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FOREWORD

The following selection of papers has recently been published in the Proceedings of the International Conference on THE ENVIRONMENT AND GEOTECHNICS: from Decontamination to Protection of the Subsoil. Paris, France - April 1993.

1. Yong, R.N. and Prost, R.
   "Decontamination, Treatment and Rehabilitation of Sites"
   pp.1-18.

2. Hadjinicolaou, J., Yong, R.N. and Bahout, E.
   "Characterization and Management of Municipal Incinerator's Bottom Ash" pp.209-216.

3. Yong, R.N. and Galvez-Cloutier, R.
   "pH Control on Lead Accumulation Mechanisms in Kaolinite-Lead Contaminant Interaction" pp.309-318.

4. Elektorowicz, M. and Yong, R.N.
   "Processus Retardant la Biorestauration des Sites Contamines par des Hydrocarbures" pp.373-380.

5. Galvez-Cloutier, R., Yong, R.N., Mourato, D. and Mulligan, C.
   "L'Utilisation du Laboratoire pour l'Etude, l'Evaluation, et le Design de Projets de Rehabilitation des Sols Contamines: le Cas du Port du Toronto" pp.389-396.

6. Mohamed, A.M.O., Yong, R.N. and Mazus, M.
   "Performance Evaluation of Engineered Clay Cover subjected to Different Environmental Conditions" pp.571-579.

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Thème 3 Rapport: DÉCONTAMINATION, TRAITEMENT ET RÉHABILITATION DES SITES

Theme 3 Report: DECONTAMINATION, TREATMENT AND REHABILITATION OF SITES

RÉSUMÉ

Une connaissance des mécanismes d'adsorption des divers contaminants dans le sol améliore les possibilités pour développement d'une décontamination plus effective et d'une technologie plus compatible. Les procédés de rétention sont abordés à la lumière de leur influence dans le choix de techniques de décontamination et réhabilitation. L'évaluation en laboratoire de l'efficacité des procédés et les études pilotes sont exigences essentielles pour le développement d'une stratégie des procédés et de réhabilitation d'une site. Le rapport de techniques et des études dans les communication du Thème 3 est fait dans le contexte d'un résumé global des procédés de rétention et des conditions essentielles pour le décontamination. Idéalement, la réhabilitation d'une site doit être compatible avec une utilisation future des terrains.

ABSTRACT

A knowledge of the mechanisms of adsorption of the various types of contaminants in soils should provide a better capability for development of more effective decontamination and compatible technology. The various contaminant retention processes are reviewed in light of their influence on choice of techniques for decontamination/remediation. Laboratory assessment of decontamination effectiveness and pilot studies are important requirements for development of remediation and site rehabilitation strategy and procedures. Reporting of the techniques and studies in the papers submitted to Theme 3 is done in the context of the summary overview on retention processes and remediation requirements. Ideally, site rehabilitation must be compatible with future land use.

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INTRODUCTION -- PRELIMINARY CONSIDERATIONS

The report on the individual papers submitted[3] to Theme 3 will be made in the context of a general summary overview of the Theme subject which briefly considers the basic processes and requirements for site/soil decontamination. It should be noted that remediation techniques are not limited to application in-situ inasmuch as processes and technology can be applied on-site, with soil material removed for treatment and reuse as rehabilitated material, or soil material removed for final disposal. In the latter case, one expects new uncontaminated soil material to be brought in as part of the site rehabilitation procedure. Preliminary consideration of some basic factors are necessary in evaluation of the appropriate procedures and technology for decontamination and rehabilitation of contaminated sites. These include considerations of:

(Factor 1)	Nature, extent, and degree of contamination, i.e. type of contaminants in the ground (site), extent of contamination (lateral and depth), and degree to which the site is contaminated (heavily or moderately contaminated, i.e.amount of contaminants);
(Factor 2)	Site specificities, i.e. lithography, stratigraphy, geology, hydrogeology, and boundary conditions, soil transmission properties, etc;
(Factor 3)	Intended land use of the reclaimed site;
(Factor 4)	Economics and compatible (feasibility?) technology.

IN-SITU? EX-SITU? OR COMBINATION?

Whereas the first three factors relate directly to the decision-making process in regard to technical feasibility for site and material decontamination, and to determination of best available technology for site decontamination and rehabilitation, it is not unusual for the fourth factor (economic factors and feasibility) to "dictate" the "solution" chosen site rehabilitation. The choice of in-situ, ex-situ (on-site or away from the site), can be made in accord with other governing considerations, e.g. risk, treatment effectiveness, and permanency of treatment. Thus, whilst some very simple guidelines exist which might quickly indicate whether the remediation procedure will be totally in-situ, ex-situ, or will consist of a combination of the two, site constraints and treatment efficiencies may however dictate otherwise. As a simple example, one can use the case of clean-up of a petroleum hydrocarbon (PHC) contaminated site. Assuming that PHCs are the only contaminants of concern in the contaminated site, and that excavation of all the contaminated material is not practical or economic, the use of in-situ biodegradation techniques, where microorganisms in the soil utilize the contaminants in their respitory process, renders this an obvious in-situ remediation solution. Alternatively, one could choose to use enhanced in-situ biodegradation techniques, or bioventing techniques such as those considered by Ong and Hinchee. However, as mentioned previously, site constraints and other requirements could alter the clean-up strategy, e.g. soil conditions not appropriate for venting, or more economic solutions available with a combined in-situ/ex-situ procedure.

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[3] A listing of the papers submitted to Theme 3 will found in the Reference listing.

A case in point has been shown by Schlegel in his discussion on a combination of in-situ and ex-situ treatment of a LNAPL contaminated substrate near the Frankfurt/Main airport. A perimeter water injection scheme to "contain" the LNAPL within the "centre" of the contaminated was implemented as the initial part of the program of decontamination. Flotation of the LNAPL on top of the aquifer facilitated extraction of the LNAPL for treatment ex-situ. For a longer term treatment of the soil, considered as the principal phase of rehabilitation, a combination of in-situ physical-microbiological treatment of venting and microbial degradation was used. The success in the treatment procedure observed over the three years of operation of the system has encouraged the development a similar set of protocols being applied to a refinery site near Frankfurt, contaminated by a group of solvents (organochlorides, aliphatic and aromatic hydrocarbons), PCB, dioxines, furans, phenols, and PCP. The principal initial requirement is to implement perimeter injection of water, not only to limit the spread of the contamination, but also to facilitate extraction of the contaminants for treatment. Research will be needed to determine the required microbial and physico-chemical treatment requirements and procedures.

The DNAPL contaminated site in Louisiana reported by Acar et al. shows a set of contaminants almost similar in complexity as that reported by Schlegel. Contaminants which consistED of sludge-like wastes, free phase organic wastes and dissolved phase organics found on the site included hexachlorobutadiene (HCBD), hexachlorobenzene (HCB), hexachloroethylene (HCE), halogenated organic solvents (DCE, TCE), volatile aromatic hydrocarbons (benzene, toluene) and polynuclear aromatic hydrocarbons (PAHs). The underlying geology shows a complex formation which includes clayey deposits with low permeabilities and alluvial deposits with higher permeabilities. Because of the high cost of specimen retrieval and sample analyses, mapping of extent and distribution of contaminants has been restricted. The remedial plan consists of both in-situ and ex-situ procedures, requiring removal of the on-site contaminated material for solidification and placement in a prepared landfill, and the implementation of a recovery well system to recover the dissolved phase organics in the groundwater for treatment.

The question which is often asked, "how clean should the site be", i.e. "how clean is clean"? has been rephrased by Martins and Barnoud who argue that the question is better posed as "how dangerous is dangerous" in their presentation concerning effective investigation, assessment and remediation of contaminated sites. In essence, the assessment procedure depends on one's evaluation of the risk potential for public health and security posed by the presence of the contaminants in the substrate. The extension of this viewpoint suggests that the extent of the remediation will be governed by the degree or level of risk, i.e. "how dangerous is dangerous". This attitude which has been adopted in several instances in the determination of the technology and associated expenditures for site remediation, requires that one renders "infallible" judgement in risk assessment, and that a definitive link can be established between "what constitutes a health threat" and threshold limits. One is required to consider not only "hazard identification" but also "toxicity and exposure" and "risk characterization or evaluation".

The U.S. EPA has given a good listing of innovative techniques for clean-up of hazardous waste sites. Some of these have been summarily reviewed by Acar et al., include: "integrated vapour extraction and/or air vacuum stripping, membrane microfiltration, freezing separation, in-situ/ex-situ biological treatment, in-situ/ex-situ solidification/stabilization, liquid/solid contact digestion, etc." Successful implementation of any of the techniques requires a good assessment of effectiveness of contaminant removal or fixation. There is common agreement however that total pristine clean-up is not always a necessary end condition, and that it is unusual to achieve total contaminant removal from a contaminated soil "at a reasonable cost". If "clean-up" criteria are written in regard to land use requirements, a more reasonable set of goals can generally be specified.

The implementation or development of a particular set of technologies for remediation and site rehabilitation requires a good working knowledge of how the contaminants are retained within the soil-water system. Categorization of remediation techniques in relation to contaminant retention processes (i.e. contaminant-soil interactive processes) is a means to establish the most likely effective principal techniques for remediation (decontamination) of contaminated soils. A typical set of groupings can be listed as follows:

(Group 1) Physical-Chemical, e.g. techniques relying physical and/or chemical procedures for removal of the contaminants, e.g. precipitation, desorption, washing, stripping, vapour extraction, demulsification, etc;
(Group 2) Biological, i.e. generally bacterial degradation of organic compounds;
(Group 3) Thermal, e.g. vitrification, closed-loop detoxification, super critical water oxidation, circulating fluidized-bed combustion;
(Group 4) Combination of any or all of the preceding three groups.

With the grouping procedure given, it becomes possible to design the method or technology by which any of the processes available can be implemented, taking into account the four factors described above. Whereas the options posed in both in-situ and ex-situ remediation treatments may have the same basis for "treatment", e.g. removal of solubilized metals by chemical precipitation, the challenges facing implementation of the decontamination process are likely to be different, partly because of the quantities of contaminated material to be treated, and partly because of the constraints present in in-situ operations. The challenge is in the development of appropriate technology for in-situ remediation, i.e. site rehabilitation, the outcome of which will impact heavily on the risk of failure (ineffective clean-up) or the likelihood of success.

CONTAMINANT RETENTION: MECHANISMS AND REMOVAL

Whether one chooses to use a physical-chemical, biological or thermal method (or a combination thereof) for soil decontamination, in-situ or ex-situ, evaluation of the effectiveness of a decontamination procedure can usefully benefit from a closer consideration of how the contaminants are held (retained, "bonded") to the soil constituents. It needs to be reminded that the contaminant retention mechanisms for the soil constituents differ, depending on the nature of the soil constituent (mineral, amorphous material, soil organic, etc.). and on the type/nature of the contaminant. An evaluation of the relative ease (or difficulty) in removal of a contaminant can be made if one obtains a better appreciation of how the contaminants are held to the soil constituents or within the soil-water system. Experience shows that whereas contaminants can be conveniently grouped into classes such as acids, bases, solvents, etc., very few leachates or contaminated sites show contaminants consisting of only one single species. Mixtures of various kinds of contaminants, inorganic and organic are often encountered, making it difficult to fully structure treatment techniques that can address all the kinds of contaminants in the affected material. The preceding notwithstanding, it is useful to determine the principal processes which control retention of the various kinds of contaminants, on the assumption that one can design a treatment system that would selectively address the various contaminants. Accordingly, a simple classification scheme reduces the contaminants to two broad classes: inorganic and organic contaminants.

Inorganic Contaminants

Retention of contaminants in a soil substrate is a function of the interaction mechanisms operative between contaminants and soil constituents. These mechanisms are greatly influenced by the nature of the soil constituents, the contaminants, and the pH of the system. In assessing the type of treatment required for removal of contaminants from a soil, it is useful to determine how the contaminants are retained within the soil-water system, i.e. the operative contaminant retention mechanisms. A proper knowledge of the type of contaminant is essential inasmuch as the types of contaminant-soil relationships are greatly influenced by whether the contaminants are inorganic or organic, since adsorption reactions are processes which are governed by the surface properties of the soil solids (inorganic and organic), and the chemistry of the contaminants. Whereas it is often not necessary to fully establish the exact extent of the contaminant-soil bonding, i.e. to fully quantify the bonding, a good working knowledge of the retention mechanisms however is useful if one wants to devise an effective compatible decontamination protocol and the corresponding appropriate technology.

