc = 96487.0d0
      iads = 0
      iter = 0
c
      do 110 i = 1, nydim
         c(i) = 0.0d0
         gc(i) = 0.0d0
         gk(i) = 0.0d0
         idy(i) = 0
         spcz(i) = 0.0
         dha(i) = 0.0
         dhb(i) = 0.0
         gfw(i) = 0.0
         dh(i) = 0.0d0
         maxgk(i) = 0.0
         mingk(i) = 0.0
         name(i) = ' '
         gamma(i) = 0.0d0
         alkfct(i) = 0.0
```

```
  100 continue
c
c NOW READ IN ANALYTICAL EXPRESSIONS FOR LOG K
c WITH TEMPERATURE FOR MINERALS AND SOLIDS ONLY
c REMEMBER MINERALS AND SOLIDS ARE STORED IN THE
c FIRST PART OF FILE LUN07.
c
      i = 1
  110 read (lun07,9060) id(i),ta(i),tb(i),tc(i),td(i),te(i),tf(i),tg(i
     *   )
      if (id(i).eq.0) then
         rewind lun07
         go to 120
      endif
      i = i+1
      go to 110
  120 num = i-1
c
      nlines = 0
      ipage = 1
      write (lunout,5750) 6
      call tstamp
      if (state.eq.'both ') then
        write (lunout,9020)
      else if (state.eq.'over ') then
        write (lunout,9021)
      else if (state.eq.'under') then
        write (lunout,9022)
      end if
c
      write (lunout,9050)
      rewind lun04
c
c READ IN THE DATA FOR ONLY ONE MINERAL
c
  130 read (lun04) midt,minnam,dht,gkt,maxgkt,mingkt,
     *   spz,spcdha,spcdhb,spcgfw,alkft,ncmp,(at(j),
     *   idt(j),j=1,ncmp)
      if (midt.eq.0) go to 999
c
      match = '  '
      v = 0.0d0
      do 150 i = 1, ncmp
         n = iadx(idt(i))
         if (n.eq.0) go to 130
         v = v+at(i)*gx(n)
  150 continue
c
c CHECK FOR INSERTED SPECIES WITH THE SAME ID AS TYPE 6 SOLIDS
c
      if (kount.eq.0) go to 170
      do 160 i = 1, kount
         if (idydum(i).ne.midt) go to 160
         match = '**'
  160 continue
c
  170 tmpk = vhoff(gkt,dht)
c
```

```
c CALCULATE LOG K WITH T
c
      do 220 i = 1, num
         if (id(i).ne.midt) go to 220
         tmpk = ta(i)+tb(i)*tempk+tc(i)/tempk+td(i)*dlog10(tempk)+te(
     *      i)*(tempk*tempk)+tf(i)/(tempk*tempk)+tg(i)/dsqrt(tempk)
         go to 230
  220 continue
  230 continue
      si = v+tmpk
      if (state.eq.'over '.and.si.lt.0.0) go to 130
      if (state.eq.'under'.and.si.gt.0.0) go to 130
      if (ncmp.le.3) then
         nlines = nlines + 1
         write (lunout,9030) match,midt,minnam,si,(oparen,at(j),cparen,
     *      idt(j),j=1,ncmp)
      elseif (ncmp.ge.4.and.ncmp.le.6) then
         nlines = nlines + 2
         write (lunout,9035) match,midt,minnam,si,(oparen,at(j),cparen,
     *      idt(j),j=1,ncmp)
      elseif (ncmp.ge.7.and.ncmp.le.9) then
         nlines = nlines + 3
         write (lunout,9040) match,midt,minnam,si,(oparen,at(j),cparen,
     *      idt(j),j=1,ncmp)
      elseif (ncmp.ge.10.and.ncmp.le.12) then
         nlines = nlines + 4
         write (lunout,9045) match,midt,minnam,si,(oparen,at(j),cparen,
     *      idt(j),j=1,ncmp)
      endif
      if (ipage.eq.1) then
        if (nlines.le.42) go to 130
      else
        if (nlines.le.50) go to 130
      end if
c
      ipage = ipage + 1
      nlines = 0
      write (lunout,9000)
      write (lunout,9050)
      go to 130
c 999 write(*,*)  "  state   ****************************************"
  999 return
c
 9000 format ('1'//)
 9020 format ('0','Saturation indices and stoichiometry of all',
     *        ' minerals')
 9021 format ('0','Saturation indices and stoichiometry of all',
     *        ' supersaturated minerals')
 9022 format ('0','Saturation indices and stoichiometry of all',
     *        ' undersaturated minerals')
 9030 format (' ',a2,i7,1x,a12,1x,f8.3,4x,3(a1,f7.3,a1,1x,i3,2x))
 9035 format (' ',a2,i7,1x,a12,1x,f8.3,4x,3(a1,f7.3,a1,1x,i3,2x),
     *      /,' ',                    35x,3(a1,f7.3,a1,1x,i3,2x))
 9040 format (' ',a2,i7,1x,a12,1x,f8.3,4x,3(a1,f7.3,a1,1x,i3,2x),
     *      /,' ',                    35x,3(a1,f7.3,a1,1x,i3,2x),
     *      /,' ',                    35x,3(a1,f7.3,a1,1x,i3,2x))
 9045 format (' ',a2,i7,1x,a12,1x,f8.3,4x,3(a1,f7.3,a1,1x,i3,2x),
     *      /,' ',                    35x,3(a1,f7.3,a1,1x,i3,2x),
```

```
     *      /,' ',                      35x,3(a1,f7.3,a1,1x,i3,2x),
     *      /,' ',                      35x,3(a1,f7.3,a1,1x,i3,2x))
 9050 format ('0',4x,'ID #',5x,'NAME',6x,'Sat. Index',8x,
     *    'Stoichiometry in [brackets] ')
 9060 format (i7,1x,7(e10.3,1x))
5750  format ('1',//,' ________________________________________',
     *        '_________________________________________',
     *      /,' ______________________________ PART ',i1,' of',
     *        ' OUTPUT FILE ___________________________')
c
      end
c**************************    subroutine # 28   ***********************
       subroutine dupcmp (idnew,i)
c***********************************************************************
c  -- The purpose of this routine is to duplicate (i.e., copy) the
c     TYPE 1 entry "i".   The newly created species will have the
c     id number "idnew" and will also be of TYPE 1 and identical to
c     the original in all respects.   This is useful for preserving
c     the identity of a TYPE 3 species as a TYPE 1 species
c     (Subroutine SWITCH moves fixed component species from TYPE 1 to
c     TYPE 3 without preserving TYPE 1 identity).
c
      include 'CHESP.INC'
      integer idnew
      i0 = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)  + 1
      idy(i0) = idnew
      do 10 j = 1, nxdim
        a(i0,j) = a(i,j)
        b(i0,j) = b(i,j)
   10 continue
      gk(i0) = 0.0
      dha(i0) = dha(i)
      dhb(i0) = dhb(i)
      gfw(i0) = gfw(i)
      spcz(i0) = spcz(i)
      dh(i0) = dh(i)
      name(i0) = name(i)
      maxgk(i0) = maxgk(i)
      mingk(i0) = mingk(i)
      gamma(i0) = gamma(i)
      c(i0) = c(i)
      j0 = nn(1) + 1
      n = j0+i0-nn(1)-2
      do 30 l = j0, n
        call exrow (l,i0)
   30 continue
      nn(1) = nn(1) + 1
c
      return
c
      end
c**************************subroutine #29   **************************
      subroutine pointer
c**********************************************************************
c     ****************************************************************
c
c  -- The purpose of this routine is to load the indices of all
c     non-zero stoichiometry elements for each species in an
```

```
c     array and to store the number of such elements in a
c     corresponding vector.  The array is accessed in Subroutine
c     Solve to avoid the overhead of multiplying or adding
c     non-zero stoichiometries in mass action and related equations
c     by "pointing" to non-zero stoichiometries only.
c
c     *************************************************************
      include 'CHESP.INC'
c
c  -- Re-create the pointer arrays.
c     jmax(i) stores the number of non-zero elements of array "a"
c     for species i.  jpta(i,j) stores the column number address of
c     the jth component which has non-zero stoichiometry in species i.
      nc = nn(1) + nn(2)
      nx = nnn - nn(3) - nn(4)
      do 100 i = 1, nc
        jmax(i) = 0
        do 110 j = 1, nx
c  -- Because 0.001 is the absolute value of the smallest legitimate
c     input stoichiometry and 99.999 is the absolute value of the
c     largest legitimate input stoichiometry, 1e-08 is then the
c     absolute value of the smallest legitimate results from the
c     modification of the stoichiometry arrays above.  Any element whose
c     absolute value is smaller than this is regarded as zero.
            if (abs(b(i,j)) .ge. 1.0e-8) then
              jmax(i) = jmax(i) + 1
              jpta(i,jmax(i)) = j
            end if
 110    continue
 100  continue
c
c     imax(j) stores the number of non-zero elements of array "a"
c     for component j.  ipta(j,i) stores the row number address of
c     the ith species which has non-zero stoichiometry of component j.
      do 120 j = 1, nx
        imax(j) = 0
        do 130 i = 1, nc
          if (abs(b(i,j)) .ge. 1.0e-8) then
            imax(j) = imax(j) + 1
            ipta(j,imax(j)) = i
          end if
 130    continue
 120  continue
c
      return
      end
c*************************   subroutine   30 *********************
      subroutine alkcor
c**************************************************************
c ***************************************************************
c
c  -- The purpose of this routine is to calculate the total dissolved
c     concentration of component 140, CO3-2, from the user-supplied
c     value of alkalinity.  The alkalinity is stored in t(j) where
c     j = the component index corresponding to id # 140.  Alkalinity
c     as used here means that the value supplied represents the
c     acid-neutralizing capacity of the solution as determined by
c     titrating the solution to the CO2 equivalence endpoint.
```

```
c     This corresponds to an operational definition implemented here
c     which is:  The alkalinity is the negative of the TOTH expression
c     when the components are the principal components at the CO2
c     equivalence point.  BEYOND THIS, THE EXACT DEFINITION OF
c     ALKALINITY AS USED IN ANY PARTICULAR PROBLEM DEPENDS ON THE
c     CONTENT OF THE FILE ALK.DBS.
c
c     In general, the principal components of an aqueous solution are
c     those components that result when the following component
c     selection rules are obeyed:
c
c       Choose components for the system in the following order:
c
c          1 - Choose H2O.
c          2 - Choose H+.
c          3 - Choose species with fixed activities, i.e., solids
c              or gases at fixed partial pressures.
c          4 - Choose the most abundant soluble species.
c
c
c     CHESP has a pre-defined set of components not all of which
c     are the principal components at the CO2 equivalence point, but
c     this does not invalidate the applicability of the operational
c     definition of alkalinity.  It simply means that the alkalinity
c     expression will incorporate species that may also be
c     components.  Practically, the procedure for determining the
c     alkalinity factors needed for carbonate containing species in
c     THERMO.DBS and for entries in ALK.DBS is to write (outside of
c     CHESP) the TOTH expression derived using the principal
c     components at the CO2 equivalence point.  The negative of the
c     coefficient for each of species as it occurs in the TOTH
c     equation is the alkalinity factor for that species.  Stated
c     differently, the contribution of each species in solution to the
c     alkalinity is given by the negative of the stoichiometry of
c     H+ in that species times that species concentration.
c
c     The only species that are implicitly included as contributors to
c     the entered alkalinity are the TYPE 1 component species CO3-2
c     and those TYPE 2 species for which there is a non-zero entry for
c     the alkalinity factor in THERMO.DBS (such as for HCO3-).  For
c     these species, it is not necessary for the user to know the
c     alkalinity factor; the appropriate factor is already in
c     THERMO.DBS.
c
c     If other species are to be included as contributors to
c     alkalinity, the id number and the proper alkalinity factor, as
c     given by the TOTH expression derived using the principal
c     components at the CO2 equivalence point, must be entered in
c     ALK.DBS.  Entries for species containing CO3-2 MUST NOT be
c     included in that file.  Suppose for example that the sample you
c     wish to model and for which you've measured the alkalinity
c     contains appreciable dissolved phosphate.  You may wish to
c     account for the phosphate contribution to the measured
c     alkalinity so as to arrive at a more correct value for total
c     dissolved carbonate.  Procedure:
c
c     1 -   Principal components at CO2 equivalence point:
c           (H+, CO2, H2PO4-, ..., other components)
```