Inorganic contaminants that are considered to be physically adsorbed "onto" soil particles (i.e. surfaces of particles) reflect the general phenomenon of attraction of ionic contaminants (cationic and/or anionic) to the soil solids' surfaces because of the unsatisfied charges (attractive forces) of the soil particles. It matters greatly whether the contaminant ions are: (a) non-specifically adsorbed ions, i.e. indifferent ions that are held primarily by electrostatic forces and interact in the diffuse ion-layer; they only affect the magnitude of the zeta potential (ζ), or (b) specifically adsorbed ions, i.e. ions adsorbed by forces other than the electric potential, and thus have the ability to influence the sign of ζ, inasmuch as this (distinction) will affect the method chosen to remove the contaminant ions from the soil. Thus for example, contaminant cations specifically adsorbed in the inner part of the double layer (inner Helmholtz layer) will lower the point of zero charge (pzc), -- thereby showing a lower pH value at which charge reversal will occur. Contaminant extraction techniques requiring pH control will need to consider this aspect of the problem, e.g. chemical precipitation techniques which depend on pH of the "treated" system. Carrying the example further, one notes that specific adsorption of contaminant anions on the other hand will tend to shift the pzc to a higher value, i.e. charge reversal occurs at a higher pH value.

Working with non-specifically adsorbed indifferent sodium cations, Yeung suggests that electro-osmotic flow can be used as a mechanism to control the movement of the contaminant ions. In essence, using electrokinetics -- as for example in the type of system used for determination of the zeta potential (ζ) -- it is suggested that an electro-kinetic fence could be constructed that would restrict passage of contaminant ions. The requirement for implementation includes attention to the efficiency of the system, the amount of driving forces (energy) needed for the electrodes, the number and spacing of the electrodes, the periodic cleaning or replacement of the electrodes over the life of the contained wastepile (or clean-up). As in the experience with in-situ electro-osmosis procedures, the permeability of the soil exerts a very dramatic influence on the cost-efficiency of the technique.

The alternative to the electro-kinetic approach taken by Yeung would be to construct impermeable barriers for containment of the waste materials, such as those proposed by Violas using the procedure SANIPAROI, or composite clay-geomembranes using non woven geotextiles and HDPE geomembranes as discussed by Marcotte and Behaxeteguy. Whereas all three techniques are better applied as design/construction techniques, the use of barriers as post-facto barriers for control of movement of contaminants in a contaminated region also constitutes a valid consideration. A case in point is the rehabilitation of a polluted and damaged site in Germany using geosynthetics as reported by Genske et al. The site restoration requirement is in response to land use pressures, and the contaminated site is the former mine and coking plant identified as "Graf Moltke", located in the northwestern part of the Ruhr-District close to Essen. The hydrocarbon contaminants appear to have migrated through the substrate porous sediments into the fractured rock where percolation has occurred in the joint network. Of the three methods proposed for site remediation, sealing of the contaminated ground in combination with hydraulic and reinforcing measures was chosen in favour of the in-situ chemical treatment and soil replacement techniques. The composite soil-geosynthetic system which was designed to be waterproof and gasproof has been discussed in detail by Genske et al. together with the pilot plant built to field test the system.

The use of force fields to generate movement and control of contaminant ions becomes very unattractive in situations where chemical adsorption occurs. Under such circumstances, the contaminant ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via *O* and *OH* groups to the structural cations. The ions have the ability to influence the sign of ζ, and are referred to as the potential determining ions. The three principal types of chemical bonds include ionic, covalent, and coordinate-covalent. The valence forces bind atoms to form chemical compounds of definite shapes and energies. In structuring or developing chemical decontamination techniques, one needs to remember that in the contaminant chemisorption process, the reactions can be endothermic or exothermic, and that the chemical bond formation is generally very strong in processes of adsorption where the exothermic heat of reaction is high. Removal of the first layer is difficult, and the strategy for removal of the contaminant should count on "working" with the additional layers of contaminants held to the soil solids since these are by and large held by van der Waals forces. Complete removal of the contaminants is not a practical exercise.

Removal of metallic cations such as transitional metals and alkaline earth metals, retained in soil by *complexation* can be difficult since the process involves the reaction of the metallic cations with anions that function as inorganic ligands, e.g. OH^-, Cl^-, SO_4^{2-}, CO_3^{2-}, PO_3^{3-}, CN^-, etc. However, since the complexes formed between the metal ions and inorganic ligands are much weaker than those complexes formed with organic ligands, decontamination techniques could either try to dissociate the complex, or remove the metallic cations as complexed ions. The latter is probably easier or more effective as a "removal" technique.

The problem of decontamination becomes considerably more difficult when organic ligands, such as the amines, phenols, etc. are involved, since by and large, the attachment to the two or more organic groups is by coordinate covalent bonding. The presence of ligands or functional groups (carboxyl, carbonyl, phenolic, alcoholic) that can form chelates with heavy metals makes the organic component of soil constituents a very strong "adsorber" of heavy metals. It is surmised that the efficiencies obtained by Groenendijk et al. in their soil washing clean-up treatment of removed soil organics and clay (maximum removal efficiency of 86%) could be due to the strong attachment of the heavy metals for the organics. Because of the increased ionization of the functional groups, with increasing pH, the stabilities of the complexes (chelates) are likely to increase. An alternative to removal of the complexed metals is to stabilize and solidify the contaminated "region", since the metals are difficult to remove. This procedure requires determination of the chemical that can both penetrate the soil medium and also "fix" the metals. In the complexed state, the order for the stability of heavy metals complexes given by Jones and Jarvis (1981) is as follows:

$$Cu^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$$

Retention of heavy metals in the substrate soil is highly dependent on pH, in that the heavy metals tend to precipitate around neutral pH by forming compounds such as hydroxides, sulfates and chlorates species. The ability of the soil substrate to retain and attenuate the movement of heavy metals is thus seen to be susceptible to changes in the local soil-water environment. Chemical precipitation is one of the "chemical" methods favourably considered in removal of heavy metals from contaminated soils, and generally "works" with the solubilized metals in the pore water. "Natural" precipitation which occurs in the soil because of changes in the local soil-water pH environment is generally a two stage event: nucleation, and particle growth. Resultant precipitation can occur on the surfaces of the soil solids or in the pore water. One needs to be aware that because of the in-situ precipitation processes, precipitation washing and flushing of the heavy metals as a technique for removal of the contaminant will not necessarily remove all the heavy metals. An example of the problem can be seen in the heavy metals which are attached to amorphous or poorly crystallized Fe, Al, and Mn oxides. These metals show several types of association with the poorly crystallized oxides: e.g. exchangeable forms via surface complexation with functional groups (e.g. hydroxyls, carbonyls, carboxyls, amines, etc.) and interface solutes (electrolytes), moderately fixed via precipitation and co-precipitation (amorphous) and relatively strongly bound. Thus, implementation of precipitation washing for heavy metals removal could show results similar in "form" to those obtained by Yong and Galvez-Cloutier (paper for this Conference). In that particular controlled sets of laboratory experiments, the results indicate partitioning of lead as a function of pH of the system and initial concentration of the contaminant lead in the soil-water system. The pH_0 (i.e. pH at the pzc) is of particular significance inasmuch as maximum adsorption of lead apparently occurs within this pH region. One needs to study further whether in-situ chemical washing techniques designed to precipitate and flush the heavy metals (Pb in the case of the Yong and Galvez-Cloutier study) will remove all the heavy metals attached to the soil particles. The question can be begged if one asks whether it is indeed necessary to remove the contaminants that will not "move" (fixed?) in the soil substrate.

Elliott et al. (1986) established that at high pH levels, aqueous metal cations hydrolyse, resulting in a suite of soluble metal complexes according to the generalized expression for divalent metals given as:

$$M^{2+}(aq) + nH_2O \rightleftharpoons M(OH)_n^{2-n} + nH^+$$

This hydrolysis, according to Elliot et al. (1986) results in precipitation of metal hydroxides onto soils, which is experimentally indistinguishable from removal of metals from solution by adsorption. Yong and Phadungchewit (1993) confirmed from their experiments with various kinds of soils, that the adsorption affinity of heavy metals in soils can be related to the pK of the first hydrolysis product of the metals, where K is the equilibrium constant for the reaction in the above equation and where $n = 1$. From calculations of pK, and from the set of confirming experiments reported by Yong and Phadungchewit (1993) for the heavy metals studied, the selectivity order for preferential adsorption was obtained as Pb > Cu > Zn > Cd. One however needs to use this type of relationship carefully in that mixed composition contaminants which report more than heavy metals in the contaminant stream will likely encounter other controlling sets of bonding forces.

A good example of the effect of retention processes established between heavy metals and soil constituents can be seen in the case study described by Groenendijk et al. In this particular instance the problem of removal of arsenic and chromium adsorbed to the soil and fluoride in the groundwater is discussed by Groenendijk et al. with respect to clean-up of a contaminated site in the province of Groningen. The contamination problem was complicated by the presence of oil in the soil and groundwater -- originating from a leaking buried oil tank. Because in-situ soil flushing was considered not to be effective in removing the adsorbed arsenic and chromium, it was concluded that removal of the organic and clay fractions from the soil for treatment would be required. Soil washing was used to remove the adsorbed arsenic and chromium, with removal efficiencies obtained ranging from 62% to 86% depending on composition of soil material. With respect to the contaminated groundwater, a precipitation technique was used. The addition of caustic soda raised the pH to a level for optimum precipitation of arsenic and chromium, using iron chlorite as a precipitant to aid the precipitation process. Floc formation was enhanced by the addition of a polymeric flocculant. Bio-degradation techniques were used to treat the soil.

One could take the another point of view and suggest that instead of removal of the contaminants, one should (by design) "fix" (immobilize) or retard the movement of the contaminants in the affected region, i.e. keep them there "forever", thus ensuring that no further contamination will occur. In a sense, this view has been discussed by Horvath in regard to control of soil and groundwater contamination using surface-active soil constituents in the subsoil to inhibit contaminant transport. The results given show that the retardation factor, Rf, ($Rf = 1 + \rho Kd/n$), increased from a value of 90 to 620 in the case of pesticide transport when the soil organic and clay contents in the soil were increased from 0.1% and 0.35% to 0.7% and 2.5% respectively. Because of the "natural" heterogeneity of the substrate, permeability contrasts and microhydrogeological differences will require proper monitoring to ensure that proper substrate containment of contaminant plume can be achieved. One cannot overemphasize the importance of monitoring in problems and solutions which address groundwater contamination control.

A similar type of approach has been taken by Smith and Booker in their consideration of the option of "no treatment", for situations where the contaminated site is deemed to pose no immediate threat to the environment. Under such circumstances, it is suggested that an interceptor trench be constructed as a perimeter trench, and that an adsorbent material be placed in the trench to adsorb all the leachate emanating from the contaminated site. The argument is made that "when all the contaminants that can move have moved", the material in the trench can be removed for final safe disposal. In a sense, this is consistent with the "risk" evaluation procedure discussed by Martins and Barnoud, i.e. implementation of a remediation procedure consistent with the risk that the problem poses.

To determine "what can move and how far" requires knowledge of the contaminant transport phenomenon and prediction of contaminant plume advance. Determination of the transport coefficients reflective of the transport properties of the substrate constitutes a challenging task, not only because of the varied nature of the contaminants that need to be studied, but also because of the retention relationships formed by the contaminants with the different types of soils, and the problem of accountability for advective and diffusive transport "forces". Hensley and Savvidou report on the use of centrifuge modelling for experimental determination of the transport coefficients -- with attention to advective transport of contaminants. The technique worked well for the type of soils used (fine sand, coarse sand, and silt), and for gradients of total potential which were governed by gravity. As might be expected, so long as the primary transport mechanism is advective, the centrifuge modelling procedure can provide useful information.

It is necessary to note that since diffusive transport is not controlled by gravitational forces, it would be difficult to use of centrifuge modelling to model diffusive transport. For Peclet numbers less than one, the diffusion (movement) of solutes in water is faster than the advective flow movement of water. By and large, the corresponding k (coefficient of permeability) value for soils which produce Peclet numbers less than one in "flow" experiments is of the order of 10^{-7} cms/sec or less, i.e. clay soils. When sorbant materials are considered, i.e. materials which demonstrate substantial Rf values, as would be used in the Smith and Booker "no treatment" option, the combination of sorption and diffusion processes would introduce limits to the use of centrifuge modelling.

The capability of a sorbant soil material to retain contaminant ions is fundamental to the Rf factor, and also to the whole problem of attenuation of contaminants in the transport of contaminants in the substrate. The two groups of assumptions necessary in the "no-treatment" option are those with respect to "when decontamination is deemed to be complete", and those in regard to application of the advection-dispersion transport equation used in determination of the thickness of the trench material to fully adsorb all the contaminants. The Rf factor appears to be the critical issue inasmuch as this impacts directly on the capability of the trench material to fully contain the transported contaminants. How Rf varies with sorbant material, with time (when the sorbant adsorbs the contaminants), and with contaminant chemistry, will need to be determined. The variation of the partition coefficient Kd with respect to time, and contaminant chemistry needs proper attention.

The studies by Espagne et al, on zeolites with respect to potassium selectivity confirm the viability of the sorbant material approach taken by Smith and Booker, and further testify to the need for studies to determine adsorption characteristics and partitioning. Adsorption compatibility between contaminant ions and sorbant material would be a prime consideration. The results shown by Espagne et al. are very instructive in that information on adsorption efficiency in relation to concentration of ions, competing ions, particle size (surface area available), and "exposure" time (path length). One becomes more aware of the phenomenon of "competition for adsorption sites", influence of "other ions", speciation, reaction times, and available surface area. The logical conclusion that one can reach with adsorption studies is in regard to the final "carrying capacity" of the sorbant material. In effect, one needs to determine the effective sorbant life of the material, and the characteristics of the Rf factor.

Techniques for removal of heavy metals from the different soil components (constituents such as soil organics and amorphous materials) can be developed with the aid of information gained in sequential selective extraction (SSE) studies (Yong et al 1993). In selective sequential extraction (SSE) of heavy metals from soils, one chooses appropriate chemical reagents to destroy the "binding phase" between the heavy metals and the soil constituents, thereby releasing the different heavy metal fractions from the soil, and allowing the heavy metals to be removed from the soil by washing techniques. The extractant reagents can be classified as: concentrated inert electrolytes, weak acids, reducing agents, complexing agents, oxidising agents, and strong acids. With a knowledge of which soil constituents are responsible for holding on to "what proportion of the heavy metals and by what mechanisms" from SSE studies, a broad outline of decontamination requirements might be obtained. Thus for example, one observes that metals held by exchange mechanisms are considered to be non-specifically adsorbed and ion exchangeable, i.e. they can be replaced by competing cations, and that in general, the sorbent soil constituent solids are mostly clay minerals, organic materials, and amorphous materials. Neutral salts such as $MgCl_2$, $CaCl_2$, and $NaNO_3$, can be used as flushing fluids with concentrations higher than 1M, i.e. they can be used as ion-displacing extractants to promote the release of ions physically bound by electrostatic attraction to the negatively charged sites on the soil particle surfaces. One notes that other types of salts such as NH_4Cl and NH_4OAc, may dissolve considerable amounts of compounds such as $CaCO_3$, $MgCO_3$, $BaCO_3$, $MgSO_4$, and $CaSO_4$, and that NH_4OAc can, in addition, cause some dissolution of Mn-oxyhydrates and metal oxide coatings. Mn-oxides and carbonates can be removed by using hydroxylamine hydrochloride solution buffered with NaOAc (Chester and Hughes, 1967).

Metals precipitated or co-precipitated as natural carbonates can be released by application of a acid (e.g. acidified acetate). A solution of 1M HOAc-NaOAc (pH 5) appears to be sufficiently efficient in dissolving calcite and dolomite, releasing the metals bound to them without dissolving organic matter, oxides, or clay mineral particle surfaces. Since there is need to preserve the integrity of the soil, the extractant selected for oxyhydrates should not attack either the silicate minerals or the organic matter. Chester and Hughes (1967) used an extractant which combined an acid reducing agent (1M hydroxylamine hydrochloride) with 25% (v/v) acetic acid for extraction of ferromanganese oxides to avoid reducing the natural organic carbon. Tessier et al (1979) point out however that this acid-reducing combination may release Al and Si if hot digestion is used as part of the extraction technique.

The binding mechanisms for metals in respect to retention of the metals with soil organic matter include complexation, adsorption, and chelation. These are strong retention mechanisms. The general technique used for removal of the metals is to obtain release of the metals as a result of oxidation of the organic matter. If one chooses to use aggressive oxidants, solubility of the organic matter could result.

Organic Contaminants

The use of bio-remediation techniques for clean-up of organics-contaminated soil has received considerable attention, to a very large extent because of the capability for treatment in-situ, using the in-place contaminants in the respiration process for the microorganisms. The many factors that need to be considered for development of effective bio-remediation have been discussed by Elektorowicz and Yong, who point out that without proper accountability for the many field and local environmental interactive parameters, it is possible for bio-remediation treatment to fail -- even when treatability studies under "simulated" laboratory conditions indicate otherwise.

The use of soil microorganisms which exist in the soil substrate to metabolize (biodegrade) synthetic organic compounds (SOCs) benefits from the similarity between many of the SOCs and naturally occurring organic compounds. The following table (from Hopper, 1989) shows the "similarity" between the two types of organic compounds.

Natural Organic Compounds		Synthetic Organic Compounds
	Aromatics	
Phenylaianine		Benzenes, toluenes
Vanillin		Xylenes
Lignin		Chlorophenols
Tannins		Polynuclear aromatic hydrocarbons
		Phenols, Naphthalenes, Phthalates
	Sugars	
Glucose		Cyclohexane
Cellulose		Cyclohexanol
Sucrose		Chlorocyclohexanes
Pectin		Heptachlor
Starch		Toxaphene
	Aliphatics	
Fatty acids		Alkanes
Ethanol		Alkenes
Acetate		Chloroalkenes
Glycine		Chloroalkanes
Cyanides		Cyanides, Nitriles, Paraffins

The use of bioventing techniques for enhancement of the respiration rates of the indigenous microorganisms is an attractive proposition -- for organic contaminants that show biodegradability. Ong and Hinchee describe the various requirements concerning soil type, type of contaminants and biodegradability potential for successful implementation of the technique. One would expect that controls on the rate of air entry into the system, and the composition of the "air" are significant issues, and that more permeable soils that permit adequate air entry are more amenable for treatment. The experience reported by Yong et al (1991) in regard to bio-remediation studies of soil samples from a site contaminated by PAHs, PCBs and heavy metals, using bioventing, is a good example of the need for laboratory treatability evaluation of the interacting physical-chemical and biological parameters. In the reported study, the extent of disappearance of PAHs under forced aeration was measured, with different parameters used to distinguish biological degradation from chemical/physical degradation. The use of sterile and non-sterile samples demonstrated that biological degradation was responsible for 20% of PAH disappearance over 20 days of forced aeration. Various soil microorganisms were isolated in soil extract media in order to identify biodegrading activity, using the PAHs which showed the most susceptibility to biodegradation: phenanthrene, anthracene and fluorene. The results obtained suggested that bioremediation as the sole decontamination method may not be as effective as anticipated, and that chemical/physical mechanisms such as volatilization and masking (transformation into an altered compound) are also of importance. One concludes that procedures for forced aeration bioremediation should monitor soil atmospheric parameters to account for possible volatilization effects, and that this be factored into evaluation of the efficacy of in-situ bioremediation of hydrocarbon contaminated sites.

The use of soil venting (specifically, soil vapour extraction, SVE) as a combination physical/chemical means for removing volatile organic compounds has been addressed by Boersma et al., with respect to contaminated groundwater and soil at a solvent transfer facility in Michigan, by Armstrong et al. in regard to rate-limiting processes which control the SVE process, and by Bürmann with respect to the use of a vacuum-vapourizer-well UVB) technique for clean-up of groundwater contaminated by chlorinated hydrocarbons (CHC). In the UVB technique, a circulation flow within the surrounding groundwater is created, and soil air from the unsaturated area of the aquifer is permitted to be sucked into the UVB and may also be cleaned. Because the stripping air loop is closed the contaminants that are not adsorbed by the activated carbon are kept from escaping into the atmosphere.

As with bio-remediation procedures, the central sets of problems lie not in the capability of the "theory", but in the determination of the control parameters and the various treatability coefficients (rate coefficients). To increase VOC removal from the groundwater and the saturated zone soil, Boersma et al. used a nitrogen sparging system which increased the concentrations of PCE and toluene in the soil vapour by a factor of 4 and 20 respectively. Air was not used in the sparging system because of the high iron concentrations in the aquifer and the concern for iron precipitation in an oxidative environment. In the case of the studies by Armstrong et al., the test results indicate that vapour extraction of dissolved and sorbed phase contamination is rate-limited, and that the first-order model is inappropriate for simulating longterm SVE data. The controlling physical processes appear to be microscale diffusion processes, and the model developed using an exponential function to decrease the rate coefficient by several orders of magnitude during the experiment time period appears to be more representative of the physical processes.

In evaluating compatible remediation techniques for removal of organic molecules using chemical techniques, a knowledge of the interactions between the functional groups of the organic contaminants and soil would indicate likely "removal" techniques. It is useful to note that the chemical properties of the functional groups of the soil particles will influence the surface acidity of the soil particles, -- a significant property of the soil, since surface acidity is very important in the adsorption of ionizable organic molecules by clays. Surface acidity is a major factor in clay adsorption of amines, *s*-triazines, amides and substituted ureas where protonation takes place on the carbonyl group. One recalls that many organic molecules (amine, alcohol and carbonyl groups) are positively charged by protonation and are adsorbed on clays, the extent of which depends on the cation exchange capacity of the clay constituents (minerals), the amount of exposed surfaces, and the molecular weight of the organic cations. It is useful to note that large organic cations are adsorbed more strongly than inorganic cations by clays because they are longer and have higher molecular weights (Morrill et al, 1982).

Furthermore, polymeric hydroxyl cations are adsorbed in preference to monomeric species not only because of the lower hydration energies, but also because of the higher positive charges and stronger interactive electrostatic forces. With lower hydration energies, a smaller amount of energy is needed to transfer the polymeric hydroxyl cations from the soil solution to the interface. The hydroxyl groups in organic contaminants consist of two broad classes of compounds: (a) alcohols; e.g. methyl, ethyl, isopropyl, and n-butyl, and (b) phenols; e.g. monohydric (aerosols) and polyhydric. In addition to the hydroxyl group, two other types of compound functional groups exist: (1) functional groups having a *C-O* bond, e.g. carboxyl, carbonyl, methoxyl, and ester groups, and (2) nitrogen-bonding functional groups, e.g. amine and nitrile groups.

Carbonyl compounds (aldehydes, ketones, and carboxylic acids) have dipole moments because the electrons in the double bond are unsymmetrically shared and whereas they can accept protons, the stability of complexes between carbonyl groups and protons is very weak. The carbonyl groups of ketones are adsorbed on clay minerals by hydrogen bonding between the *OH* group of the adsorbent and the carbonyl group of the ketone, or via a water bridge. Acetone and nitrobenzene form double-layer complexes with clay. On the other hand the carboxyl group of organic acids such as benzoic and acetic acids interacts either directly with the interlayer cation or by forming a hydrogen bond with the water molecules coordinated to the exchangeable cation on the clay complex. Water bridging is an important mechanism in the adsorption process.

Amines possess the NH_2 functional group, and can protonate in soil, replacing inorganic cations from the clay complex by ion exchange. They can be adsorbed with their hydrocarbon chain perpendicular or parallel to the clay surface, depending on their concentration. The phenolic functional group, which consists of a hydroxyl attached directly to a carbon atom of an aromatic ring, can combine with other components such as pesticides, alcohol, and hydrocarbons to form new compounds. The sulfoxide group, which is a polar organic functional group forms complexes through either the sulfur or oxygen atom. One has complexes with transition metals with exchangeable cations.