```
c
c     2 -   TOTH = (H+) - (HCO3-) - 2(CO3-2) + (H3PO4) - (HPO4-2)
c                  - 2(PO4-3) + ... other species
c
c     3 -   Noting that the pKl for H3PO4 is 2.2, we might choose to
c           omit that species altogether due to its negligible
c           concentration above pH 4.  Retaining it here for
c           illustration, entries in ALK.DBS would look like this:
c
c                      3305802 -1.00
c                      3305800  1.00
c                          580  2.00
c                      3300020  1.00
c                          330 -1.00
c
c           where the 7 and 3 digit numbers are species id numbers:
c                      3305802 = H3PO4
c                      3305800 = HPO4-2
c                          580 = PO4-3
c                      3300020 = OH-
c                          330 = H+
c           and the rightmost digit in each id number is in column 7
c           and the first line in the file holds the first entry.
c
c
c     Thus, in this case, the alkalinity equation to which the value
c     input for alkalinity corresponds is:
c
c     alk = [HCO3-] + 2[CO3-2] - [H3PO4] + [HPO4-2] + 2[PO4-3]
c            + [OH-] - [H+]
c
c     In most natural systems, the phosphate species are at much
c     lesser concentration than the carbonate and can thus be
c     neglected.  But, as shown above, the user controls the
c     alkalinity equation by preparing ALK.DBS.
c
c     If this same file is used in a CHESP run for which component
c     id # 580 (PO4-3) is not included, then those entries in ALK.DBS
c     that involve component 580 are simply ignored and the alkalinity
c     equation that would be used is:
c
c     alk = [HCO3-] + 2[CO3-2] + [OH-] - [H+]
c
c     Let the contribution of non-carbonate containing species to the
c     input alkalinity be called non-carbonate alkalinity.  Then, the
c     dissolved total inorganic carbon (TIC) is given by
c
c                    TIC = alk - excrb - noncrb + c(iyh2co3)
c
c     where  alk = The input alkalinity value converted to eq/L.
c
c          excrb = The total number of excess equivalents of acid
c                  consumed per mole of carbonate containing species,
c                  (total meaning summed over all such species).
c                  For each carbonate species, the alkalinity factor
c                  gives the total number of equivalents of acid
c                  consumed per mole.  Therefore, the excess
c                  equivalents for each such species is given by the
```

```
c                  difference between the alkalinity factor and the
c                  stoichiometry of CO3-2 in that species times the
c                  the number of moles, that is, times the
c                  concentration (per liter basis).
c
c         noncrb = The total number of equivalents of non-carbonate
c                  alkalinity (total meaning summed over all species
c                  contributing to non-carbonate alkalinity).
c                  For each non-carbonate species, the alkalinity
c                  factor is the number of equivalents of acid
c                  consumed per mole.  Therefore, the number of
c                  equivalents of non-carbonate alkalinity for
c                  each such species is the alkalinity factor times
c                  the species concentration (per liter basis).
c
c     c(iyh2co3) = The concentration of H2CO3(aq).
c
c
c  -- REFERENCES:
c         Morel, Francois M.M., PRINCIPLES of AQUATIC CHESPISTRY,
c                Wiley, New York, 1983, pp. 105,131-141.
c
c **********************************************************************
c
      include 'CHESP.INC'
c
      real*8 alk,excarb,fact,factor
c
      dimension ialk(30),fact(30),iidt(30)
      include 'CONST.INC'
c
c
c  -- Addresses of relevant species in component space (x) and species
c     space (y).
      ixco3 = iadx(140)
      iyco3 = iady(140)
      iyh2co3 = iady(3301401)
c
c  -- The input value for alkalinity, t(ixco3), is initially
c     in whatever units the user has chosen in PRODEFA2 and is
c     converted to mol/L in Subroutine PREP.  Convert to eq/L by
c     by multiplying by 2.  Also, the alkalinity factor for the
c     component species CO3-2 is 2.0; alkalinity factors for TYPE
c     2 species are in THERMO.DBS.
      if (iter.eq.0) then
         alk = t(ixco3)*2.0d0
         alkfct(iyco3) = 2.0
      endif
c
c  -- Compute the excess equivalents of acid that can be neutralized
c     by HCO3-, CO3-2, and any other aqueous species having non-zero
c     carbonate stoichiometry for which the components are present
c     and the alkalinity factor in the database THERMO.DBS is
c     non-zero.
      excarb = 0.0d0
      ll = nn(1)+nn(2)
      do 100 i = 1, ll
         if (alkfct(i).lt.D0MIN) go to 100
```

```
         excarb = excarb + c(i) * (alkfct(i)-a(i,ixco3))
  100 continue
c
c  -- Read the noncarbonate alkalinity file ALK.DBS on the first trip
c     through this routine only.  No need to re-read it on subsequent.
c     iterations.  Assignment of ALK.DBS to lun10 and file OPEN occurs
c     in Program CHESP.
      if (iter.eq.0) then
         i = 0
         rewind lun10
  110    read (lun10,9040) idt,factor
         if (idt.eq.0) go to 120
         k = iady(idt)
         if (k.eq.0) go to 110
         i = i+1
         ialk(i) = k
         iidt(i) = idt
         fact(i) = factor
         go to 110
  120    ii = i
      endif
c
c  -- Compute the total number of equivalents of acid-neutralizing
c     capacity represented by non-carbonate species (i.e., those
c     species which are included as TYPE 1 or TYPE 2 species in this
c     problem and for which entries are present in ALK.DBS).
      noncrb = 0.0d0
      if (ii.eq.0) go to 150
      do 130 i = 1, ii
c
c  -- The bounds on the following IF block seem ridiculously large;
c     If c(ialk(i)) is anywhere near 1e37, we've got big problems.
         if (dabs(c(ialk(i))).lt.1.0d37) then
           noncrb = noncrb + c(ialk(i)) * fact(i)
         end if
  130 continue
c
c  -- The following calculation arrives finally at the main objective:
c     to use the known value of alkalinity, the computed excess
c     acid-neutralizing capacity represented by carbonate species, the
c     computed acid-neutralizing capacity represented by non-carbonate
c     species, and the concentration of H2CO3 to compute the total
c     dissolved inorganic carbon in the system.
c  -- The bounds on the following IF block also seem ridiculously
c     large for the same reason as above.
      if (excarb.lt.1.0d37.and.c(iyh2co3).lt.1.0d37) then
         t(ixco3) = alk - excarb - noncrb + c(iyh2co3)
      else
         t(ixco3) = alk
      endif
c
c
      if (idebug.eq.2) then
         write (lunout,9010)
         do 140 i = 1, ii
            write (lunout,9020) iidt(i),fact(i),idx(ialk(i)),idy(ialk
     *         (i)),c(ialk(i)),x(ialk(i)),gamma(ialk(i)),ialk(i)
  140    continue
```

```
         write (lunout,9030) noncrb,excarb
      endif
c
c  -- Prevent total dissolved inorganic carbon from becoming less than
c     or equal to zero during iterations.
  150 if (t(ixco3).le.0.0) t(ixco3) = alk
c
      return
c
 9010 format ('0',5x,'ALK ID ',' FACTOR',2x,'  IDX  ',2x,'  IDY  ',2x
     *   ,'     C    ',2x,'     X    ',2x,'  GAMMA   ',2x,'IALK ')
 9020 format (5x,i7,2x,f5.2,2x,i7,2x,i7,2x,1pe10.3,2x,1pe10.3,2x,
     *   0pf10.5,2x,i3)
 9030 format (5x,'NONCRB= ',1pe11.4,' CO3ALK = ',e11.4)
 9040 format (i7,1x,f5.2)
c
      end
c*************  subroutine # 31  ***********************************
      subroutine guess1 (actH,actE)
c*******************************************************************
c  -- The purpose of this subroutine is to make better activity
c     guesses for certain components.
c
      include 'CHESP.INC'
c
      real*8 k1, k2, k3, k4, k5, k6, k7, k8, k9, k10,
     *       total, actH, actE, coefa, coefb, coefc
      include 'CONST.INC'
c
c
c
      do 10 j = 1, nnn
      if (t(j).lt.DOMIN.or.reguess(j).eq.'n') go to 10
c
c  -- Carbonate
      if (idx(j).eq.140) then
        k1 = 10.0d0**gk(iady(3301400))
        k2 = 10.0d0**gk(iady(3301401))
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k1*actH + k2*actH**2)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Phosphate
      else if (idx(j).eq.580) then
        k1 = 10.0d0**gk(iady(3305800))
        k2 = 10.0d0**gk(iady(3305801))
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k1*actH + k2*actH**2 + k3*actH**3)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Aluminum
      else if (idx(j).eq.030) then
```

```
        k1 = 10.0d0**gk(iady(0303300))
        k2 = 10.0d0**gk(iady(0303301))
        k3 = 10.0d0**gk(iady(0303303))
        k4 = 10.0d0**gk(iady(0303302))
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k1/actH + k2/actH**2 + k3/actH**3
     *          + k4/actH**4)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c  -- Sulfate
      else if (idx(j).eq.732) then
        k2 = 10.d0**gk(iady(3307320))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k2*actH)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c  -- Bi-sulfide
      else if (idx(j).eq.730) then
        k3 = 10.d0**gk(iady(3307300))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k3*actH)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Fe+3
      else if (idx(j).eq.281) then
        k4 = 10.d0**gk(iady(2813300))
        k5 = 10.d0**gk(iady(2813301))
        k6 = 10.d0**gk(iady(2813302))
        k7 = 10.d0**gk(iady(2813303))
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k4/actH + k5/actH**2
     *          + k6/actH**3 + k7/actH**4)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Fe+2
      else if (idx(j).eq.280) then
        k2 = 10.d0**gk(iady(2803300))
        k3 = 10.d0**gk(iady(2803302))
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k2/actH + k3/actH**2)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Manganese
```

```
      else if (idx(j).eq.470) then
        k2 = 10.d0**gk(iady(4703300))
        k3 = 10.d0**gk(iady(4703301))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 +  k2/actH + k3/actH**3)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
c  -- Arsenic
      else if (idx(j).eq.061) then
        k6 = 10.d0**gk(iady(3300611))
        k7 = 10.d0**gk(iady(3300612))
        k8 = 10.d0**gk(iady(3300613))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k6/actH + k7/(actH**2)
     *              + k8/(actH**3))
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
      else if (idx(j).eq.060) then
        k2 = 10.d0**gk(iady(3300600))
        k3 = 10.d0**gk(iady(3300601))
        k4 = 10.d0**gk(iady(3300602))
        k5 = 10.d0**gk(iady(3300603))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 + k1*(actE**2)*(actH**2)
     *              + k2/actH + k3/(actH**2)
     *              + k4/(actH**3) + k5*actH)
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
       end if
c
c  -- Chromium
      else if (idx(j).eq.211) then
        k2 = 10.d0**gk(iady(2113300))
        k3 = 10.d0**gk(iady(2113301))
        k4 = 10.d0**gk(iady(2113302))
        k5 = 10.d0**gk(iady(2113303))
        k6 = 10.d0**gk(iady(2113304))
c
        total = t(j)
        if (total.gt.DOMIN) then
          x(j) = total / (1.0 +  k2*(actH**2) + k3*actH
     *              + k4/actH + k5/(actH**2) + k6/(actH**2))
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
        end if
c
      else if (idx(j).eq.212) then
        k8 = 10.d0**gk(iady(2123300))
        k9 = 10.d0**gk(iady(2123301))
```

```
          k10= 10.d0**gk(iady(2123302))
c
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total / (1.0 + k8*actH + k9*(actH**2)
     *              + k10*(actH**2))
            gx(j) = dlog10 (x(j))
            reguess(j) = 'r'
          end if
c
c  -- Mercury
        else if (idx(j).eq.361) then
          k3 = 10.d0**gk(iady(3613300))
          k4 = 10.d0**gk(iady(3613302))
          k5 = 10.d0**gk(iady(3613303))
c
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total / (1.0 + k3*(actH**2) + k4*actH + k5/actH)
            gx(j) = dlog10 (x(j))
            reguess(j) = 'r'
          end if
c
        else if (idx(j).eq.360.and.iady(3600000).ne.0) then
          k2 = 10.d0**gk(iady(3600000))
c
          coefa = k2*actE
          coefb = 2.0d0
          coefc = -2*t(j)
          x(j) = (-coefb + dsqrt((coefb**2)-4.0d0*coefa*coefc))
     *             /(2.0d0*coefa)
          if (dabs(x(j)).lt.DOMIN) x(j) = -coefc/coefb
          x(j) = x(j)**2
          gx(j) = dlog10 (x(j))
          reguess(j) = 'r'
c
c
c  -- Copper
        else if (idx(j).eq.231) then
            k2 = 10.d0**gk(iady(2313300))
            k3 = 10.d0**gk(iady(2313301))
            k4 = 10.d0**gk(iady(2313302))
            k5 = 10.d0**gk(iady(2313303))
            k6 = 10.d0**gk(iady(2313304))
c
            coefa = k6/(actH**2)
            coefb = 1.0 + k2/actH + k3*(actH**2) + k4/(actH**3)
     *               + k5/(actH**4)
            coefc = -t(j)
            x(j) = (-coefb + dsqrt((coefb**2)-4.0d0*coefa*coefc))
     *               /(2.0d0*coefa)
            if (dabs(x(j)).lt.DOMIN) x(j) = -coefc/coefb
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
c
c
c  -- Selenium
        else if (idx(j).eq.760) then
```