PILOT TESTS, AND FIELD APPLICATIONS

Laboratory experiments designed to test or evaluate application of theories regarding contaminant retention, removal, or treatability, are valuable in that they permit application of controlled situations and proper parametric variations. However, scale-up of laboratory experiments for direct application to field problems suffer not only from scale effects, but also from lack of control of soil and contaminant compositions and uniformity, and local physical/chemical environmental control. Biological, chemical and physical reactions do not appear to scale linearly, and interactive relationships are likewise affected. Galvez-Cloutier et al. describe the laboratory tests used for control of the pilot-scale experiments conducted to clean-up the contaminated sediments of Toronto harbour. In that contaminated sediment problem, a combination of soil washing for removal of the heavy metals, and pre-conditioning and biodegradation of the organic contaminants is being used as the pilot test technique, prior to design of the full scale clean-up.

Arnaud et al. describe a large scale experimental basin created under a joint Franco-German Institute research project, designed to permit the study of protection of aquifers against contamination by hydrocarbons. The objectives of the joint program of study with the experimental basin is to better understand the mechanisms of pollution of alluvial aquifers by petroleum products, validate techniques for decontamination, and to validate mathematical polyphase models of transport. As in the case of the Galvez-Cloutier et al. experience, complementary laboratory tests are conducted to study certain phenomena associated with penetration of the oil and plume advance.

The reuse of wastewater from water treatment plants and from waste piles has always been an option that presents itself in situations where water availability is scarce or where water conservation is important. Guiton describes the experimental wastewater treatment plant for the town of Oppede which uses plants, anaerobic microorganisms and a soil percolation trap for an ecologically-based wastewater treatment procedure. Dia et al. on the other hand have utilized the leachate generated from a non-toxic waste pile, collected and treated in lagoons prior to use. The discussion includes procedures and protocol and the capture of methane gas for use as an alternative energy source.

Whereas methane production can be useful alternative energy source, it can on the other hand be a noxious substance in situations where gas permeation (diffusion/flow) through the ground, thereby creating a health hazard for the general population located in the region. Similar problems exist for the production of radon gas in cases uranium rich rocks in the substrate -- e.g. pegmatites and some granites. Case studies, control requirements and procedures for monitoring for these kinds of noxious gases are given by O'Riordan, leading to procedures for amelioration of these gases.

CONCLUDING REMARKS

The problem of decontamination and remediation of contaminated sites as part of the requirement for site rehabilitation needs careful attention to "what is in the substrate", and "what will the use of rehabilitated site". The papers submitted to Theme 3 confirm that new innovative technology is needed to address many of the complex problems. By and large, it is clear that for treatment of the contaminated groundwater, one attractive option is to extract the contaminated groundwater for treatment on-site by methods well-proven for wastewater treatment. Treatment in-situ can become complicated when complex mixtures of contaminants are encountered. Aeration or air stripping, steam stripping, SVE and thermal adsorption are techniques that are suited for "removal" of volatile organics. Chemical precipitation and soil washing can be used for "removal" of many of the heavy metals in the soil-water in in-situ treatment procedures. However, complete "removal" will be difficult because of high affinity and specific adsorptions of the contaminant ions. Soil removal for "washing" would be more appropriate, provided that soil removal is economic. A good working knowledge of contaminant-soil "bonding" relationships would provide for better structuring of appropriate options and compatible technology for soil decontamination and site remediation.

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CARACTERISATION ET GESTION DES CENDRES DES MACHEFERS PROVENANT DES INCINERATEURS MUNICIPAUX

CHARACTERIZATION AND MANAGEMENT OF MUNICIPAL INCINERATOR'S BOTTOM ASH

RESUME

Contenant des quantités considérables de métaux lourds lixiviables et d'autres contaminants organiques/inorganiques, les cendres des mâchefers ont suscité de nombreux problèmes, notamment en ce qui concerne les scénarios de disposition finale orientés vers la sauvegarde des sols et des eaux souterraines.

Plusieurs possibilités ont été investiguées pour la disposition finale -autre que l'enfouissement- de ces residus, principalement; 1) remblais pour la construction des routes, 2) stabilisateurs pour les sols, 3) additifs dans le béton, et 4) materiaux de construction en blocs.

Les facteurs de base affectant l'utilisation des cendres des mâchefers incluent principalement l'acceptabilité de l'impact environmental, la faisabilité aussi bien technique qu'économique, et la présence d'un marché viable.

Deux techniques de traitement ont été considérées, notamment, un traitement chimique visant à récupérer certains métaux par la technique d'éléctroplaquage, et un traitement physique consistant d'une part à une analyse granulométrique et de l'autre à une séparation magnétique des métaux.

Un procédé d'optimisation a été suggeré dans le but de définir, d'une part, la quantité de résidus devant être traités et la technique de traitement appliquée, et de l'autre, les facteurs économiques allant de pair avec cette action.

ABSTRACT

Since the bottom ash residues obtained from municipal solid waste incinerators contain considerable amounts of leachable heavy metals and organic/inorganic contaminants, problems have been encountered in deciding upon final disposal scenarios based on concerns about soil and groundwater contamination.

Several possibilities have been investigated for the ultimate disposal -other than landfilling- of these residues such as; 1) structural fill for road subbases, 2) soil stabilizers, 3) concrete additives, and 4) building block materials.

The basic factors influencing ash utilization scenarios include concerns of environmental impacts acceptability, technical and economical feasibility, and market availability.

Two treatment techniques have been initially considered, namely the metal recovery from the ash residues utilizing electro-chemical treatment techniques and a physical process which involves magnetic removal of metal and sieve analysis.

An optimization process has been suggested in an effort to define the amount of residues to be treated and the treatment technique applied on the one hand and the economic factors that accompany such an action on the other.

INTRODUCTION

Municipal solid waste (MSW) incineration (with energy recovery) has become a widely used alternative, especially in countries where landfill areas are scarce and difficult to site. Fortunately or unfortunately, MSW incineration is considered as a potential viable alternative in any waste management plan.

The incineration of solid waste produces three main types of solid residues: (1) fly ash (10 to 30% by weight of total residues), which is the fine dust collected from the flue gas by emission control devices; (2) slag (around 1% of total weight); and (3) bottom ash (70 to 90% of total residue), which is the remaining heavy material residue collected at the bottom of the combustion chamber. Although the incineration of the MSW provides a reduction of 70 to 80% by weight, the amount of the remaining residues to be disposed of is still substantial.

The bottom ash component consists of a metallic and a non-metallic fraction. The non-metallic inert material has properties very similar to sand and gravel. This fact leads to considering some useful utilization scenarios of bottom ash other than landfilling, e.g., aggregate material in construction works. Hartlen and Rogbeck (1989) presented the possibility of using "ash-gravel" in road construction and abutment fills. Some implications of such a practice would be the conservation of natural aggregate and the diversion of significant volumes of "waste material" from landfill, thus extending the operating life span of the landfill and saving on the tipping fees.

However, the environmental acceptability of such a practice is still debatable and should be addressed. The overriding concerns as to the best method of solid waste combustion ash management are the content and leachability of heavy metals (e.g., lead, cadmium, copper, zinc, etc.), salts and sulfates contained in the ash and the potential public health effects that may result from improper ash management. In addition, other concerns include the presence of trace organics and inhalation of contaminants from the dust generated by the ash.

Moreover, if ash should be beneficially reused as a raw material, e.g., structural fill for road subbases or building block materials, regulatory requirements are necessary.

The scope of this paper is to present the preliminary results of a bottom ash characterization and the basic considerations for treating MSW incinerator ash residues to improve their suitability in utilization scenarios.

DESCRIPTION OF THE INCINERATOR

The Montreal Des Carrières incinerator started its operations in 1969. It consists of 4 parallel mass burning incinerator units designed to handle a total of 1200 tons of municipal refuse per day.

The incinerator chamber is fed by gravity via a vibrating feeder, and the refuse moves thereof to the incineration chamber via vibrating gates. To control the formation of acid gases, lime powder is directly injected at the point where the refuse is fed. The flue gases pass through a water walled/bailer economizer heat recovery chamber, enter a multicyclone unit which is followed by a 3-stage electrostatic precipitator.

All three types of ashes are conveyed to a quench tank, then transported by a drag chain through an incline and dumped in a hauling truck.

SAMPLING AND TESTING

Since all of the ash streams are combined in the quench tank, it was not possible to obtain a separate bottom ash sample after quenching.

The samples of bottom ash were collected off the finishing gate, just prior to entering the quench tank. Thus, by doing so, it is not known whether or not quenching alters the bottom ash characteristics.

Composite samples of bottom ash were prepared and separated into different particle size fractions; namely, greater than 2mm (i.e., retained on sieve #10), between 2 and 0.595mm (i.e., passing sieve #10 and retained on #30), between 0.595 and 0.297 mm (i.e., passing sieve #30 and retained on #50), and less than 0.297mm (i.e., passing sieve #50). The total amount of some of the various metals (Pb, Zn, Cd, Cr, Cu) present in these four particle size fractions, and for a ground ash sample passing sieve #100, was determined using the Aqua Regia Digestion method[12].

The total solids content of the bottom ash was determined by sample weight loss after 24 hour period at 104°C according to ASTM method D2216-71. The fixed solids content of each ash was based upon weight loss of a dry sample placed in a 550°C muffle furnace for one hour (APHA standard method 290E).

The bottom ash was subjected to a multiple batch extraction procedure (MBEP) to determine the potential for metal solubility under non-aggressive leaching conditions. The test consists of five subsequent extractions using the same starting material. The extracting liquid used was demineralized water at a liquid to solid ratio of 10 to 1. The tests were performed in triplicates and the leachate samples were analyzed for pH, total dissolved solids (TDS) and chloride content. A sub-sample of each leachate was preserved with concentrated nitric acid and analyzed for metal content using the Flame Atomic Absorption (FAA).

RESULTS AND DISCUSSION

The particle size distribution of the Des Carrières incinerator bottom ash is shown in Table 1 below.

Table 1. Particle Size Distribution of a Bottom Ash Sample

Sieve No.	Sieve opening (mm)	% retained	cumulative % retained	% finer
3/4"	19.0	0.9	0.9	99.1
1/2"	12.7	14.6	15.5	84.5
5/16"	8.0	28.6	44.1	55.9
4	4.76	23.6	67.7	32.3
10	2.00	18.8	86.5	13.5
30	0.595	10.8	97.3	2.7
50	0.297	1.2	98.5	1.5
100	0.15	0.4	98.9	1.1
200	0.075	0.4	99.3	0.7
PAN	_	0.7	100.0	0.0

It can be seen from Table 1 that around 14% of the total mass of bottom ash is smaller than 2.00mm and 86% is larger. The total amounts of Pb, Zn, Cd, Cr, and Cu present in each of the above mentioned four particle size fractions are shown in Table 2.

It can be seen from Table 2 that the particle size fraction larger than 2mm has the lowest metal content, as compared to the smaller size fractions; namely, less than 1% of total Pb, less than 2% of total Zn, less than 9% of total Cd, less than 18% of total Cr, and less than 2% of total Cu. The highest content of Pb, Zn and Cu was found in the particle size fraction between 0.595 and 2mm. Not only is the total amount of contaminants (metals) in bottom ash particles smaller than 2mm greater than that found in the larger size, but it is also more leachable, as was pointed out by Stegemann and Schneider (1991) and by Gavasci et.al. (1990).

Based on these results, it is then suggested to discard the fraction of bottom ash with size smaller than 2mm, when it is desired to utilize the material in a construction work. By doing so, no more than 20% by weight of the total bottom ash would be discarded, thus leaving at least 80% by weight to be effectively utilized.

However, if some fine material is needed in a particular job, the numbers shown in Table 2 suggest the use of particles with size less than 0.297mm or the use of the fraction of a ground bottom ash passing #100 sieve. This recommendation is solely based on the amount of total metal present in the ash, without taking into consideration the effect of such a practice on the leachability characteristics of the composite material.