```
          k2 = 10.d0**gk(iady(3307600))
          k3 = 10.d0**gk(iady(3307601))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k2*actH + k3/actH)
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
c
      else if (idx(j).eq.761) then
          k4 = 10.d0**gk(iady(3307610))
          k5 = 10.d0**gk(iady(3307611))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k4*actH + k5/actH)
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
      else if (idx(j).eq.762) then
          k7 = 10.d0**gk(iady(3307620))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k7*actH)
            gx(j) = dlog10(x(j))
           reguess(j) = 'r'
          end if
c
      else if (idx(j).eq.740) then
          k2 = 10.d0**gk(iady(7403302))
          k3 = 10.d0**gk(iady(7400020))
          k4 = 10.d0**gk(iady(7403301))
          k5 = 10.d0**gk(iady(7403300))
          k6 = 10.d0**gk(iady(7400021))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k2*actH + k3/actH + k4/actH
     *              + k5*actH + k6)
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
c
      else if (idx(j).eq.741) then
          k7 = 10.d0**gk(iady(7413300))
          k8 = 10.d0**gk(iady(7410021))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k7*(actH**2) + k8)
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
c
c  -- Thallium
      else if (idx(j).eq.870) then
          k2 = 10.d0**gk(iady(8703300))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k2/actH)
            gx(j) = dlog10(x(j))
```

```
            reguess(j) = 'r'
          end if
c
      else if (idx(j).eq.871) then
          k3 = 10.d0**gk(iady(8713300))
          k4 = 10.d0**gk(iady(8713301))
          k5 = 10.d0**gk(iady(8713302))
          k6 = 10.d0**gk(iady(8713303))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k3*(actH**3) + k4*(actH**2)
     *             + k5*actH + k6/actH)
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
c
c  -- Silica
      else if (idx(j).eq.770) then
          k1 = 10.d0**gk(iady(3307700))
          k2 = 10.d0**gk(iady(3307701))
          total = t(j)
          if (total.gt.DOMIN) then
            x(j) = total/(1.0d0 + k1/actH + k2/(actH**2))
            gx(j) = dlog10(x(j))
            reguess(j) = 'r'
          end if
        end if
   10 continue
c
c
c
      return
c
      end
c*************** Subrountine  # 32  ************************
      subroutine adsorb
c**********************************************************
c *************************************************************
c
c THIS SUBROUTINE PERFORMS ALL ADSORPTION CALCULATIONS
c FOR THE TRIPLE LAYER SITE BINDING MODEL YATES ET AL.(1975)
c AND FOR THE CONSTANT CAPACITANCE MODEL (SEE HOHL AND STUMM).
c THE SUBROUTINE IS BROKEN INTO THREE ENTRY POINTS.
c
c ENTRY ADSID INITIALIZES SOME USEFUL CONSTANTS AND LOCATES
c THE COLUMN HEADERS FOR THE ELECTROSTATIC COMPONENTS.
c
c ENTRY ADINIT INITIALIZES THE TOTAL MASSES OF THE SURFACE
c SITE AND ELECTROSTATIC COMPONENTS.
c
c ENTRY ADSJAC INCLUDES THE DERIVATIVES OF TJ/PSI(J) FOR
c THE ELECTROSTATIC COMPONENTS IN THE JACOBIAN
c
c *************************************************************
c
      include 'CHESP.INC'
c
      real*8 cnvft(5),econv,lambda,w
```

```
      integer*4 m0(5),m1(5)
      include 'CONST.INC'
c
      entry adsid
      if (iter.eq.0) then
         econv = dlog(10.0d0)*rj*tempk/fcc
         lambda = rj*tempk/fcc
         w = 1.0d0/(2d0*lambda)
      endif
c
      do 100 i = 1, 5
         IF (SOLCON(I).lt.DOMIN) GO TO 100
         cnvft(i) = ssa(i)*solcon(i)/fcc
         m0(i) = iadx(813+(i-1)*10)
         if (iads.eq.3) then
            m1(i) = iadx(814+(i-1)*10)
            m2(i) = iadx(815+(i-1)*10)
         endif
  100 continue
c
      return
c
c
      entry adinit
      do 110 i = 1, 5
         IF (SOLCON(I).lt.DOMIN) GO TO 110
         psi0(i) = -econv*gx(m0(i))
         if (iads.eq.3) then
            psib(i) = -econv*gx(m1(i))
            psid(i) = -econv*gx(m2(i))
         endif
         if (iads.eq.2) then
            sig0(i) = psi0(i)*cap1(i)
            t(m0(i)) = sig0(i)*cnvft(i)
         elseif (iads.eq.3) then
            sig0(i) = (psi0(i)-psib(i))*cap1(i)
            sigd(i) = (psid(i)-psib(i))*cap2(i)
            sigb(i) = -sig0(i)-sigd(i)
            t(m0(i)) = sig0(i)*cnvft(i)
            t(m2(i)) = sigd(i)*cnvft(i)
            t(m1(i)) = -t(m0(i))-t(m2(i))
         elseif (iads.eq.4) then
            sig0(i) = ee*sqrt(xmu)*dsinh(w*psi0(i))
            t(m0(i)) = sig0(i)*cnvft(i)
         endif
  110 continue
c
c
      return
c
      entry adscaly
      do 120 i = 1, 5
         IF (SOLCON(I).lt.DOMIN) GO TO 120
         y(m2(i)) = y(m2(i))+(-ee*sqrt(xmu)*dsinh(w*psid(i))*cnvft(i))
  120 continue
c
      return
c
```

```
      entry adsjac
      do 130 i = 1, 5
         IF (SOLCON(I).lt.DOMIN) GO TO 130
         if (iads.eq.2) then
            z(m0(i),m0(i)) = z(m0(i),m0(i))+cap1(i)*lambda/x(m0(i))*
     *         cnvft(i)
         elseif (iads.eq.3) then
            z(m0(i),m0(i)) = z(m0(i),m0(i))+cap1(i)*lambda/x(m0(i))*
     *         cnvft(i)
            z(m1(i),m2(i)) = z(m1(i),m2(i))-cap2(i)*lambda/x(m2(i))*
     *         cnvft(i)
            z(m2(i),m1(i)) = z(m2(i),m1(i))-cap2(i)*lambda/x(m1(i))*
     *         cnvft(i)
            z(m2(i),m2(i)) = z(m2(i),m2(i))+(cap2(i)+w*ee*dsqrt(xmu)*
     *         dcosh(w*psid(i)))*lambda/x(m2(i))*cnvft(i)
            z(m0(i),m1(i)) = z(m0(i),m1(i))-cap1(i)*lambda/x(m1(i))*
     *         cnvft(i)
            z(m1(i),m0(i)) = z(m1(i),m0(i))-cap1(i)*lambda/x(m0(i))*
     *         cnvft(i)
            z(m1(i),m1(i)) = z(m1(i),m1(i))+(cap1(i)+cap2(i))*lambda/
     *         x(m1(i))*cnvft(i)
         elseif (iads.eq.4) then
            z(m0(i),m0(i)) = z(m0(i),m0(i))+w*ee*dsqrt(xmu)*dcosh(w*
     *         psi0(i))*lambda/x(m0(i))*cnvft(i)
         endif
  130 continue
      return
c
      entry adsprnt
c
c  -- Print out information about adsorbents.
c
      if (iads.eq.2) then
         write (lunout,9000)
      elseif (iads.eq.3) then
         write (lunout,9010)
      elseif (iads.eq.4) then
         write (lunout,9020)
      endif
c
      do 140 i = 1, 5
         IF (SOLCON(I).lt.DOMIN) GO TO 140
         write (lunout,9030) i
         write (lunout,9040) psi0(i), sig0(i), psib(i), sigb(i),
     *                       psid(i), sigd(i)
         write (lunout,9050) solcon(i)
         write (lunout,9060) ssa(i)
  140 continue
      return
c
c
c
 9000 format (//,1x,'**** CONSTANT CAPACITANCE ADSORPTION MODEL ****'
     *   )
 9010 format (//,1x,'******** TRIPLE LAYER ADSORPTION MODEL ********'
     *   )
 9020 format (//,1x,'******* DIFFUSE LAYER ADSORPTION MODEL ********'
     *   )
```

```
 9030 format (//,1x,' **** Parameters For Adsorbent Number ',i1,
     *    ' ****')
 9040 format (1x,'  Electrostatic Variables:  psi0 = ',f8.6,4x,
     *    ' sig0 = ',f8.6,
     *      /,1x,'                            psib = ',f8.6,4x,
     *    ' sigb = ',f8.6,
     *      /,1x,'                            psid = ',f8.6,4x,
     *    ' sigd = ',f8.6)
 9050 format (1x,'  Adsorbent Concentration (g/l): ',f7.3)
 9060 format (1x,'  Specific Surface Area (sq. meters/g): ',f7.2)
c
      end
c************************* subroutine  # 33  ***********************
      subroutine simq (z,y,n,nxdim,ierr)
c*******************************************************************
c ****************************************************
c
c THIS SUBROUTINE SOLVES THE JACOBIAN MATRIX
c VIA GAUSSIAN ELIMINATION AND BACK SUBSTITUTION.
c
c THIS PROCEDURE IS FASTER THAN GAUSS-JORDAN ELIMINATION
c BY AT LEAST 50%.   (N^3+3N^2-N)/3
c ****************************************************
c
      include 'CONST.INC'
      real*8 z,y,zmax,v
      dimension z(nxdim,nxdim),y(nxdim)
c
c     PROVISION FOR N=1
c
      if (n.ne.1) go to 100
      y(1) = y(1)/z(1,1)
      return
  100 continue
c
c     ELEMENT OF ELIMINATION
c
      n1 = n-1
      do 160 m = 1, n1
         zmax = 0.0d0
         imax = 0
c
c     FIND MAX OF COLUMN
c
         do 110 i = m, n
            if (dabs(z(i,m)).le.zmax) go to 110
            imax = i
            zmax = dabs(z(i,m))
  110    continue
c
c     ERROR RETURN
c
         if (imax.ne.0) go to 120
         ierr = 9
         call error
         go to 999
  120    continue
c
```

```
c     ROW INTERCHANGE
c
         if (imax.eq.m) go to 140
         v = y(m)
         y(m) = y(imax)
         y(imax) = v
         do 130 j = m, n
            v = z(m,j)
            z(m,j) = z(imax,j)
            z(imax,j) = v
  130    continue
  140    continue
c
c     DIAGONALIZE
c
         m1 = m+1
         do 150 i = m1, n
            if (dabs(z(i,m)).lt.DOMIN) go to 150
            v = z(i,m)/z(m,m)
            y(i) = y(i)-v*y(m)
            do 155 j = m, n
              z(i,j) = z(i,j) - v * z(m,j)
  155       continue
  150    continue
  160 continue
c
c     BACK SUBSTITUTE
c
      y(n) = y(n)/z(n,n)
      n1 = n-1
      do 180 k = 1, n1
         i = n-k
         i1 = i+1
         do 170 j = i1, n
            y(i) = y(i)-y(j)*z(i,j)
  170    continue
         y(i) = y(i)/z(i,i)
  180 continue
  999 return
      end
c****************** subroutine  # 34   ****************************
      subroutine newx
c
c ******************************************************************
c
      include 'CHESP.INC'
      include 'CONST.INC'
c
      call display (6)
      nx = nnn-nn(3)-nn(4)
      do 10 j = 1, nx
c
         x(j) = x(j)-y(j)
c     non-conventional  x(j) = exp (log(x(j)) - y(j))
c
         if (x(j).le.((-1)*DOMIN)) then
            x(j) = (x(j)+y(j))/10.0d0
            gx(j) = dlog10(x(j))
```

```
         else if (dabs(x(j)).lt.DOMIN) then
            gx(j) = 0.0d0
         else
            gx(j) = dlog10 (x(j))
         end if
c
 10   continue
c      return
c
      end
c*******************************************************************
      real*8 function vhoff (k,dhv)
c
c *******************************************************************
c VHOFF
c
c THIS ROUTINE RETURNS THE EQUILIBRIUM CONSTANT CORRECTED FOR
c TEMPERATURE. THE COMMON VARIABLE VH WAS SET IN INPUT TO:
c
c  VH=(1/T0 - 1/T1)/2.303*R
c
c
********************************************************************
      include 'CHESP.INC'
      real*8 dhv,k
c
      vhoff = k-dhv*vh
      return
      end
c********************** subroutine # 35  ****************************
      subroutine switch (l,ltype,i)
c
c ***************************************************************
c THE PURPOSE OF THIS SUBROUTINE IS TO CHANGE THE TYPE
c OF A SPECIE FROM TYPE L TO LTYPE. THIS REQUIRES
c CHANGING THE ROW THE SPECIE IS STORED IN WHICH IS
c ACCOMPLISHED BY CALLING EXROW
c
      include 'CHESP.INC'
c
c     MOVE SPECIES I FROM TYPE L TO LTYPE
c
      if (l.eq.ltype) go to 130
      k = 1
      ii = 0
      do 100 ll = 1, l
         ii = ii+nn(ll)
 100  continue
      if (ltype.gt.l) go to 110
      k = -1
      ii = ii-nn(l)+1
 110  continue
      nn(l) = nn(l)-1
      nn(ltype) = nn(ltype)+1
      l2 = l
 120  call exrow (i,ii)
      l2 = l2+k
      i = ii
```