Table 2. Total Metal Concentrations in the various Particle Size Fractions

Size, x (mm)	Total Metal Concentration (mg/kg)				
	Pb	Zn	Cd	Cr	Cu
x>2	102	275	3.3	74	110
0.595<x<2	9974	4677	4.2	83	3464
0.297<x<0.595	3554	4428	5.8	60	2855
x<0.297	886	2976	12.3	92	1275
Ground Bottom Ash passing sieve #100	861	2284	11.4	112	1365

The concentrations of cations and anions were again higher in the leachates from the smallest particle size fraction, with the same applying for the pH and buffering capacity. The total solids content of the bottom ash was greater than 99.6%, indicating that the ashes were essentially dry.

The fixed solid content, on the other hand, was greater than 97%, indicating that the non-combusted carbon and volatile organic content of the bottom ash, reported as loss of weight on ignition (LOI) was greater than 3%.

The extracted fluids, obtained from the MBEP which was performed on the portion of bottom ash smaller than 2mm, were analyzed for pH, TDS, chloride and metal content. The pH of the leachates remained alkaline throughout the test. It decreased from 12.12, after cycle 1, to 11.38, at the end of cycle 5.

The average cumulative TDS in the leachates from the MBEP was less than 5% of the bottom ash.

The chloride dissolution was observed to occur during the first and second cycles. This fact was of course expected since, even under alkaline conditions, chlorides are known to readily dissociate in water.

The average cumulative fractions of each metal leached out at the end of the fifth cycle were determined by dividing the mass of the contaminant measured in the leachates to the mass of that contaminant in the original sample, expressed as a percentage. Typically, less than 1% of Zn, and less than 2% of Pb were leached out during the test. It was noted that the amount of metals (Pb and Zn) leached out decreased from cycle 1 to cycle 5, i.e., decreased as the pH of the ash decreased from 12.12 to 11.38, indicating therefore the amphoteric nature of the metals. Hence, the pH (and redox potential) environment is an important parameter in that respect.

What has been presented indicates the advantage of removing the fraction of bottom ash with particle size smaller than 2mm. Moreover, the fraction of the ash with particle size greater than 2mm could be subjected to a process where the metallic fraction would be magnetically removed. The cost associated with this "physical treatment technique" should be minimal especially when compared to an electro-chemical treatment technique. Legiec et al. (1988) and Vehlow et al. (1989) have presented the technical possibility of operating a continuous process for heavy metal removal. The extraction studies presented by Legiec et al. (1988) revealed information on the leaching characteristics of the ashes and on the ability of some extraction solutions to separate these metals from the ash matrix. The electrochemical plating techniques was then utilized to recover the metals, in a relatively pure form, from the extraction solution. Although the results were promising, the cost of implementing such a technique on a full-scale basis, without mentioning the operating problems that are likely to occur, has yet to be addressed, and since the amount of metals present in the bottom ash is much less than that found in the fly ash, such a technique would not be warranted for bottom ash conditioning.

Thus, the preferred approach for improving the suitability of MSW incinerator bottom ash in utilization scenarios is to separate the fractions with size smaller than 2mm.

CONCLUSION AND RECOMMENDATIONS

In order to conserve natural aggregates and reduce, or eliminate, the cost associated with MSW incinerator bottom ash disposal, it is strongly recommended to make use of this "aggregate-like" material in construction use. However, the content and leachability of some heavy metals, especially lead and zinc, present in these ashes raised concern about adverse potential effects that accompany any utilization scenario.

Considering the amount of bottom ash, an expensive and laborious treatment technique, such as metal recovery by electrochemical treatment processes will not be advantageous if compared to a process which involves the magnetic removal of the bottom ash metallic fraction and its segregation into two different fractions; namely, the fraction with size greater than 2mm and the fraction with size smaller than 2mm.

Preliminary study showed the fraction of bottom ash with size greater than 2mm, which consists of around 80% by weight of total amount, contain the lowest level of heavy metals (less than: 1% of total Pb, 2% of total Zn, 9% of total Cd, 18% of total Cr, and 2% of total Cu), the leachability of which is also less, as compared to the fractions with size smaller than 2mm.

It is therefore suggested to magnetically remove the metallic fraction from the ash and to discard the fraction with size smaller than 2mm (less than 20% of total weight), while retaining the remaining part for constructive utilization.

Since the characteristics of solid waste can vary substantially over short periods of time (based upon the nature of the waste burned and the incinerator operating parameters), the remaining residue, i.e., the ash, is very heterogeneous. Therefore, in order to provide statistically valid results which will present a basis for assessing the environmental acceptability of a given ash utilization scenario, it is necessary to take daily samples on an hourly basis over a very long time period (e.g., a year) and correlate the results of the ash characterization (which affect the short and long-term behaviour of the ash in the environment) with the quality of the influent waste and the operating parameters of the incinerator.

There is a need to develop some reliable and reproducible lab tests to predict leachate characteristics at the site where the ash is utilized in one way or another.

It is essential that the ash residue streams be handled in a well-designed closed-system to prevent the generation of fugitive air borne dust.

At this point in time, and before starting to utilize bottom ash on a large scale, it is recommended to wait for additional research and guidelines to regulate bottom ash utilization scenarios, in order not to endanger the public health nor the environment.

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LE CONTRÔLE DU pH DANS LES MÉCANISMES D'ACCUMULATION LORS DE L'INTÉRACTION KAOLINITE-PLOMB

pH CONTROL ON LEAD ACCUMULATION MECHANISMS IN KAOLINITE-LEAD CONTAMINANT INTERACTION

RÉSUMÉ

Les mécanismes d'adsorption et de précipitation ont été étudiés à l'aide de la technique des titrations potentiométriques en paralléle, la capacité tampon a été mesurée à partir des titrations et à partir des valeurs du potentiel zeta. La force ionique du système sol-contaminant, l'acidité de la solutions contaminante et la capacité tampon ont été des paramètre considérés dans l'évaluation du processus d'accumulation. Une suspension de kaolinite a été utilisée de façon à permettre un maximum d'exposition des surfaces des particules. Ceci a permis en même temps une étude sans l'interférence de contraintes physiques dûes à la granulométrie, laquelle cause des surfaces "cachés" dans le cas des agglomerats et floccons.

ABSTRACT

The Pb adsorption and precipitation mechanisms were studied using parallel potentiometric titrations, and the soil buffering capacity was calculated from potentiometric titration measurements and also from zeta potential measurements. The ionic strength of the soil-contaminant system, the acidity of the leachate solution, and the soil buffering capacity were all considered in the evaluation of the Pb-soil accumulation processes. To permit maximum soil particle surface area for the interaction processes, a kaolinite soil suspension system was used. This permitted the accumulation processes to be examined without interference from physical pore size constrictions and "hidden" surface areas arising from flocs and aggregate groupings.

INTRODUCTION

The transport and fate of heavy metals in soils, and the influence of pH of the leachate and the soils, on the retention and attenuation of heavy metals have been of considerable interest in the design and evaluation of clay soil barriers, inasmuch as (1) heavy metals are one of the contaminant groups considered to be noxious with respect to human health, and (2) the possibility of changes to the pH regime of the soil-water system due to the chemical nature of the leachate and/or the likelihood of acid precipitation. Since water in the atmosphere is generally in equilibrium with the prevailing carbon dioxide pressure, and will in general exhibit pH values of less than 6, the presence of other air-borne "smoke-stack" emissions capable of producing acid precipitation, will have the tendency or capability of influencing the transport processes and fate of the heavy metals in the contaminant leachate.

The retention of heavy metals by soil constituents is seen to be pH sensitive, especially in the case of soils containing soil organics, oxides and hydroxides, carbonates, etc. The processes of accumulation, e.g. adsorption and precipitation or co-precipitation etc. are directly influenced by the pH of the system. Previous studies (e.g. Yong et al, 1992, 1993) show that heavy metals can be retained by clay soils and that they can be partitioned into five operationally defined "phases" such as exchangeable, carbonate, hydroxide/oxide, organic and "residual" phases -- where the operationally defined phase refers to the "binding phase or mechanism of attachment of the heavy metal" which is assessed via selective sequential extraction (SSE) methods of analyses. The use of SSE permits one to apply appropriate chemical reagents in such a manner that the heavy metals in the contaminated soil can be "released" from the soil solids (constituents) once the "binding phase" is destroyed.

If one considers the chemical interaction of a inorganic contaminant leachate with a soil-water system in terms of resultant changes in the pH of the system, there is a convenient procedure that one could use to determine the capability of the soil-water system to maintain its potential for accumulation of the inorganic chemical leachate. This procedure is akin to the one used in solution chemistry vis-a-vis determination or evaluation of the chemical buffering potential of the chemical solution. One recalls that the capacity of a solution to resist a change in pH with the addition of strong acids or bases is defined as its *buffer capacity (or potential)* . The studies performed (Yong et al., 1990) show that there is considerable promise in the application of this potential for evaluation of the fate of heavy metals in heavy metal contaminant leachate transport in clay soils.

As part of the continuing study of the overall problem, this study reports on the interaction between a lead (Pb) contaminant and a kaolinite soil, with particular attention to the influence of pH on the accumulation processes involved. Attention is directed towards the status of Pb^{2+}, since the amount of Pb^{2+} available for retention depends on pH, cation exchange capacity CEC, soil buffering capacity, and initial concentration of Pb in the contaminant solution. One generally studies pH control on Pb solubility and precipitation (and/or co-precipitation) since the amount of soluble Pb^{2+} adsorbed is conditioned by how much remains in solution after precipitation at a particular pH. Whereas this study is directed specifically to Pb, if one accounts for the influence of the unhydrated ionic radii of other heavy metals, and their respective pKs of the first hydrolysis product (to account for selectivity) the heavy metal contaminants such as cadmium, copper, zinc, would also exhibit similar patterns of contaminant-soil interaction and accumulation processes.

MATERIALS AND METHODS

The kaolinite soil which was obtained from the Georgia Kaolin Co. was identified as a hydrite PX kaolin soil. The mineralogical composition of the clay was determined by conducting XRD tests on plain, acid treated, and heated samples, using a Siemens D-500 diffractometer. The results indicated only kaolinite present as the clay mineral with about 1.2% of amorphous material -- (0.5% Al_2O_3 , and 0.7% SiO_2). The grain size analysis showed at least 84% clay ($<2\mu$), with the remaining soil fraction as silt (2 - 53μ). Consistency tests indicated that the liquid limit was 61% , with a plastic limit of 35%. The specific surface area measured, using the ethylene glycol-monoethyl ether technique (Eltantawy and Arnold, 1973), was 24 m^2/g.

The lead leachate was prepared as a lead solution (1000 ppm Pb^{2+}) using 1.3422 g of $PbCl_2$ salt dissolved in 200 mL of double-distilled water, adding 1.5 mL of concentrated HCl acid and diluting to 100 mL with distilled water. This provided a stock solution such that 1.00 mL = 1.00 mg of Pb^{2+}, with a pH value of 3. This stock solution served as the basis for preparation of all lower Pb^{2+} concentrations (by dilution) of test solutions (50, 100, 200, 300, 400, 500, and 600 ppm).

Measurement of pH of the soil, especially in regard to determination of the pH value as influenced by adsorption processes, poses several problems, not the least of which is "where does one measure the pH"? A general solution to the problems of measuring pH has been to use soil-water dilution ratios. However, both dilution ratios and equilibrium salt concentration values will influence the value of pH obtained. Schofield and Taylor (1955) suggested that the main criterion for selecting an extractant for pH measurement is one which causes the minimum of disturbance in the distribution of ions between soil surfaces and the surrounding solution. This means that the extractant must have the same ionic strength (I.S.) as the soil solution, and should also contain the most common ions present in the soil. The study reported by Conyers and Davey (1988) show that for the three types of soil suspensions (i.e. soil mixed with water, pH_W; 0.01 M $CaCl_2$, pH_C; and 0.M KCl, pH_K), the pH_C values did not vary for soil-fluid ratios between 1:2 and 1:10, whereas the values for pH_W and pH_K varied linearly within the same soil-fluid ratio range. Accordingly, from the initial tests conducted in this study, it was decided that a soil-fluid ratio of 1:10 was acceptable and from other tests conducted to determine the equilibration periods and optimal saline concentrations, it was established that the pH should be measured after 0, 1,2,3,4, and 5 days following reaction, and the varying saline concentrations would be obtained by addition of KCl (0 - 0.25N KCl) as the required salt. This choice of salt was predicated on the requirement for a saline solution which would not introduce a cationic form that would compete with Pb for the adsorption sites, and would not introduce other anionic forms "foreign" to those already present in the system. pH was measured with a BECKMAN Φrm pH12/ISE meter with combination electrode (glass-calomel) after a double-buffer calibration, with temperature compensation obtained by an automatic temperature compensator probe immersed in the suspension during the measurement process.