```
c                       number of reactions in which the composite
c                       ligand is a reactant.  The value of nrxcl is
c                       assigned in subroutine INPUT.
c
c            idxcl   =  An array containing the component id numbers
c                       of all components involved in composite
c                       ligand reactions.  Does not include the
c                       id number of the composite ligand component
c                       itself.
c
c           nidxcl   =  The number of entries in idxcl.  The number of
c                       components involved in reactions with the
c                       composite ligand (not counting the ligand
c                       itself).
c
c            stoica  =  A 2-d array having one row for each complex
c                       involving the composite ligand (thus, each
c                       row corresponds to an entry in idrxcl and there
c                       are nrxcl rows).  Each column represents
c                       a component involved in a reaction with
c                       the composite ligand (the ligand itself
c                       has no corresponding column).  Thus, each
c                       column is identified with an entry in the
c                       array idxcl and there are nidxcl columns.
c                       The entries themselves give the stoichiometry
c                       of the component (represented by that column
c                       index) in the species (represented by the
c                       row index).
c
c            jmaxcl  =  An integer array containing the number of non-
c                       zero entries along a particular row of stoica.
c
c           jptacl  =  A 2-d integer array containing the column indices
c                       of the non-zero elements of a particular row
c                       of stoica.
c
c            gamma   =  A global array containing the common log of
c                       the activity coefficients as computed in
c                       Subroutine ACTVTY.
c
c            idy     =  A global array containing the id numbers
c                       of ALL species; includes components as
c                       free species.
c
c            idx     =  A global array containing the 3-digit id
c                       numbers of ALL components involved in
c                       this problem.
c
c            nnn     =  The total number of components in this
c                       problem.
c
c            sigma   =  A variable containing the standard deviation
c                       in log K for a complex involving a
c                       composite ligand.  In this implementation
c                       of the composite ligand model, all reactions
c                       have identically the same value of sigma.
c
c            t       =  A global array containing the total
```

```
c                       dissolved concentrations of ALL components
c                       involved in this problem.
c
c
c     --------------------------------------------------------------
c     LOCAL**LOCAL**LOCAL**LOCAL**LOCAL**LOCAL**LOCAL**LOCAL**LOCAL
c
c       npts    = The total number of points and weights (32).
c
c       zp      = An array containing the Gaussian-Hermite points.
c
c       wt      = An array containing the Gaussian-Hermite weights.
c
c       sqr2    = Square root of 2.
c
c       wtsum   = A normalization factor for the integration equal to
c                 the sum of the weights and to the reciprocal of pi.
c
c       jxlig   = The array index address of the composite ligand
c                 component.
c
c       xnum    = An array containing the numerator portion of the
c                 expression for the concentration of metal/ligand
c                 complex.  A value of xnum is computed for each
c                 point zp along the integration path by multiplying
c                 by the appropriate weight.
c
c       xdenom  = An array containing the denominator portion of the
c                 expression for the concentration of metal/ligand
c                 complex.  A value of xdenom is computed for
c                 each point zp along the integration path.
c
c       cxnum   = The resulting numerator in the expression for bound
c                 metal if the individual quoients corresponding to
c                 each point in the Gaussian quadrature integration
c                 are summed after finding a common denominator.
c
c       cxdenom= The common denominator of all the individual quoients
c                 of the Gaussian quadrature.
c
c       gkclc   = An array to which is assigned the corrected mean
c                 log K values pertaining to each reaction involving
c                 the composite ligand.  "Corrected" means multiplied by
c                 the activity coefficient pertaining to the free ligand
c                 and divided by the activity coefficient pertaining
c                 to the metal-ligand complex.  The uncorrected
c                 mean log K values are retained in the global array
c                 gkcl.
c
c       term    = An array whose elements contain the terms of the
c                 denominator that arise from all the composite
c                 ligand complexes including the one for which we are
c                 calculating the concentration in a call to this
c                 routine.  Each term is represented by the left
c                 hand side of a mass action equation for the
c                 corresponding reaction given that the equation is
c                 arranged so that only one product, the metal/ligand
c                 complex, appears on the right-hand side.
```

```
c
c       conc   = The intermediate result of the Gaussian-Hermite
c                  quadrature integration and finally, the concentration
c                  of the complex whose id is idy(iy); i.e., the answer
c                  we seek.  The common log of conc is returned to the
c                  calling program unit as the answer.
c
c       tmp1   = A temporary storage buffer used for intermediate
c                  results in calculating the terms contributing to
c                  xdenom and in calculating the partial derivatives.
c
c       tmp2   = A temporary storage buffer used for intermediate
c                  results in calculating the partial derivatives.
c
c
c
c
c     --------------------------------------------------------------
c     OUTPUT**OUTPUT**OUTPUT**OUTPUT**OUTPUT**OUTPUT**OUTPUT**OUTPUT
c
c     Primary output:
c
c       vlig = The log concentration of the metal/ligand complex
c              whose id number is idy(iy).
c
c
c     Variables in CHESP.INC common blocks modified by COMPOSIT:
c
c       z(j,k) =  The gradients or partial derivatives.  More
c                 specifically, the change in the mass imbalance of
c                 component j as a function of change in the
c                 activity of component k.  Only those gradients
c                 involving components that complex the composite
c                 ligand are modified.  Note that for every
c                 component,  each z(j,k) is actually a summation
c                 of contributing terms.  Each term is computed by
c                 taking the partial derivative of a species
c                 concentration (the species must have non-zero
c                 stoichiometry in component j, else the computation
c                 is pointless).  The derivative is taken with respect
c                 to the activity of component k.  The "partial
c                 gradients" computed here are for those
c                 terms where the species of interest is the
c                 metal/ligand complex with id number idy(iy).
c
c
c
c
c     ****************************************************************
c     BEGIN**BEGIN**BEGIN**BEGIN**BEGIN**BEGIN**BEGIN**BEGIN**BEGIN
c     ****************************************************************
c
      real*8 zp(32), wt(32), gkclc(14), term(14), xdenom(32), xnum(32),
     &       conc, vlig, wtsum, tmp1, tmp2, cxdenom, cxnum
c
      include 'CHESP.INC'
c
c
```

```
c  -- The set of 32 points for the Gaussian-Hermite quadrature:
      data (zp(i), i = 1, 32) / 0.7125813909830728E+01,
     *         0.6409498149269661E+01,
     *         0.5812225949515914E+01,
     *         0.5275550986515880E+01,
     *         0.4777164503502596E+01,
     *         0.4305547953351199E+01,
     *         0.3853755485471445E+01,
     *         0.3417167492818571E+01,
     *         0.2992490825002374E+01,
     *         0.2577249537732317E+01,
     *         0.2169499183606112E+01,
     *         0.1767654109463202E+01,
     *         0.1370376410952872E+01,
     *         0.9765004635896828E+00,
     *         0.5849787654359324E+00,
     *         0.1948407415693993E+00,
     *        -0.1948407415693993E+00,
     *        -0.5849787654359324E+00,
     *        -0.9765004635896828E+00,
     *        -0.1370376410952872E+01,
     *        -0.1767654109463202E+01,
     *        -0.2169499183606112E+01,
     *        -0.2577249537732317E+01,
     *        -0.2992490825002374E+01,
     *        -0.3417167492818571E+01,
     *        -0.3853755485471445E+01,
     *        -0.4305547953351199E+01,
     *        -0.4777164503502596E+01,
     *        -0.5275550986515880E+01,
     *        -0.5812225949515914E+01,
     *        -0.6409498149269661E+01,
     *        -0.7125813909830728E+01/
c
c
c  -- The set of 32 points for the Gaussian-Hermite quadrature:
      data (wt(i), i = 1, 32) / 0.7310676427384062E-22,
     *         0.9231736536518204E-18,
     *         0.1197344017092854E-14,
     *         0.4215010211326414E-12,
     *         0.5933291463396681E-10,
     *         0.4098832164770878E-08,
     *         0.1574167792545590E-06,
     *         0.3650585129562368E-05,
     *         0.5416584061819989E-04,
     *         0.5362683655279717E-03,
     *         0.3654890326654427E-02,
     *         0.1755342883157342E-01,
     *         0.6045813095591263E-01,
     *         0.1512697340766425E+00,
     *         0.2774581423025300E+00,
     *         0.3752383525928024E+00,
     *         0.3752383525928024E+00,
     *         0.2774581423025300E+00,
     *         0.1512697340766425E+00,
     *         0.6045813095591263E-01,
     *         0.1755342883157342E-01,
     *         0.3654890326654427E-02,
```

```
     *        0.5362683655279717E-03,
     *        0.5416584061819989E-04,
     *        0.3650585129562368E-05,
     *        0.1574167792545590E-06,
     *        0.4098832164770878E-08,
     *        0.5933291463396681E-10,
     *        0.4215010211326414E-12,
     *        0.1197344017092854E-14,
     *        0.9231736536518204E-18,
     *        0.7310676427384062E-22/
c
c
c
      npts = 32
      wtsum = dsqrt (4.0d0 * datan (1.0d0))
      sqr2 = dsqrt(2.0d0)
c
c  -- Find the array index address of the composite ligand component.
      do 10 j = 1, nnn
        if (b(iy,j).gt.0.0d0
     &     .and.(idx(j).ge.idclf.and.idx(j).le.idcll)) jxlig = j
  10  continue
c
c  -- Find the array index address (irxn) of the complex
c     whose concentration is to be computed.
      do 20 i = 1, nrxcl
        if (idy(iy) .eq. idrxcl(i)) irxn = i
  20  continue
c
c  -- Find the array index address in species space of all species
c     competing for the composite ligand.  We need to correct their
c     log K values for ionic strength by using previously computed
c     (Subroutine ACTVTY) log gamma's.   Store the corrected log K 's
c     in local array gkclc, preserving the originals in gkcl for use
c     in future corrections.
      do 30 k = 1, nrxcl
        n1 = iady(idrxcl(k))
        n2 = iady(idx(jxlig))
        gkclc(k) = gkcl(k) - gamma(n1) + gamma(n2)
  30  continue
c
c
c     Each element of the array term(k) corresponds to a term
c     in the denominator xdenom.  The denominator is a summation
c     of these terms including a term involving the complexing component
c     of the species for which we seek the concentration (that term is
c     also the numerator), as well as all other competing components.
c
      do 40 k = 1, nrxcl
        tmp1 = gkclc(k)
        do 50 j = 1, jmaxcl(k)
          jjj = jptacl(k,j)
          n = iady(idxcl(jjj))
          tmp1 = tmp1 + stoica(k,jjj)*(gc(n)+gamma(n))
  50    continue
        term(k) = 10.0d0**tmp1
  40  continue
c
```

```
c
c  -- Main computation loop
c
c     This loop computes and accumulates conc = xnum / xdenom for each
c     index i.  Values of xnum and xdenom are computed to
c     correspond with each value of zp(i) and wt(i).  The quoient
c     xnum/xdenom is summed (accumulated) in the variable conc, the
c     concentration of the species of interest.
c
      conc = 0.0d0
c
      do 60 i = 1, npts
        xnum(i) = term(irxn) * t(jxlig) / wtsum
c
        xdenom(i) = 1.0d0 / 10.0d0**(sigma * sqr2 * zp(i))
c
        do 70 k = 1, nrxcl
          xdenom(i) = xdenom(i) + term(k)
  70    continue
c
c
c  -- Compute the value of the quoient
        xnum(i) = xnum(i) * wt(i)
        conc = conc + xnum(i) / xdenom(i)
c
  60  continue
c
c  -- COMPUTE DERIVATIVES
c
c  -- Compute the common denominator of the overall quoient.  This
c     is just the product over all point denominators xdenom(i).
      cxdenom = xdenom(1)
      do 110 i = 2, npts
        cxdenom = cxdenom * xdenom(i)
 110  continue
c
c
c  -- Compute the numerator of the overall quoient.  This is
c     computed by:
c
c          npts                    npts
c          SUM  [xnum(i)    *      PROD (xdenom(j)) ]
c          i=1                  j=1,j.ne.i
c
c     This can be computed by accumulating the sum over i of each
c     xnum(i) times cxdenom/xdenom(i).
      cxnum = 0.0d0
      do 120 i = 1, npts
        cxnum = cxnum + xnum(i) * cxdenom/xdenom(i)
 120  continue
c
c
c  -- Compute the partial derivatives using the quoient rule:
c
c
c
c            d (conc)        d   (cxnum/cxdenom)
c            ---         =   ---
```