Lead was measured by atomic absorption spectrophotometry (AAS) using a GBS model 902-double beam atomic absorption spectrophotometer. Measurements were

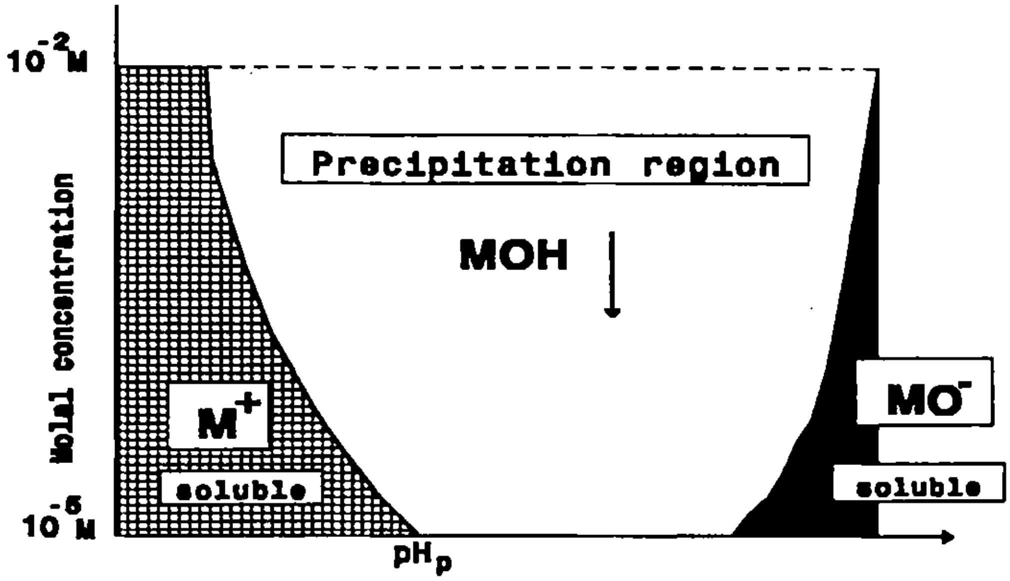

Fig. 1 - Solubility of metal hydroxide in relation to pH.

performed after precipitation (due to pH adjustment), and centrifugation of the samples (in polypropylene tubes for 10 minutes at 10,000 rpm in a DAMON/IEC centrifuge) was performed prior to AAS measurements.

For potentiometric titration, the type of salt (10 ml of 0.025N KCl) was kept constant and total electrolyte concentration variation was obtained by the addition of different loads of Pb. pH variation was obtained by adding increasing amounts of 0.1N HCl or NaOH in 0.5 mL increments.

The zeta potential, which is calculated from a measurement of the electrophoretic mobility of the particle, and which represents the electrical potential at some distance from the particle, was determined from measurements with a ZETA Meter, using the Helmholtz-Smoluchowsky relationship for calculation of the actual zeta potential.

RESULTS AND DISCUSSION

The first series of $PbCl_2$-soil interaction studies were conducted as precipitation experiments, using soil suspensions consisting of 4g of clay in 40 mL lead solutions. The results showed (as expected) that the amount of Pb precipitated (solid hydroxide species) depended on the pH and initial metal concentration. For this study, it was determined that the amount of Pb^{2+} remaining in solution (after precipitation) is the Pb^{2+} available for adsorption onto the clay particles. The dependence of solubility of hydroxide species on pH can be seen in the pictorial relationship shown in Fig. 1, where M indicates metal ions, MOH = hydroxide compounds.

The solubility curves obtained for the experiments conducted showed that the higher the concentration of Pb^{2+}, the higher is the position of the solubility curve (represented on the left hand side, LHS, in Fig. 1), and that the precipitation pH_p, which is the intercept of the LHS solubility curve with the abscissa, varies between pH 6 and 7.5, with the higher pH_p value associated with the higher initial Pb^{2+} concentration, as seen in Fig. 2.

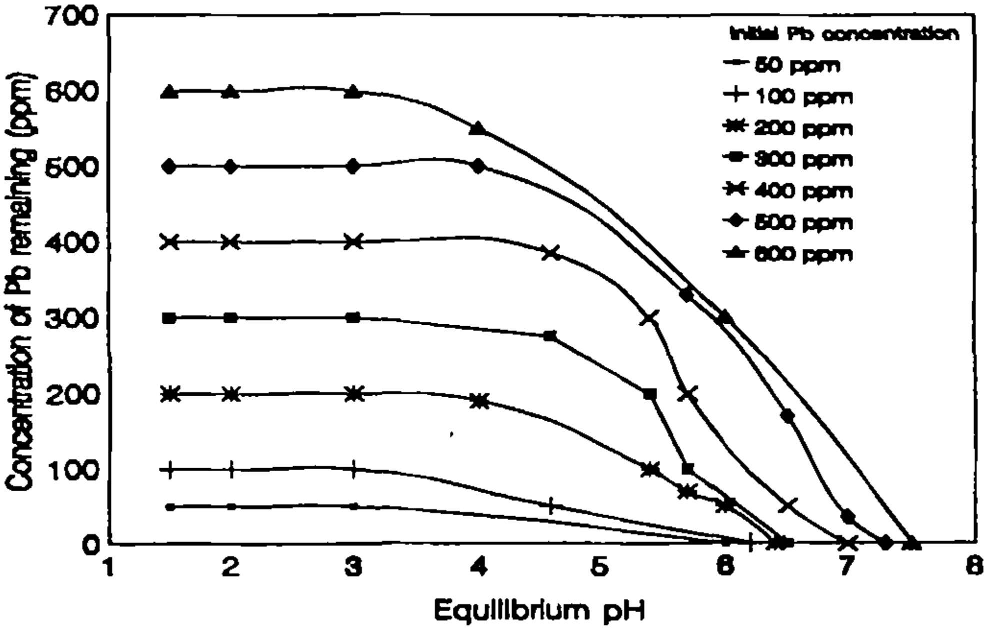

Fig. 2 - Pb^{2+} solubility curves for different initial concentrations.

The adsorption tests which were performed under the same conditions as those for the precipitation experiments (with soil suspensions), showed that the equilibrium pH values decreased with incremental input of lead, due primarily to the acidity of the lead solution. The amounts of Pb^{2+} adsorbed by the clay were computed by taking into account the difference between the total amounts of Pb^{2+} applied to the soil suspension minus the amount of free Pb^{2+} at the specific pH.

Considering kaolinite to be a combination of fixed and variable-charged mineral (because of its hydroxylated edges), and taking into account the pH influence on both precipitation and the particle charge of variable-charged surfaces, it is to be expected that the amount of lead adsorbed will be a function of the pH of the system. The results obtained from this series of experiments can be seen in Fig. 3 in relation to the role of pH and initial Pb concentration. The maximum adsorption of Pb^{2+} is seen to occur in the pH range of from 2.5 to 6. At pH values higher than 6, one begins to encounter significant precipitation effects which appear to dramatically reduce the cation adsorption of Pb^{2+}. As shown in Fig. 3, the amounts of Pb^{2+} adsorbed reached a maximum value of about 60% of the quantity available for adsorption at a pH value between 4 and 5. The relationship between available Pb^{2+} and amount adsorbed can be better visualized by "looking" at a the superposition of the results obtained in Figs. 2 and 3 -- as shown schematically in Fig. 4.

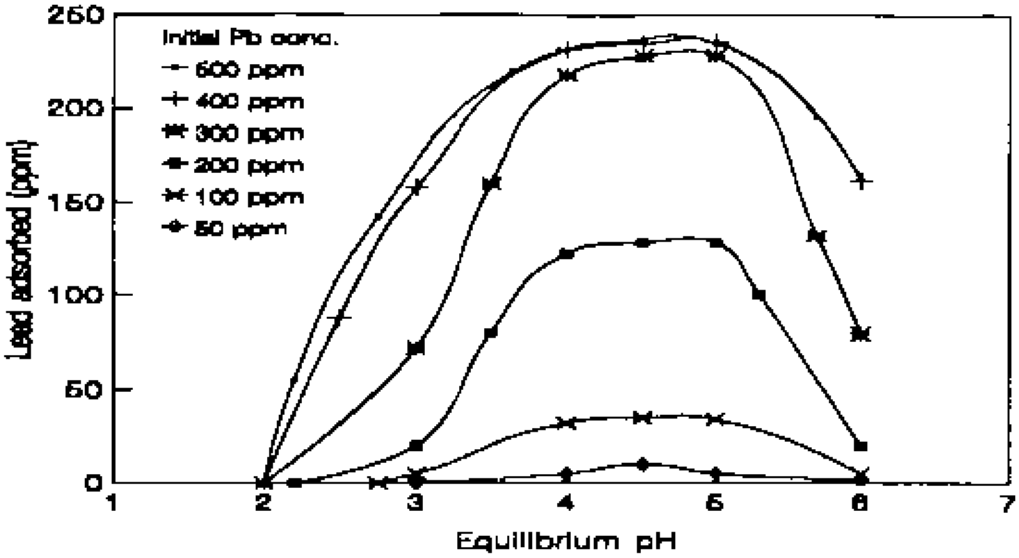

Fig. 3 - Adsorption of Pb^{2+} as a function of pH and initial Pb^{2+} load.

With the aid of Fig. 4, one can obtain a better visualization of the role of pH and initial Pb^{2+} concentration in the lead leachate (solution) on the amount of Pb^{2+} adsorbed and the various other forms of Pb remaining in solution and/or precipitated.

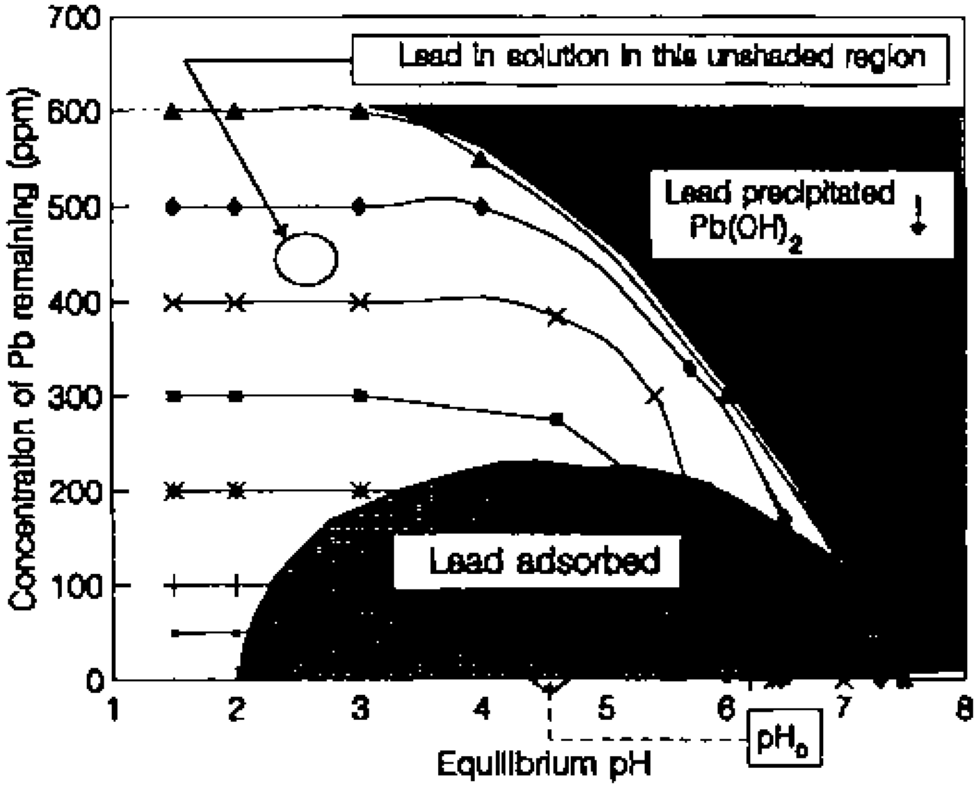

Fig. 4 - Schematic representation of superposition of Figs. 2 and 3, demonstrating the various lead (Pb) forms.

As indicated in the figure, for the lead which is not precipitated, the lead remaining in solution (shown as the unshaded region in Fig. 4) can take the form of free Pb^{2+}, $PbOH^+$, $PbCl^+$, etc. depending upon ligand availability. The pH_o shown in the abscissa refers to the point of zero charge (zero point charge zpc) which is seen to occur when lead adsorption is at its maximum -- as indicated in Fig. 3.

Potentiometric titration tests were conducted with various solutions containing the kaolinite clay particles and various Pb^{2+} concentrations. The titration curves constructed by plotting (H^+-OH^-) as the ordinate against the equilibrium pH values as the abscissa showed that the titration curves (not shown in this paper because of "space" constraints) all crossed the equilibrium pH abscissa at a pH value of about 4.5. This represents the pH_o of the clay, which confirms the indications obtained from the adsorption tests. Maximum buffering capability is obtained at this pH level.

It is useful to note that except for zeta potential measurements on the kaolinite soil suspension without any Pb^{2+} in the solution (i.e. "blank" clay suspension), all the other zeta potential measurements on the clay-Pb^{2+} solutions also confirmed the pH level at the zpc. This was obtained from a graphical representation of the zeta potential in relation to pH variation for the various clay-Pb^{2+} solutions. The graphical representation of results is similar in format to the representation for titration results, except that in this case, the ordinate is represented by the zeta potential measurements. As with the titration curves, all the curves appear to intersect the equilibrium pH abscissa (which represents a zero value for the zeta potential) at also about a pH value of 4.5. This common intersection point on the pH abscissa "plot" between all the "curves" which represents the pH at zero point charge appears to confirm the pH_o value found from the titration tests and the pH "region" indicated in Fig. 3.

The zeta potential measurement results for the "blank" clay suspension showed that the zeta potential curve intersected the equilibrium pH abscissa at a value of about 4, i.e. indicating that the natural zpc of the kaolinite was about 4. The shift in the pH at the zpc (i.e. pH_o) from 4 to 4.5 was immediately evident with the first Pb^{2+} solution. Pyman et al., (1979) and Uehara (1981) suggest that this is indicative of specific adsorption processes. If this thesis is accepted, for the test results obtained, one would expect that a certain amount of Pb^{2+} would be specifically adsorbed by the clay particles, and in consequence, this part of the Pb^{2+} adsorption would be more difficult to "overcome" if removal of Pb^{2+} is sought in a remediation exercise. However, more work needs to be done to pursue this particular thesis.

CONCLUDING REMARKS

The results obtained indicate that maximum adsorption occurred at a pH value equivalent to the zero point of charge (zpc) of the soil. For values of pH higher than the pH at zpc (pH_o), adsorption decreased until the precipitation pH (pH_p) of the lead was reached, at which time Pb retention was mostly achieved through precipitation mechanisms. For pH values between 6.5 and 8.5, precipitation may account for as much as 90% of Pb retention. However, ionic strength, dilutions ratios, initial concentrations, and elapsed time were found to modify soil pH and thus influence total amounts of Pb retained by the kaolinite. Zeta potential measurements were found to provide good indicators of the surface charge modifications resulting from Pb adsorption onto the clay particles, and also as a means for determination of the specific adsorption of Pb. The role of soil buffering capacity, and its influence on metal accumulation processes can be seen from the results obtained. This permits evaluation of clay barrier compatibility and capability to serve as a heavy metal contaminant barrier material.

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PROCESSUS RETARDANT LA BIORESTAURATION DES SITES CONTAMINÉS PAR DES HYDROCARBURES

RETARDATION OF BIOREMEDIATION OF HYDROCARBON CONTAMINATED SITES

RÉSUMÉ

La biodégradation des hydrocarbures dans le sol est une technique de plus en plus reconnue et appliquée. Pourtant, malgré les études de faisabilité en laboratoire, les résultats de la biodégradation sont souvent loin des attentes. Chaque nouvelle expérience produit de nouveaux aspects des processus complexes ayant lieu durant la restauration des sites contaminés. Ces processus mal contrôlés peuvent retarder et même arrêter la biodégradation. L'article présente les aspects qui peuvent influencer le plus la technique de biorestauration tant in-situ qu'ex-situ. Les conclusions sont tirées à partir de la bibliographie et des études de faisabilité effectuées en laboratoire avant l'application de la technique particulière sur le site. Les paramètres environnementaux tels que la température, le pH, la tension osmotique ainsi que la sorption à la surface des particules, l'aspect de la compétition entre les microorganismes, l'impact du prétraitement du sol sont décrits. En se basant sur ces données, on peut optimiser les paramètres techniques au cours de l'application de la biodégradation dans le sol sur le site contaminé.

ABSTRACT

The bioreclamation of hydrocarbon contaminated soils is a very common technique these days. However, in practice, the results of bioreclamation are very often far from expectations. Each case brings new aspects of the complex process taking place during the bioreclamation. These processes controlled the wrong way can retard and even stop bioreclamation. The paper presents these aspects which can most influence the bioreclamation technique in-situ as well as ex-situ. The conclusions are developed on the basis of the review of numerous references and the feasibility studies done in laboratory before the application of a technique on site. The environmental parameters such as temperature, pH, osmotic pressure as well as sorption, microorganism competition, impact of pretreatment of soil are presented. From these data the optimisation of parameters during the bioremediation is possible.

INTRODUCTION

On sait déjà depuis 100 ans que certains microorganismes ont l'habilité de métaboliser des hydrocarbures (Miyoshi, 1895). Dans des conditions favorables, le développement des microorganismes peut être utilisé afin de restaurer des sols contaminés. La réduction des contaminants se fait grâce aux processus biochimiques se produisant dans le sol pollué si les conditions environnementales favorables sont accomplies. L'objectif de chaque technique de biodégradation est d'améliorer ces conditions afin d'accélérer l'activité des microorganismes dans le sol.

Pratiquement, la biodégradation à l'échelle industrielle est incitée par la croissance contrôlée des microorganismes indigènes ou par l'inoculation dans le sol des microorganismes spécifiques, développés en laboratoire. Ce deux techniques peuvent être appliquées soit in-situ soit ex-situ dans les sols excavés, en les plaçant dans les cellules spécialement conçues dans ce but.

Le processus de croissance comprend six phases: la phase de décalage, la phase d'accélération, la phase exponentielle, le déclin de croissance, la phase stationnaire et la phase endogène (fig.1). Le but de chaque technique est de diminuer le temps de décalage, d'augmenter la phase d'accélération, d'étendre la phase stationnaire et de retarder la phase endogène. Pourtant, au cours de la biodégradation, les processus biochimiques peuvent retarder le traitement en freinant la croissance et en diminuant la biodégradation.

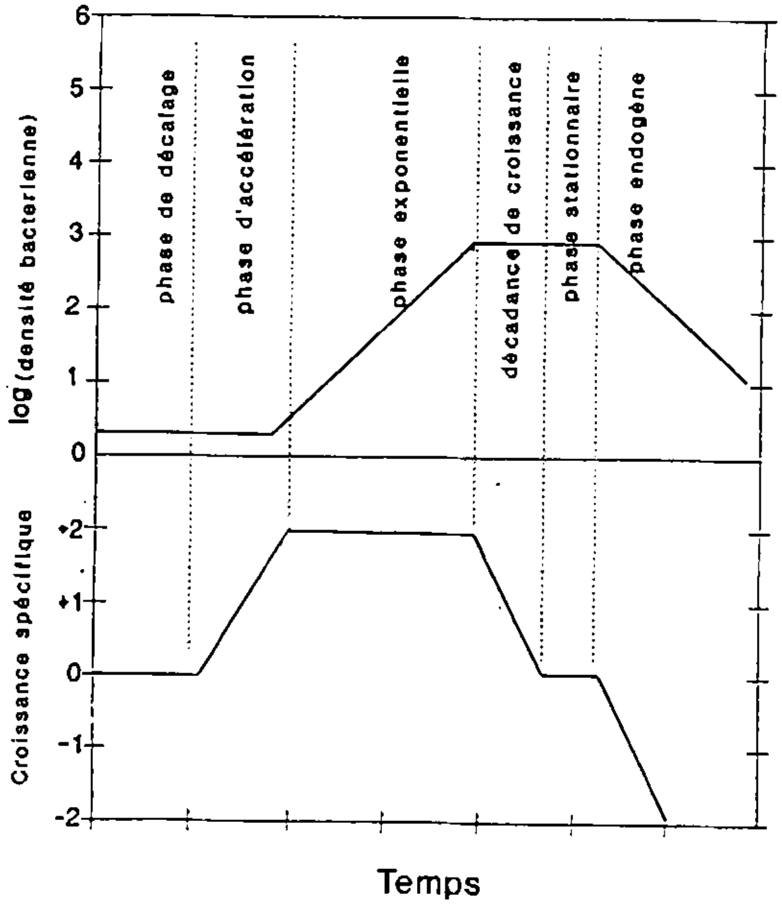


Fig.1 La courbe de la croissance des microorganismes (selon Mond ,1949)

Le retard dans la croissance des microorganismes capables de dégrader des hydrocarbures se concentre sur les aspects suivants:

- compétition parmi les microorganismes,
- indisponibilité des nutriments,
- variation du pH,
- humidité inadéquate,
- variation de la température,
- sorption,
- impact des additifs,
- toxicité des sous-produits,
- mutagénèses.

COMPÉTITION PARMI LES MICROORGANISMES

La microflore tellurique est composée d'espèces appartenant aux groupes suivants; bactéries, actinomycètes, moisissures, champignons, algues et protozoaires. Les virus ne sont pas des microorganismes telluriques puisque ce sont des parasites intracellulaires stricts, cependant, ils jouent un rôle indirect dans le sol. Il est évident que la faune du sol (*Nématodes, Arthropodes, Annélides*) joue aussi un rôle indirect dans les processus interactifs de l'écosystème.

Il est reconnu que les moisissures qui démontrent une haute activité dans les hydrocarbures sont *les Cladosporium resinae, Fusarium sp., Stysanus sp. et Alternaria sp.*. Une activité modérée est présentée par les *Céphalosporines sp., Cladosporium sp. (ou Cladosporium resinae), Aspergillus sp. et Pénicilliums sp.*. Parmi des microorganismes non-actifs, on retrouve *les Pullularia sp.* et les actinomycètes variés. Plusieurs d'entre eux se retrouvent au milieu du sol.

Les bactéries sont la population la plus répandue dans le sol. Parmi les bactéries, les *Corynébactériacées* occupent 65%, *Bacilles Sporulés* - 25%, les bactéries mieux connues comme *Agrobacterium, Nitrobacter, Azotobacter, Achromobacter* n'en occupent que 10%. La distribution de ces microorganismes varie selon le site ainsi que selon la profondeur.

La densité bactérienne totale et la distribution verticale reflètent la distribution de la matière organique dans le sol. Donc, théoriquement, les bactéries du sol, en majorité des hétérotrophes, sont capables de se placer en profondeur, en utilisant les hydrocarbures comme source d'énergie. Pourtant, leur distribution est si peu connue que les tests de la faisabilité doivent être effectués avant l'implantation de la technologie sur le site. Ces tests peuvent détecter la présence des microorganismes actifs dans la biodégradation des hydrocarbures.

En tenant compte des processus complexes, il convient de dire plutôt que la bonne technique "contrôle" les processus interactifs dans l'écosystème du sol. Le développement de la technique doit, donc, conduire à une approche de la connaissance des interactions entre les microorganismes et le sol, des interactions entre les microorganismes et les contaminants, et des interactions entre les microorganismes telluriques eux-mêmes.