```
c           dx             dx
c
c
c
c                            d (cxnum)        cxnum  d (cxdenom)
c                           ---                     ---
c                      =    dx           -          dx
c                         ------------     -------------------
c                           cxdenom             cxdenom**2
c
c
c     The second term of this expression is divided by xdenom
c     squared, a very large number.  Thus, this term is negligible
c     and will be omitted from the calculations.
c
c  -- For those components for which the metal/ligand concentration
c     just computed enters into the mass balance equation:
      do 80 j = 1, jmaxcl(irxn)
        jjj = jptacl(irxn,j)
        jj = iadx(idxcl(jjj))
c
c  -- The partial derivative of the metal/ligand concentration is
c     taken with respect to the activity of each component having
c     non-zero stoichiometry in species irxn (i.e., that complexes
c     the ligand):
        do 90 k = 1, jmaxcl(irxn)
          kkk = jptacl(irxn,k)
          kk = iadx(idxcl(kkk))
          n = iady(idxcl(kkk))
c  -- Take the derivative of cxnum with respect to component idxcl(kkk)
c     and then divide by cxdenom.  This is the first term in the
c     quoient rule expression.  The second term is negligible and
c     is omitted from the calculations.
          tmp1 = (stoica(irxn,kkk) * cxnum / (c(n)*10.0d0**gamma(n)))
     *             / cxdenom
c
c     ****************************************************************
c     SPECIAL NOTE:
c
c     The following code segment shows how to compute the second
c     term should it ever prove necessary to do so.  Test runs with
c     this code not commented out show that tmp2 will be very
c     small.  (A value of 1e-80 was the largest tmp2 observed in
c     the tests).
c
c  -- Take the derivative of cxdenom, with respect to component
c     idxcl(kkk), multiply by cxnum, and divide by cxdenom**2.  This
c     is the second term in the quoient rule expression.
c          tmp2 = 0.0d0
c          do 100 m = 1, nrxcl
c            tmp2 = tmp2 + stoica(m,kkk)*term(m)/(c(n)
c     *             *10.0d0**gamma(n))
c 100      continue
c          tmp2 = cxnum * tmp2 / cxdenom**2.0d0
c      ***************************************************************
c
c
c  -- Add the partial gradient to the current gradient after
```

```
c     multiplying by the stoichiometry of this component in the
c     mass balance expression.  The partial gradient is the
c     difference tmp1-tmp2, but since tmp2 is negligible, we
c     just use tmp1.
          z(jj,kk) = z(jj,kk) + tmp1 * stoica(irxn,jjj)
  90    continue
  80  continue
c
c
c
c
c  -- Take the common log for return to calling program unit.
      vlig = dlog10 (conc)
c
      return
c
      end
c*****************************************************************
      function iadx (idxt)
c
c ***********************************************************
c
c THIS FUNCTION RETURNS THE COLUMN HEADER INDEX. THE
c FUNCTION IS IDENTICAL TO FUNCTION IADX IN MINEQL
c (WESTALL 1976) EXCEPT FOR CHANGES IN THE COMMONBLOCK
c
c ***********************************************************
c
      include 'CHESP.INC'
c
      jj = nnn
      do 100 j = 1, jj
         if (idx(j).eq.idxt) go to 110
  100 continue
      j = 0
  110 iadx = j
      return
      end
c***********************************************************************
      function iady (idyt)
c
c ************************************************************
c
c THIS FUNCTION RETURNS THE ROW HEADER INDEX. THE FUNCTION
c IS IDENTICAL TO FUNCTION IADY IN MINEQL(WESTALL ET AL 1976)
c EXCEPT FOR CHANGES IN COMMONBLOCK.
c
c ************************************************************
c
      include 'CHESP.INC'
c
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      if (ii.lt.1) go to 110
      do 100 i = 1, ii
         if (idy(i).eq.idyt) go to 120
  100 continue
  110 continue
      i = 0
```

```
  120 iady = i
      return
      end
c***************  subroutine # 37     ******************************
      subroutine exrow (i0,ii)
c
c *******************************************************************
c
c THIS SUBROUTINE EXCHANGES ROWS IN THE A AND B MATRICES ALONG
c WITH THE APPROPRIATE ROW HEADERS.
c
c *******************************************************************
c
      include 'CHESP.INC'
c
      character*12 nm
      real*8 v,vb,v1
      iv = idy(ii)
      idy(ii) = idy(i0)
      idy(i0) = iv
      do 100 j = 1, nxdim
         v = a(i0,j)
         a(i0,j) = a(ii,j)
         a(ii,j) = v
         vb = b(i0,j)
         b(i0,j) = b(ii,j)
         b(ii,j) = vb
  100 continue
c
      v = gk(i0)
      gk(i0) = gk(ii)
      gk(ii) = v
c
      v = dha(i0)
      dha(i0) = dha(ii)
      dha(ii) = v
c
      v = dhb(i0)
      dhb(i0) = dhb(ii)
      dhb(ii) = v
c
      v = gfw(i0)
      gfw(i0) = gfw(ii)
      gfw(ii) = v
c
      v = spcz(i0)
      spcz(i0) = spcz(ii)
      spcz(ii) = v
c
      v = dh(i0)
      dh(i0) = dh(ii)
      dh(ii) = v
c
      nm = name(i0)
      name(i0) = name(ii)
      name(ii) = nm
c
      v = maxgk(i0)
```

```
      maxgk(i0) = maxgk(ii)
      maxgk(ii) = v
c
      v = mingk(i0)
      mingk(i0) = mingk(ii)
      mingk(ii) = v
c
      v = gamma(i0)
      gamma(i0) = gamma(ii)
      gamma(ii) = v
c
      v1 = c(i0)
      c(i0) = c(ii)
      c(ii) = v1
c
      v = alkfct(i0)
      alkfct(i0) = alkfct(ii)
      alkfct(ii) = v
c
      return
      end
c****************   subroutine #  38 **********************************
      subroutine excol (j0,jj)
c
c ********************************************************************
c
c THIS SUBROUTINE IS IDENTICAL TO SUBROUTINE EXCOL IN MINEQL
c (WESTALL 1976). THE COMMONBLOCK WAS ALL THAT WAS CHANGED.
c
c ********************************************************************
c
      include 'CHESP.INC'
      real*8 v,vb
c
      iv = idx(jj)
      idx(jj) = idx(j0)
      idx(j0) = iv
      v = x(j0)
      x(j0) = x(jj)
      x(jj) = v
      v = gx(j0)
      gx(j0) = gx(jj)
      gx(jj) = v
      v = t(j0)
      t(j0) = t(jj)
      t(jj) = v
      do 100 i = 1, nydim
         v = a(i,j0)
         a(i,j0) = a(i,jj)
         a(i,jj) = v
         vb = b(i,j0)
         b(i,j0) = b(i,jj)
         b(i,jj) = vb
  100 continue
c
      return
c
      end
```

```
c*************** subroutine # 39   *****************************
      subroutine output (lastime)
c
c *********************************************************************
c
c OUTPUT
c
c THIS SUBROUTINE PRINTS THE INPUT DATA AS WELL AS THE RESULTS OF
c THE AQUEOUS SPECIATION AND MASS TRANSFER CALCULATIONS. SATURATION
c INDICIES FOR ALL SOLIDS ARE PRINTED IN SUBROUTINE IAP.
c
c THE ENTRY POINTS: OINCMP,OINSPC,OUTCMP,OUTSPC AND OUTPC HAVE
c ESSENTIALLY THE SAME FUNCTIONS AS IN THE ORIGINAL MINEQL CODE.
c THEY HAVE BEEN MODIFIED ONLY TO ACCEPT HE DIFFERENT VARIABLES
c FROM THE WATEQ DATA.
c
      include 'cem.INC'
c
      real*8 alf,alfa,cc1,cc2,cc3,diff,gam,pc,v,sv,sd,totmass,
     *   vprcnt,svprcnt,sdprcnt,dprml23(8),sprml23(8),pprml23(8),
     *   concl23(8)
c
      integer idw123(8)
      character lastime*1
      include 'CONST.INC'
c
c
c INPUT DATA COMPONENTS
c
      entry oincmp
      if (kkthr.eq.2) go to 105
      jj = nnn
      write (lunout,9070)
      write (lunout,9080)
      do 100 j = 1, jj
         i = iady(idx(j))
         write (lunout,9090) idx(j),name(i),x(j),gx(j),t(j)
         write (lunout,*) 'ya mahdi'
  100 continue
  105 return
c
c INPUT DATA SPECIES
c
      entry oinspc
c
      write (lunout,5750) 2
      call tstamp
      write (lunout,9100)
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      jj = nnn
      l = 0
      m = 1
      do 130 i = 1, ii
         if (m.ne.i) go to 120
  110    l = l+1
         if (nn(l).eq.0) go to 110
         m = m+nn(l)
         write (lunout,9110)
```

```
          write (lunout,9115)
c  -- Write input information pertaining to all species types.
          if (l.eq.1) then
            write (lunout,9121)
          else if (l.eq.2) then
            write (lunout,9122)
          else if (l.eq.3) then
            write (lunout,9123)
          else if (l.eq.4) then
            write (lunout,9127)
          else if (l.eq.5) then
            write (lunout,9128)
          else if (l.eq.6) then
            write (lunout,9126)
          end if
          write (lunout,9130)
  120     continue
          write (lunout,9140) idy(i),name(i),dh(i),gk(i),maxgk(i),mingk(
     *       i),spcz(i),dha(i),dhb(i),gfw(i)
  130 continue
      return
c
c COMPONENT OUTPUT
c
      entry outcmp
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      jj = nnn
      write (lunout,9150)
      do 170 j = 1, jj
         i = iady(idx(j))
         gam = 10.0d0**gamma(i)
c         if (idx(j).eq.999) go to 170
c         write (lunout,9160) idx(j),name(i),t(j),c(i),x(j),gx(j),gam,gk
c    *       (i),y(j)
         write (lunout,9160) idx(j),name(i),t(j),c(i),gx(j),gam,y(j)
  170 continue
      return
c
c SPECIES OUTPUT
c
      entry outspc (lastime)
      if (kkthr.eq.2) go to 205
      ii = nn(1)+nn(2)+nn(3)+nn(4)+nn(5)+nn(6)
      jj = nnn
      l = 0
      m = 1
      do 200 i = 1, ii
         if (m.ne.i) go to 190
  180    l = l+1
         if (nn(l).eq.0) go to 180
         m = m+nn(l)
         write (lunout,9110)
         write (lunout,9115)
c  -- Write output information pertaining to all species types.
         if (l.eq.1) then
           write (lunout,9121)
         else if (l.eq.2) then
           write (lunout,9122)
```

```
         else if (l.eq.3) then
           write (lunout,9123)
         else if (l.eq.4) then
           if (lastime.eq.'y') then
             write (lunout,9124)
           else
             write (lunout,9127)
           end if
         else if (l.eq.5) then
           if (lastime.eq.'y') then
             write (lunout,9125)
           else
             write (lunout,9128)
           end if
         else if (l.eq.6) then
           write (lunout,9126)
         end if
         if (l.ge.3) then
            write (lunout,9240)
         else
            write (lunout,9170)
         endif
  190    continue
         if (l.ge.3) then
            if (l.eq.4.and.c(i).lt.0.0d0) c(i) = 0.0d0
            write (lunout,9250) idy(i),name(i),c(i),gc(i),gk(i),dh(i)
         else
            alfa = gc(i)+gamma(i)
            alf = 10.0d0**alfa
            gam = 10.0d0**gamma(i)
            write (lunout,9180) idy(i),name(i),c(i),alf,alfa,gam,gk(i)
         endif
  200 continue
  205 return
c
c OUTPUTS PERCENTAGES
c
      entry outpc (lastime)
      jj = nnn
c
      write (lunout,5750) 4
      call tstamp
c
      write (lunout,9190)
c
      do 390 k = 1, 8
         idw123(k) = 0
  390 continue
      do 400 k = 1, jj
         if (idx(k).eq.330) idw123(1) = 330
         if (idx(k).eq.001) idw123(2) = 001
  400 continue
      idw123(3) = id123(1)
      idw123(4) = id123(2)
      idw123(5) = id123(3)
      idw123(6) = id123(4)
      idw123(7) = id123(5)
      idw123(8) = id123(6)
```

```
      i1 = 1
      i2 = nn(1)+nn(2)
      do 230 j = 1, jj
         write (lunout,9110)
         i = iady(idx(j))
         write (lunout,9200) name(i)
c
         v = 0.0d0
         do 210 i = i1, i2
            if (ABS(b(i,j)).le.0.001) go to 210
            v = v+b(i,j)*c(i)
  210    continue
         if (dabs(v).lt.DOMIN) then
           go to 230
         endif
        do 220 i = i1, i2
            if (ABS(b(i,j)).le.0.001) go to 220
            pc = b(i,j)*c(i)/v
c  - Do not include in printing percent distribution if species
c    is less than 1 percent of total component dissolved mass.
            if (pc.lt.0.01d0) go to 220
            pc = pc*100.0d0
            if (pc.gt.1000.0d0) then
               write (lunout,9220) idy(i),name(i)
            else
               write (lunout,9210) pc,idy(i),name(i)
            endif
  220    continue
  230 continue
c
c --- THE FOLLOWING SECTION MODIFIED 04/04/88 BY JD ALLISON.
c --- CALCULATE AND PRINT DISSOLVED, ADSORBED, AND PRECIPITATED
c     MASS TOTALS FOR EACH COMPONENT EXCEPT DON'T BOTHER WITH
c     THE PRECIPITATED TOTALS FOR H2O, H+1, OR E-1.  EXPRESS
c     RESULTS AS PERCENT IN EACH PHASE FOR EACH COMPONENT.
c
      write (lunout,5750) 5
      call tstamp
      if (lastime.eq.'y') then
        write (lunout,9260)
      else
        write (lunout,9261)
      end if
      write (lunout,9270)
c
c --- SET INDICES THAT DEFINE BOUNDARIES OF DISSOLVED SPECIES, THAT I
c     TYPES 1 AND 2, AND PRECIPITATES (TYPE 4) IN THE ARRAYS IDY AND
c
      i0 = nn(1)+nn(2)
      i1 = i0+nn(3)+1
      i2 = i1+nn(4)-1
c
      do 270 j = 1, nnn
         v = 0.0d0
         sv = 0.0d0
         if (idx(j).ge.811.and.idx(j).le.859) go to 270
         do 250 i = 1, i0
            if (ABS(b(i,j)).le.0.001) go to 250
```

```
            if (idy(i).ge.8110000.and.idy(i).le.8599999) then
               sv = sv+b(i,j)*c(i)
            else
               v = v+b(i,j)*c(i)
            endif
  250    continue
         sd = 0.0d0
         if (idx(j).gt.002.and.idx(j).ne.330) then
            do 260 i = i1, i2
               if (ABS(b(i,j)).le.0.001) go to 260
               sd = sd+b(i,j)*c(i)
  260       continue
         endif
c
c --- CALCULATE TOTAL MASS IN THE SYSTEM FOR THIS COMPONENT.  THIS
c     MAY BE THE SAME AS WAS INPUT BUT NOT NECESSARILY DUE TO MASS
c     TRANSFER BETWEEN REDOX COUPLES.
c
         totmass = v+sv+sd
c  -- For use in further calculations, i.e., titrations, calclculate
c     the new total dissolved concentrations.  For this purpose,
c     sorbed fraction is considered part of the "dissolved" phase.
c
c --- CALCULATE PERCENT OF TOTAL MASS THAT IS DISSOLVED, ADSORBED AND
c     PRECIPITATED.
c
         if (dabs(totmass).gt.DOMIN) then
            vprcnt = v/totmass*100.0d0
            svprcnt = sv/totmass*100.0d0
            sdprcnt = sd/totmass*100.0d0
         else
            vprcnt = 0.D0
            svprcnt = 0.D0
            sdprcnt = 0.D0
         endif
         n = iady(idx(j))
         write (lunout,9280) idx(j),name(n),v,vprcnt,sv,svprcnt,sd,
     *      sdprcnt
c --- Modify to write the dissolved, sorbed, and precipitated
c     totals in molal and as percent of total to a separate file opened
c     in the main program (on unit 11) ONLY for the
c     component that is first in the component list of the input file.
c     Write the pH as well, all on one line.  The purpose is to allow
c     quick assessment of results for multiple runs.  The id number of
c     that component is assigned to variable IDRESULT in SUBROUTINE
c     INPUT.
         if (lastime.eq.'y') then
           if (n123.gt.0.and.(ntyp123.eq.1.or.ntyp123.eq.2)) then
             if (idx(j).eq.idw123(3)) then
               if (ntyp123.eq.1) then
                dprm123(3) = vprcnt
                sprm123(3) = svprcnt
                pprm123(3) = sdprcnt
               else if (ntyp123.eq.2) then
                dprm123(3) = v
                sprm123(3) = sv
                pprm123(3) = sd
               end if
```

```
             else if (idx(j).eq.idwl23(4)) then
               if (ntyp123.eq.1) then
                dprml23(4) = vprcnt
                sprml23(4) = svprcnt
                pprml23(4) = sdprcnt
               else if (ntyp123.eq.2) then
                dprml23(4) = v
                sprml23(4) = sv
                pprml23(4) = sd
               end if
             else if (idx(j).eq.idwl23(5)) then
               if (ntyp123.eq.1) then
                dprml23(5) = vprcnt
                sprml23(5) = svprcnt
                pprml23(5) = sdprcnt
               else if (ntyp123.eq.2) then
                dprml23(5) = v
                sprml23(5) = sv
                pprml23(5) = sd
               end if
             else if (idx(j).eq.idwl23(6)) then
               if (ntyp123.eq.1) then
                dprml23(6) = vprcnt
                sprml23(6) = svprcnt
                pprml23(6) = sdprcnt
               else if (ntyp123.eq.2) then
                dprml23(6) = v
                sprml23(6) = sv
                pprml23(6) = sd
               end if
             else if (idx(j).eq.idwl23(7)) then
               if (ntyp123.eq.1) then
                dprml23(7) = vprcnt
                sprml23(7) = svprcnt
                pprml23(7) = sdprcnt
               else if (ntyp123.eq.2) then
                dprml23(7) = v
                sprml23(7) = sv
                pprml23(7) = sd
               end if
             else if (idx(j).eq.idwl23(8)) then
               if (ntyp123.eq.1) then
                dprml23(8) = vprcnt
                sprml23(8) = svprcnt
                pprml23(8) = sdprcnt
               else if (ntyp123.eq.2) then
                dprml23(8) = v
                sprml23(8) = sv
                pprml23(8) = sd
               end if
             end if
           end if
         end if
  270 continue
c
      if (ntyp123.eq.3) then
        do 275 i = 1, i0
         do 277 j = 1, n123
```

```
           if (idy(i).eq.idw123(2+j)) conc123(2+j) = c(i)
 277     continue
 275    continue
      end if
c
c
c CALCULATE AND PRINT CHARGE BALANCE
c
      cc1 = 0.0d0
      cc2 = 0.0d0
      i0 = nn(1)+nn(2)
c
      do 280 i = 1, i0
         if (spcz(i).gt.0.0d0) then
            cc1 = cc1+spcz(i)*c(i)
         else
            cc2 = cc2-spcz(i)*c(i)
         endif
  280 continue
c
      diff = 0.0d0
      cc3 = cc1+cc2
      if (dabs(cc3).gt.DOMIN) diff = DABS((cc2-cc1)/(cc2+cc1))
      diff = diff*100.0d0
      write (lunout,9020)
      write (lunout,9030) cc1,cc2
      write (lunout,9040) diff
      if (lastime.eq.'y'.and. icoralk.eq.1) write (lunout,9050) noncrb
      if (lastime.eq.'y') then
         write (lunout,9060) xmu
      else
         write (lunout,9061) xmu
      end if
      if (idw123(1).eq.330.and.lastime.eq.'y') then
        write (lunout,9065) -gx(iadx(330))
      end if
      if (idw123(2).eq.001.and. lastime.eq.'y') then
        ehmv = -gx(iadx(001))*(temp+273.16)*1000.0/5040.24
        write (lunout,9066) -gx(iadx(001)), ehmv
      end if
c
      if (iads.gt.1.and.lastime.eq.'y') call adsprnt
c
      if (lastime.eq.'y') then
        if (n123.gt.0) then
           write (lunout,9265) iddate, idtime, fil123
        else
           write (lunout,9266) iddate, idtime
        end if
      end if
c
      if (n123.eq.0 .or. lastime.eq.'n') go to 999
c  -- Write data to file 'fil123' in a format suitable for import
c     into LOTUS 1-2-3  or a compatible program.
      k123 = n123 + 2
      if (ntyp123.eq.1) then
        if (idw123(1).ne.0.and.idw123(2).ne.0) then
         write (lun11,7000) iddate, idtime, idw123(1),
```

```
     *                         -gx(iadx(330)),idw123(2), -gx(iadx(001)),
     *                         (idw123(i),dprm123(i),sprm123(i),
     *                          pprm123(i),i=3,k123)
         else if (idw123(1).ne.0.and.idw123(2).eq.0) then
           write (lun11,7001) iddate,idtime, idw123(1),
     *         -gx(iadx(330)), (idw123(i),dprm123(i),sprm123(i),
     *         pprm123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).ne.0) then
           write (lun11,7001) iddate,idtime, idw123(2),
     *          -gx(iadx(001)), (idw123(i),dprm123(i),
     *         sprm123(i),pprm123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).eq.0) then
           write (lun11,7002) iddate,idtime, (idw123(i),
     *          dprm123(i), sprm123(i),pprm123(i),i=3,k123)
         end if
c
       else if (ntyp123.eq.2) then
         if (idw123(1).ne.0.and.idw123(2).ne.0) then
          write (lun11,7003) iddate, idtime, idw123(1),
     *                         -gx(iadx(330)),idw123(2), -gx(iadx(001)),
     *                         (idw123(i),dprm123(i),sprm123(i),
     *                          pprm123(i),i=3,k123)
         else if (idw123(1).ne.0.and.idw123(2).eq.0) then
           write (lun11,7004) iddate,idtime, idw123(1),
     *         -gx(iadx(330)), (idw123(i),dprm123(i),sprm123(i),
     *         pprm123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).ne.0) then
           write (lun11,7004) iddate,idtime, idw123(2),
     *          -gx(iadx(001)), (idw123(i),dprm123(i),
     *         sprm123(i),pprm123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).eq.0) then
           write (lun11,7005) iddate,idtime, (idw123(i),
     *          dprm123(i), sprm123(i),pprm123(i),i=3,k123)
         end if
c
       else if (ntyp123.eq.3) then
         if (idw123(1).ne.0.and.idw123(2).ne.0) then
          write (lun11,8000) iddate, idtime, idw123(1),
     *                         -gx(iadx(330)),idw123(2), -gx(iadx(001)),
     *                         (idw123(i), conc123(i),i = 3, k123)
         else if (idw123(1).ne.0.and.idw123(2).eq.0) then
           write (lun11,8001) iddate,idtime, idw123(1),
     *         -gx(iadx(330)), (idw123(i),conc123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).ne.0) then
           write (lun11,8001) iddate,idtime, idw123(2),
     *          -gx(iadx(001)), (idw123(i),conc123(i),i=3,k123)
         else if (idw123(1).eq.0.and.idw123(2).eq.0) then
           write (lun11,8002) iddate,idtime, (idw123(i),
     *          conc123(i),i=3,k123)
         end if
c
       end if

c      write(*,*)(idw123(i),i=3,k123),k123
       ph=-gx(iadx(330))
       C1=DPRM123(3)
       C2=DPRM123(4)
       C3=DPRM123(5)
```

```
      C4=DPRM123(6)
      C5=DPRM123(7)
      C1S=SPRM123(3)
      C2S=SPRM123(4)
      C3S=SPRM123(5)
      C4S=SPRM123(6)
      C5S=SPRM123(7)
      C1P=PPRM123(3)
      C2P=PPRM123(4)
      C3P=PPRM123(5)
      C4P=PPRM123(6)
      C5P=PPRM123(7)
c     write(*,*)c1,idw123(3),'c1 out',c2,idw123(4),'c2 out',c3,idw123(5)
c    *,' ','ph=',ph,'  ','c4=',c4,'  ','c5=',c5
 999  return
 7000 format (i6,1x,i8,1x,i3,1x,f6.2,
     *        1x,i3,1x,f6.2,6(1x,i3,3(1x,f6.1)))
 7001 format (i6,1x,i8,1x,i3,1x,f6.2,6(1x,i3,3(1x,f6.1)))
 7002 format (i6,1x,i8,1x,6(1x,i3,3(1x,f6.1)))
 7003 format (i6,1x,i8,1x,i3,1x,f6.2,
     *        1x,i3,1x,f6.2,6(1x,i3,3(1x,1pe8.2)))
 7004 format (i6,1x,i8,1x,i3,1x,f6.2,6(1x,i3,3(1x,1pe8.2)))
 7005 format (i6,1x,i8,1x,6(1x,i3,3(1x,1pe8.2)))
 8000 format (i6,1x,i8,1x,i3,1x,f6.2,
     *        1x,i3,1x,f6.2,6(1x,i7,1x,1pe8.2))
 8001 format (i6,1x,i8,1x,i3,1x,f6.2,6(1x,i7,1x,1pe8.2))
 8002 format (i6,1x,i8,1x,6(1x,i7,1pe8.2))
 9020 format (/,'0',5x,'Charge Balance: SPECIATED')
 9030 format ('0',7x,'Sum of CATIONS = ',1pe10.3,' Sum of ANIONS ',
     *   1pe11.3)
 9040 format ('0',7x,'PERCENT DIFFERENCE = ',1pe11.3,2x,
     *   '(ANIONS - CATIONS)/(ANIONS + CATIONS)')
 9050 format ('0',5x,'NON-CARBONATE ALKALINITY       = ',1pe11.3)
 9060 format ('0',5x,'EQUILIBRIUM IONIC STRENGTH (m) = ',1pe11.3)
 9061 format ('0',5x,'PROVISIONAL IONIC STRENGTH (m) = ',1pe11.3)
 9065 format ('0',5x,'EQUILIBRIUM pH                 = ',f7.3)
 9066 format ('0',5x,'EQUILIBRIUM pe                 = ',f7.3,
     *        '   or Eh  = ',f8.2,' mv')
 9265 format ('0',5x,'DATE ID NUMBER:          ',i6,
     *          /,6x,'TIME ID NUMBER:        ',i8,
     *          /,6x,'ACCESSORY OUTPUT FILE: ',a12)
 9266 format ('0',5x,'DATE ID NUMBER:          ',i6,
     *          /,6x,'TIME ID NUMBER:        ',i8)
 9070 format ('0','INPUT DATA BEFORE TYPE MODIFICATIONS')
 9080 format ('0','   ID   ',2x,'    NAME    ',3x,'ACTIVITY GUESS',4x,
     *   'LOG GUESS',2x,' ANAL TOTAL')
 9090 format (' ',i7,2x,a12,7x,1pe10.3,7x,0pf7.3,2x,1pe10.3)
 9100 format ('0',' ALL SPECIES CONSIDERED IN THIS PROBLEM')
 9110 format (' ')
 9115 format (' --------------------------------------------------',
     *       '--------------------------')
 9121 format ('0',' Type I - COMPONENTS AS SPECIES IN SOLUTION')
 9122 format ('0',' Type II - OTHER SPECIES IN SOLUTION OR ADSORBED')
 9123 format ('0',' Type III - SPECIES WITH FIXED ACTIVITY ')
 9127 format ('0',' Type IV - FINITE SOLIDS (presumed present at',
     *            ' equilibrium)')
 9128 format ('0',' Type V - POSSIBLE SOLIDS')
 9126 format ('0',' Type VI - EXCLUDED SPECIES (not included in mole',
```

```
    *              ' balance)')
9124 format ('0',' Type IV - FINITE SOLIDS (present at equilibrium)')
9125 format ('0',' Type V - UNDERSATURATED SOLIDS (not present at',
    *              ' equilibrium)')
9130 format ('0','   ID   ',2x,'    NAME     ',2x,'    DH    ',2x,
    *    '     LOGK   ',2x,'MIN LOGK',2x,'MAX LOGK',2x,'  Z   ',1x,
    *    ' DHA ',1x,' DHB ',1x,'   GFW    ')
9140 format (' ',i7,2x,a12,2x,2(f10.4,2x),2(f8.3,2x),3(f5.2,1x),f9.4
    *    )
9150 format ('0',' ID   ',2x,'    NAME     ',2x,' ANAL MOL',2x,
    *    ' CALC MOL',2x,'LOG ACTVTY',2x,'   GAMMA   ',2x,' DIFF FXN')
9160 format (' ',i5,2x,a12,2(1x,1pe10.3),2x,0pf10.5,f12.6,2x
    *    ,1pe10.3)
9170 format ('0','   ID   ',2x,'    NAME     ',2x,' CALC MOL',2x,
    *    ' ACTIVITY ',2x,'LOG ACTVTY',2x,'  GAMMA   ',2x,' NEW LOGK')
9180 format (' ',i7,2x,a12,2x,1pe10.3,1x,1pe10.3,2x,0pf10.5,2x,f8.5,
    *             2x,f9.3)
9190 format (' '//,'                    PERCENTAGE DISTRIBUTION OF',
    *     ' COMPONENTS AMONG',
    *           /,'                 TYPE I and TYPE II (dissolved',
    *     ' and adsorbed) species',/)
9200 format ('+',a12)
9210 format ('+',14x,f6.1,5x,'PERCENT BOUND IN SPECIES #',i7,3x,a12/
    *    )
9220 format ('+',14x,'>1000.',5x,'PERCENT BOUND IN SPECIES #',i7,3x,
    *    a12/)
9240 format ('0','   ID   ',2x,'    NAME     ',2x,' CALC MOL ',4x,
    *    '  LOG MOL ',2x,'NEW LOGK',2x,'    DH    ')
9250 format (' ',i7,2x,a12,2x,1pe10.3,2x,0pf10.3,2x,0pf9.3,2x,f9.3)
9260 format (' ',//,16x,'----------------------------------------',
    *    '-------------',
    *               /,16X,'----------- EQUILIBRATED MASS DISTRIBUTION',
    *    ' -----------')
9261 format (' ',//,16x,'----------------------------------------',
    *    '-------------',
    *               /,16X,'----------- PROVISIONAL MASS DISTRIBUTION',
    *    ' -----------')
9270 format ('0'/,1x,'IDX',5x,'NAME',12x,'DISSOLVED',12x,'SORBED',
    *    12x,'PRECIPITATED',/,23x,'MOL/KG',3x,'PERCENT',4x,'MOL/KG',
    *    3x,'PERCENT',4x,'MOL/KG',3x,'PERCENT'/)
9280 format (' ',i3,2x,a12,2x,1pe10.3,2x,0pf6.1,2x,1pe10.3,2x,0pf6.1
    *    ,2x,1pe10.3,2x,0pf6.1)
5750 format ('1',//,' _______________________________________',
    *          '_____________________________________',
    *       /,' ______________________________ PART ',i1,' of',
    *          ' OUTPUT FILE _________________________')
     end
```

# Appendix G

## Program Listing for PET

```
C    A program to find a best value for the constant parameters associated
C     with diffusion functions
C      CU             =     CONCENTRATIONS PROFILES AT  ULTIMATE
C                             PORE VOLUMES
C      CO             =     CONCENTRATIONS PROFILES AT INITIAL PORE
C                            VOLUMES
C      RO             =     SOIL DENSITY
C      POROS          =     POROSITY
C      DX             =     SPACE  INCREMENT
C      NT             =     TIME    INCREMENT
C      DU             =     ULTIMATE DEPTH
C      DI             =     INITIAL DEPTH
C      TF             =     FINAL TIME
C      TS             =     TIME  SCALE
C      HO             =      HEAD AT UPPER BOUNDARY CONDITIONS
C      HK             =      HEAD AT LOWER BOUNDARY CONDITIONS
C      MAX            =      MAX  ITERATION
$DEBUG
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION  Cu(555),CO(555),CN(555),X(50),E(50),W(555),Y(50),
     *AHN(555),XX(555),CI(555)
      OPEN(10,FILE='INP')
      OPEN(11,FILE='out')
      OPEN(12,FILE='out.DAT')
      OPEN(33,FILE='ou.DAT')

C    ******************   READ INPUT DATA   ******************
      READ(10,*) N,N1,ML,MAX,NS,DU,DI,H0,HK
      READ(10,*) DT,TF,TS,R,T,SCAL,RO,POROS
      DO 5 J=1,N
      READ(10,*) E(J)
      READ(10,*) X(J)
    5 CONTINUE
      DO 4 J=1,N
      Y(J)=X(J)
    4 CONTINUE

C     *************  CALCULATE TIME AND SPACE INCREAMENT  ***********
      DX=(DU-DI)/N1
      NT=(TF-TS)/DT
C    ****** READ INITIAL AND FINAL NODAL VALUE FROM EQUATIONS  ******
      DO 13 I=1,N1+1
      XX(I)=DI+DX*(I-1)
```

```
      CI(I)= EXP(5.380103945-1.41339956*(XX(I)**0.5)-.04794237*EXP(XX(I)
     *))
      CU(I)=EXP(5.500557687-0.36898782*(XX(I)**2)-0.16833451*
     *EXP(-XX(I)))
      AHN(I) = H0-XX(I)
      CA=CA+Cu(I)/(N1+1)
C   CALCULATE THE HYDRUALIC HEAD AT DIFFERENT POINTS
      WRITE(11,234)  XX(I),CI(I),Cu(I)
  234 FORMAT(5(F12.4,2X))
   13 CONTINUE
      WRITE(11,*)  'DX               =',DX
      WRITE(11,*)  'DT               =',DT
      WRITE(11,*)  'No. of node      =',N1+1
      WRITE(11,*)  'No. of parameters=',N
      WRITE(11,*)  'No. of time step =',NT
      WRITE(*,*)   '                         No. of time step =',NT
      WRITE(*,*)   '                         No. of node step =',N1+1
      IPRINT=1
      CALL OPM(N,N1,DT,NT,MAX,SCAL,X,E,CN,CO,TS,CI,POROS,HK,
     *CA,ML,Y,DI,DU,TF,IT,DX,W,CU,NS,RO,H0,R,T,AHN)
      IF(IT.EQ.1) ML=ML+10
      IF(IT.GT.1) ML=IT+5
      CLOSE (10)
      OPEN(10,FILE='Inp')
      write(10,24) N,N1,ML,MAX,NS,DU,DI,H0,HK
      write(10,27) DT,TF,TS,R,T,SCAL,RO,POROS
   24 FORMAT(5(I6,1X),4(F12.6,1X))
   27 FORMAT(4(F12.6,1X),F24.7,1X,3(F7.2,1X))
      DO 1 J=1,N
      WRITE(10,*) E(J)
      WRITE(10,*) Y(J)
  1   CONTINUE

C     ***************      PRINT OUT PUT      *******************
      WRITE(12,*)"XX,CI(I),Cu(I),CN(I),DC,DS"
      DO 35 I=1,N1+1
           DC=X(1)*EXP(CN(I)*X(2))

           DS=X(3)*EXP(CN(I)*(X(4)))
           CI(I)=CI(I)
           CU(I)=CU(I)
           CN(I)=cN(I)
      WRITE(12,46) XX(I),CI(I),Cu(I),CN(I),DC,DS
   46 FORMAT(11(E12.6,1X))
   35 CONTINUE
      CLOSE(11)
      CLOSE(10)
      STOP
      END

C     *************************************************************
C     *                                                           *
C     *        A SUBROUTINE TO OPTIMIZE PARAMETERS                *
C     *                         BY                                *
C     *                USING POWELL'S METHOD                      *
C     *                                                           *
C     *************************************************************
      SUBROUTINE OPM(N,N1,DT,NT,MAX,SCAL,X,E,CN,CO,TS,CI,POROS,HK,
```

```
     *CA,ML,Y,DI,DU,TF,IT,DX,W,CU,NS,RO,HO,R,T,AHN)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Cu(555),CO(555),CN(555),X(50),E(50),W(555),Y(50),CI(555)
     *,AHN(555)
      IPRINT=1
      NOLUCK=1
      DDMAG=0.1*SCAL
      SCER=0.05/SCAL
      JJ=N*N+N
      JJJ=JJ+N
      K=N+1
      NFCC=1
      IND=1
33    INN=1
      DO 1 I=1,N
      DO 2 J=1,N
      W(K)=0.0
      IF((I-J).NE.0.0) GO TO 92
      W(K)=ABS(E(I))
      W(I)=SCAL
   92 K=K+1
    2 CONTINUE
    1 CONTINUE
      ITERC=1
      ISGRAD=2
      CALL IMP(N1,DT,NT,N,F,X,ITERD,TS,CA,CI,POROS,HK,RO,
     *Y,DI,DU,TF,ML,MAX,SCAL,E,IT,DX,CO,CU,CN,MP,MN,NS,FN,HO,R,T,AHN)
      IF(ITERD.EQ.ML) GO TO 320
      FKEEP=ABS(F)+ABS(F)
  101 ITONE=1
      FP=F
      SUM=0.0
      IXP=JJ
      DO 3 I=1,N
      IXP=IXP+1
      W(IXP)=X(I)
    3 CONTINUE
      IDIRN=N+1
      ILINE=1
      KLINE=1
  112 DMAX=W(ILINE)
      DACC=DMAX*SCER
      IF(DDMAG.LT.(0.1*DMAX)) DMAG=DDMAG
      IF(DDMAG.GE.(0.1*DMAX)) DMAG=0.1*DMAX
      IF(DMAG.LT.(20*DACC)) DMAG=20*DACC
      DDMAX=10*DMAG
      IF(ITONE.EQ.3) GO TO 184
      DL=0.0
      D=DMAG
      FPREV=F
      IS=5
      FA=F
      DA=DL
  124 DD=D-DL
      DL=D
  126 K=IDIRN
      DO 4 I=1,N
      X(I)=X(I)+DD*W(K)
```

```
      K=K+1
    4 CONTINUE
      CALL IMP(N1,DT,NT,N,F,X,ITERD,TS,CA,CI,POROS,HK,RO,
     *Y,DI,DU,TF,ML,MAX,SCAL,E,IT,DX,CO,CU,CN,MP,MN,NS,FN,H0,R,T,AHN)
      IF(ITERD.EQ.ML) RETURN
      NFCC=NFCC+1
      IF(IS.EQ.1) GO TO 191
      IF(IS.EQ.2) GO TO 180
      IF(IS.EQ.3) GO TO 176
      IF(IS.EQ.4) GO TO 170
      IF(IS.EQ.5) GO TO 141
      IF(IS.EQ.6) GO TO 258
  141 IF(F-FA) 147,142,150
  142 IF((ABS(D)-DMAX).GT.0.0) GO TO 145
      D=D+D
      GO TO 124
  145 NOLUCK=2
      GO TO 320
  147 FB=F
      DB=D
      GO TO 154
  150 FB=FA
      DB=DA
      FA=F
      DA=D
  154 IF(ISGRAD.EQ.1) GO TO 158
  155 D=DB+DB-DA
      IS=1
      GO TO 124
  158 D=0.5*(DA+DB-(FA-FB)/(DA-DB))
      IS=4
      IF(((DA-D)*(D-DB)).GE.0.0) GO TO 124
  161 IS=1
      IF((ABS(D-DB)-DDMAX).LE.0.0) GO TO 124
  163 D=DB+(ABS(DDMAX))*SIGN(DB,DA)
      IS=1
      DDMAX=DDMAX+DDMAX
      DDMAG=DDMAG+DDMAG
      IF((DDMAX-DMAX).LE.0.0) GO TO 124
      DDMAX=DMAX
      GO TO 124
  170 IF((F-FA).GE.0.0) GO TO 155
  171 FC=FB
      DC=DB
  173 FB=F
      DB=D
      GO TO 193
  176 IF((F-FB).LE.0.0) GO TO 171
      FA=F
      DA=D
      GO TO 193
  180 IF((F-FB).GE.0.0) GO TO 191
      FA=FB
      DA=DB
      GO TO 173
  184 DL=1.0
      DDMAX=5.0
      FA=FP
```

```
      DA=-1.0
      FB=FHOLD
      DB=0.0
      D=1.0
  191 FC=F
      DC=D
  193 A=(DB-DC)*(FA-FC)
      B=(DC-DA)*(FB-FC)
      IF(((A+B)*(DA-DC)).GT.0.0) GO TO 201
      FA=FB
      DA=DB
      FB=FC
      DB=DC
      GO TO 163
  201 D=0.5*(A*(DB+DC)+B*(DA+DC))/(A+B)
      DI=DB
      FI=FB
      IF((FB-FC).LE.0.0) GO TO 207
      DI=DC
      FI=FC
  207 IF(ITONE.EQ.1) GO TO 212
      IF(ITONE.EQ.2) GO TO 212
      ITONE=2
      GO TO 214
  212 IF((ABS(D-DI)-DACC).LE.0.0) GO TO 224
      IF((ABS(D-DI)-(0.03*ABS(D))).LE.0.0) GO TO 224
  214 IF(((DA-DC)*(DC-D)).LT.0.0) GO TO 220
      FA=FB
      DA=DB
      FB=FC
      DB=DC
      GOTO 161
  220 IS=2
      IF(((DB-D)*(D-DC)).GE.0.0) GO TO 124
      IS=3
      GO TO 124
  224 F=FI
      D=DI-DL
      DD=SQRT((DC-DB)*(DC-DA)*(DA-DB)/(A+B))
      DO 5 I=1,N
      X(I)=X(I)+D*W(IDIRN)
      W(IDIRN)=DD*W(IDIRN)
      IDIRN=IDIRN+1
    5 CONTINUE
      W(ILINE)=W(ILINE)/DD
      ILINE=ILINE + 1
      IF((IPRINT-1).NE.0.0) GO TO 241
  235 IF(IPRINT.EQ.1) GO TO 241
      IF(IPRINT.EQ.2) GO TO 300
  241 IF(ITONE.EQ.1) GO TO 243
      IF(ITONE.EQ.2) GO TO 297
  243 IF((FPREV-F-SUM).LT.0.0) GO TO 246
      SUM=FPREV-F
      JIL=ILINE
  246 IF((IDIRN - JJ).LE.0.0) GO TO 112
      IF(IND.EQ.2) GO TO 299
      FHOLD=F
      IS=6
```

```
      IXP=JJ
      DO 6 I=1,N
      IXP=IXP+1
      W(IXP)=X(I)-W(IXP)
    6 CONTINUE
      DD=1.0
      GO TO 126
  258 IF(IND.EQ.2) GO TO 262
      IF((FP-F).LE.0.0) GO TO 287
      D=2*(FP+F-2*FHOLD)/(FP-F)**2
      IF(((D*(FP-FHOLD-SUM)**2)-SUM).GE.0.0) GO TO 287
  262 J=JIL*N+1
      IF((J-JJ).GT.0.0) GO TO 271
      DO 7 I=J,JJ
      K=I-N
      W(K)=W(I)
    7 CONTINUE
      DO 8 I=JIL,N
      W(I-1)=W(I)
    8 CONTINUE
  271 IDIRN=IDIRN-N
      ITONE=3
      K=IDIRN
      IXP=JJ
      AAA=0.
      DO 9 I=1,N
      IXP=IXP+1
      W(K)=W(IXP)
      IF((AAA-ABS(W(K)/E(I))).GE.0.0) GO TO 281
      AAA=ABS(W(K)/E(I))
  281 K=K+1
    9 CONTINUE
      DDMAG=1.
      W(N)=SCAL/AAA
      ILINE=N
      GO TO 112
  287 IXP=JJ
      AAA=0.
      F=FHOLD
      DO 10 I=1,N
      IXP=IXP+1
      X(I)=X(I)-W(IXP)
      IF((AAA*ABS(E(I))-ABS(W(IXP))).GE.0.0) GO TO 10
      AAA=ABS(W(IXP)/E(I))
   10 CONTINUE
      GO TO 299
  297 AAA=AAA*(1.+DI)
      IF(IND.EQ.2) GO TO 319
  299 IF((IPRINT-2).GE.0.0) GO TO 235
  300 KLINE=KLINE+1
      IF(IND.EQ.2) GO TO 306
      IF((AAA-0.1).LE.0.0) GO TO 320
      IF((F-FP).LT.0.0) GO TO 307
      NOLUCK=3
      GO TO 320
  306 IND=1
  307 DDMAG=0.4*SQRT(FP-F)
      ISGRAD=1
```

```
      ITERC=ITERC+1
      IF((ITERC-MAX).LE.0.0) GO TO 101
      NOLUCK=4
      IF((F-FKEEP).LE.0.0) GO TO 320
      F=FKEEP
      DO 11 I=1,N
      JJJ=JJJ+1
      X(I)=W(JJJ)
   11 CONTINUE
      GO TO 320
  319 IF((AAA-0.1).LE.0.0) GO TO 320
      INN=1
      GO TO 307
  320 RETURN
      END


C
C***********************************************************************
C                                                                       *
C
C                                                                       *
C              A SUBROUTINE TO CUMPUTE  CONCENTRATIONS  AT TIME J+1
C                                                                      *
C                                     BY
C                                                                      *
C               USING EXPLECIT FINITE DIFFERENCE METHOD
C                                                                      *
C
C
C                                                                      *
C
C***********************************************************************

      SUBROUTINE IMP(N1,DT,NT,N,F,X,ITERD,TS,CA,CI,POROS,HK,RO,
     *Y,DI,DU,TF,ML,MAX,SCAL,E,IT,DX,CO,CU,CN,MP,MN,NS,FN,H0,R,T,AHN)
      IMPLICIT   REAL*8(A-H,O-Z)
      DIMENSION  Cu(555),CO(555),CN(555),X(50),E(50),Y(50),CI(555),
     *AHN(555)
      ITERD=ITERD+1
C     **************     UPDATE T. AND W.     ****************
      DO 14 I=1,N1+1
      CO(I)=CI(I)
      CN(I)=CI(I)
   14 CONTINUE
C     **************     BOUNDARY CONDITIONS FOR  W. & T. ***********
      TIME=TS
      C1=(Cu(1)-CI(1))/NT
      C2=(Cu(N1+1)-CI(N1+1))/Nt/0.3
      K1=0

                         DO 50 N2=1,NT
      CN(1)=CO(1)+C1
      CN(N1+1)=CO(N1+1)+C2
      if(CN(n1+1).gt.Cu(N1+1))  CN(N1+1)=Cu(n1+1)

C     ***********    COMPUTATION OF CONCENTRATION AT TIME J+1  ******
      WM=207.
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                   DO 40 I = 2 , N1
      DIF=X(1)*EXP(X(2)*CO(I))
      S2=X(3)*EXP(X(4)*CO(I))
c     KHC=X(5)*(0.01)
      KHC=KHC*X(5)
      KCH=KHC*POROS/(R*T)
      RI=KCH/HK+1.
      OSM=KCH*KHC/(2*HK)*WM

C    ****** DETERMINATION OF VELOCITIES AND CONCENTERATIONS


      HDZ=AHN(I+1)-AHN(I-1)/(2.0*DX)
      VZ=((-HK/POROS)*HDZ-((X(5)/WM)*Q2*3600*24))
      Q1=RO*X(3)*S2/POROS
      Q2=(CO(I+1)-CO(I-1))/(2.0*DX)
      Q3=(CO(I+1)-2.D0*CO(I)+CO(I-1))/(DX**2)
      Q4=(CO(I+1)**2-2.*CO(I)**2+CO(I-1)**2)/(DX**2)

      CN(I)=CO(I)+(DT/(1+Q1))*(X(2)*DIF*Q2**2+DIF*Q3-RI*VZ*Q2-OSM*Q4)
 40   CONTINUE


      DO 2 I=1,N1+1
      CO(I)=CN(I)
 2    CONTINUE
      TIME=TIME+DT

  50  CONTINUE



C     ********* CORELATION COEFFICIENT FOR DIFFUSION **********
      SUMD=0.0
      S2Y=0.0
      S2YE=0.0
      DO 51 I=1,N1+1
      SUMD=SUMD+((Cu(I)-CN(I)))**2
      S2Y=S2Y+(Cu(I)-CA)**2
      S2YE=S2YE+(CN(I)-Cu(I))**2
   51 CONTINUE
      FY=1-S2YE/S2Y
      IF(FY.LT.0) FY=4
      RW=SQRT(FY)
      F=SUMD

C     ************   RECORDING THE OBTIMIZED PARAMETER   *************
      IF (ITERD.EQ.1) FN = F
      IF (ITERD.EQ.1) GO TO 199
      IF (F.GT.FN) GO TO 199
      FN=F
      IT=ITERD
      if(iterd-mn.ne.1)  go to 13
      mp=mp+1
      go to 16
 13   mp=1
      go to 12
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 16   if(mp.ne.NS) go to 12
      f=fm
      fn=f
      mp=0
      go to 11
 12   fm=f
 11   mn=iterd
      write(*,*)'                   =============================='
      DO 88 I=1,N
      Y(I)=X(I)
   88 CONTINUE
      CLOSE(10)
      OPEN(10,FILE='Inp')
      write(10,24) N,N1,ML,MAX,NS,DU,DI,H0,HK
      write(10,27) DT,TF,TS,R,T,SCAL,RO,POROS
   24 FORMAT(5(I6,1X),4(F12.6,1X))
   27 FORMAT(4(F12.6,1X),F24.7,1X,3(F7.2,1X))
      DO 1 J=1,N
      WRITE(10,*) E(J)
      WRITE(10,*) Y(J)
  1   CONTINUE
      CLOSE(10)


  199 IF(IT.EQ.0) IT=1
      IF(ITERD.EQ.1)   GO TO 96
      IF(ITERD/22*22.NE.ITERD)   GO TO 91
      WRITE(*,*)"               **************************************"
 96   WRITE(*,*) "  ITER.       IT          k1          RW     f     Q1"
      write(*,*) "            Program running, please do not disturb it
     *."
      write(*,*) "                              Thank you."
      WRITE(*,*)"               **************************************"
C 91  WRITE(*,23) ITERD,IT,k1/NT,RW,f,mp
  91  WRITE(*,23) ITERD,IT,k1/NT,RW,f/(N1+1)/CA*100,mp,q1
C  23 FORMAT(3(I5,6x),2(F12.3,6X),I1)
   23 FORMAT(3(I5,6x),2(F9.6,6X),I1)
      RETURN
      END
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