Cette compétition est spécialement importante dans deux cas: 1) inoculation in-situ des microorganismes capables de dégrader les hydrocarbures, 2) introduction des additifs. Dans un premier cas, les microorganismes développés en laboratoire et soumis à l'impact des microorganismes telluriques autochtones perdent la compétition. Dans un deuxième cas, les additifs utilisés au cours du prétraitement, afin de changer des paramètres structuraux du milieu, introduisent les nouvelles interactions dans le milieu. Les nouveaux microorganismes peuvent, donc, gagner la compétition en diminuant le taux de biodégradation. Ces cas sont tellement fréquents qu'il semble étonnant que certains applicateurs de la méthode évitent les études de faisabilité avant d'entrer sur le site.

NUTRIMENTS

Dans le milieu des sols contaminés, les hydrocarbures offrent une source riche en carbone, cependant, leur quantité doit être en proportion exacte avec celle d'autres substances nutritives.

L'activité microbienne a lieu principalement en fonction de la quantité d'éléments nutritifs tels le phosphore, l'azote, le potassium et les sels minéraux ainsi que la présence des accepteurs d'électrons. La proportion entre le carbone, l'azote, et le phosphore le plus souvent utilisée est de 100:10:1. Afin d'augmenter l'activité des microorganismes telluriques indigènes, le développement de la technique de biodégradation aérobie consiste à assurer les conditions susmentionnées. Les substances nutritives sont utilisées sous forme liquide ou solide; l'accepteur d'électrons est injecté sous forme de gaz (air, oxygène, ozone) ou sous forme liquide (peroxyde d'hydrogène). Cette alimentation est assez facile dans les sols à perméabilité élevée, pourtant, dans le cas de perméabilité basse, la situation se complique. Les sols argileux, par exemple, ne laissent pas facilement pénétrer les substances nutritives, minimisant leur contact avec les microorganismes. Le prétraitement des sols argileux est, donc, nécessaire avant l'application de la biodégradation. Le prétraitement des sols argileux se base sur le changement de la densité et de la porosité. Les techniques tels que le broyage des sols et l'ajout des additifs sont appliquées. Chacune de ces actions est avantageuse mais peut aussi causer des inconvénients en freinant le processus de biodégradation.

TEMPÉRATURE

Les conditions de refroidissement ont un impact très limité sur la viabilité des moisissures (Hill, Thomas, 1975). Les spores de *Cladosporium resinae* et *Aspergillus fumigatus* peuvent survivre à l'exposition aux températures extrêmes tels que 80°C ou -32°C dans les combustibles. Dans le cas où les spores sont plongés dans l'eau leur résistivité diminue; la température extrême dans laquelle les spores peuvent survivre à long terme est de 60°C (Thomas, 1977). L'augmentation de la température de 2°C (de 18°C à 20°C) a quadruple la croissance de la biomasse (Elektorowicz, 1987).

LE pH

La distribution des ions H^+ dans le sol est très hétérogène contrairement à ce qui se passe dans les milieux de culture habituels. Un sol, dont le pH est déterminé par les techniques classiques comme celui de 6,0, peut renfermer des microsites où le pH est localement plus élevé (par exemple 10,0) ou plus bas (par exemple 2,0).

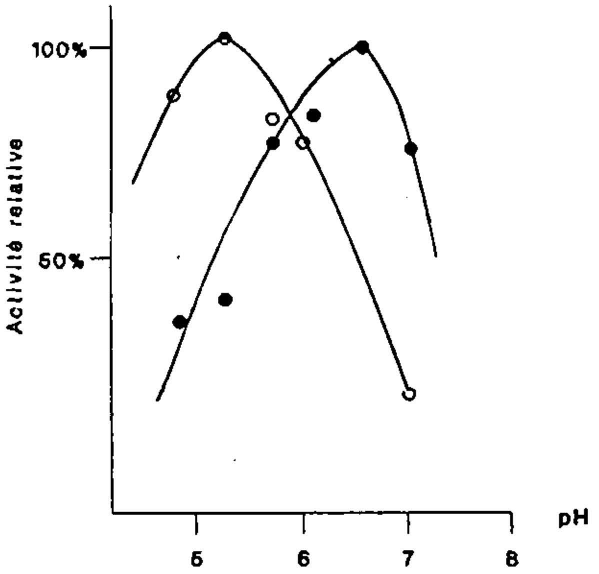


Fig.2 Décalage du pH optimum moyen d'activité de cellules microbiennes adsorbées (.) par rapport à des cellules non adsorbées (o) sur une surface électronégative.

(Selon R. Hattori et T. Hattori, 1963)

Selon les études de Hattori (1963), l'optimum moyen d'activité des cellules microbiennes absorbées sur les surfaces électronégatives (particules argileuses) est observé quand le pH atteint 7,9. Par contre, cet optimum, pour les cellules microbiennes libres, non adsorbées est observé pour le pH égal à 5,9 (fig.2). Si, à certaine étape du processus, il y a possibilité de variation du pH du milieu au cours de différents processus interactifs durant la biodégradation. La variation extrême du pH peut diminuer l'activité des espèces bactériennes capables de dégrader des hydrocarbures. La croissance du pH, par exemple, peut augmenter l'activité des champignons non-actifs dans la dégradation des hydrocarbures. Dans ce cas le compétition des microorganismes est toujours actuelle.

HUMIDITÉ

L'humidité moyennes où la tension interstitielle comprise entre 0,01 et 4 bars (pF entre 1,0 et 3,6) caractérise la plupart des sols. Ces conditions sont favorables à l'activité des microorganismes aérobies ou microaérophiles.

L'humidité faible se manifeste quand la tension est comprise entre 4 et 400 bars (pF entre 3,6 et 5,6). Au cours du dessèchement du sol quand la tension atteint le seuil de 15 bars (pF=4,2), les microorganismes telluriques présentent encore une activité non négligeable. Pourtant, l'accroissement de la tension de l'eau au-delà de 15 bars se traduit par un développement préférentiel des actinomycètes et des champignons par rapport aux bactéries. Par conséquent, il y a le développement de microorganismes qui ne sont pas actifs dans le milieu des hydrocarbures. La limite de l'activité microbienne est de 400 bars (pF = 5,6).

Les études effectuées sur les combustibles démontrent que le bactérie *Pseudomonas sp.* ne peut survivre que quelques heures dans un milieu d'hydrocarbures en absence d'eau (Hill et al., 1967).

Selon plusieurs sources la valeur de la tension de 0.3 est la plus appliquée. D'autres considèrent le taux d'humidité de 20% comme valeur optimale. L'expertise personnelle des auteurs démontre que l'activité est aussi élevée dans l'espace de 20% à 50% de taux d'humidité.

La tension diminue avec la saturation du sol. Le sol saturé acquiert des caractères hydromorphes. L'activité microbienne influe sur les propriétés physiques et chimiques du sol et en particulier sur la teneur en oxygène, et en gaz carbonique, le Eh, le pH, et la teneur en ions Fe^{++}, Mn^{++}, S^{-}. La saturation du sol n'induit pas obligatoirement au sein du sol le développement exclusif de processus anaérobies. En fait, dans les sol submergés, tous les types de métabolisme microbien existent depuis le métabolisme aérobie typique jusqu'au métabolisme anaérobie strict. Les trois orientations (aérobie, anaérobie modérée et anaérobie stricte) qui correspondent à des potentiels d'oxydoréduction du sol de plus en plus bas peuvent d'ailleurs se manifester simultanément ou successivement aux différents horizons d'un même sol.

Une pression des hydrocarbures liquides s'élevant jusqu'à 14×10^6 Nm^{-2} (2000 psi) n'influence pas la croissance des microorganismes (Hill, 1968).

SOUS-PRODUITS

Du métabolisme des organismes oxygénés des hydrocarbures, peuvent résulter des sous-produits comme alcools, acides gras, esters, acides nucléiques, protéines, pigments et vitamines. Certains d'entre eux sont utilisés par d'autres microorganismes du même milieu. La composition des sous-produits influence la croissance des microorganismes biodégradables, surtout ceux qui sont inoculés au milieu contaminé.

La situation se complique dans le cas des processus biochimiques des additifs. Les produits des réactions peuvent gravement influencer l'activité des microorganismes dégradant les hydrocarbures.

SORPTION

Le transport des contaminants dans le sol est dirigé principalement par les processus physico-chimiques: l'advection, la diffusion et la sorption. A la lumière des expériences effectuées, la sorption des substances organiques, tant dans la phase liquide que gazeuse à la surface des particules de sol, peut jouer un rôle important dans l'activité des microorganismes. Ce rôle n'est pas bien reconnu, bien que l'observation de la biodégradation de TCE confirme ce raisonnement. Les coefficients de partitition semblent être les premiers paramètres à vérifier avant l'application de la méthode. Cet aspect de la biodégradation exige encore des études approfondies.

MUTAGENESE

La mutagénèse semble être un des plus importants processus biochimiques ayant lieu au cours de la biodégradation. L'importance du phénomène est remarquée principalement dans le cas de l'inoculation des microorganismes ainsi que dans le processus de biodégradation à long terme. Ces approches ont été réalisées en laboratoire, et jusqu'à présent, aucune étude dans cette direction n'a été effectuée in-situ.

PRÉTRAITEMENT ET ADDITIFS

Très souvent, au cours du prétraitement on-site, les mottes compactes de sols argileux, excavés antérieurement, sont broyées en voletés d'un diamètre de moins de 2 cm. Afin d'assurer la pénétration facile des substances injectées, il est nécessaire de changer la densité de la masse traitée et sa transmissibilité. Diverses substances additives sont donc ajoutées dans des proportions différentes afin d'assurer la transmissibilité requise.

Le sable est une des principales substances additives. Mélangé à l'argile, il augmente la transmissibilité de la masse, cependant le changement de la densité spécifique n'est pas suffisant et limite la hauteur des andains sur le site. D'autre part, l'usage du sable peut être aussi limité à cause de sa qualité; présentement, même le sable fluvial peut contenir certains contaminants supplémentaires tant organiques qu'inorganiques. La toxicité des microorganismes et le traitement supplémentaire peuvent être nécessaires dans ces cas.

L'impact des additifs sur le processus de biodégradation des sols peut être présenté en utilisant comme l'exemple, l'application de la sciure comme additif. La sciure ou les copeaux de bois peuvent assurer la densité basse et la transmissibilité élevée de la masse traitée. Ce additif est un résidu abondant là où l'industrie des pâtes et papiers est développée. La composition chimique de la sciure varie d'une variété de bois à l'autre, en faisant une distinction spécifique entre le bois des conifères et celui des feuillus. Cette diversité de composition peut influencer le processus de biodégradation; l'origine et la qualité de la sciure utilisée doivent donc être bien reconnues.

La matière du bois est hétérogène, pourtant, on distingue trois composantes majeurs; cellulose, hemicellulose et lignine. Elles forment les structures cellulaires de chaînes polymérisés complexes. A part ces éléments principaux, le bois possède une certaine quantité infime d'éléments inorganiques ainsi qu'une grande variété de composantes organiques extractibles. Parmi les composantes extractibles, on peut citer presque toutes les séries de composantes organiques: des hydrocarbures, des alcools, des phénols, des éthers, des aldéhydes, des cétanes , des acides, des esters et des lactones. La quantité d'éléments extractibles peut varier de 1% à 50% selon le type de bois. Dans le cas où la sciure est ajoutée à 10% de la masse totale du sol contaminé, les composantes susmentionnées peuvent changer les processus interactifs dans le sol, donc, la biodégradation.

Le bois est très facilement soumis à la dégradation provoquée par deux sortes des moisissures nommées pourriture brune ("brown rots") et pourriture blanche ("white rots"). Le premier groupe procède par le système enzymatique hydrolysant la cellulose, en laissant la lignine intacte. Les organismes qui peuvent libérer des lignines de manière enzymatique sont avant tout *les Letinus lepidus, les Poria vaillanties et les Lenzites separia.* Le résidu change alors de couleur et devient brun. La pourriture blanche décompose tous les éléments du bois incluant la lignine, et on observe la couleur blanche du résidu. La plupart des microorganismes dégradant le bois appartiennent aux *Basidiomycètes.* Certaines moisissures sont aussi classées comme *Acomycètes.* Les microorganismes isolés dans le sol, capables de dégrader les bois sont: *le Falvobacterium, le P. versicolore et le F. formentarius.*

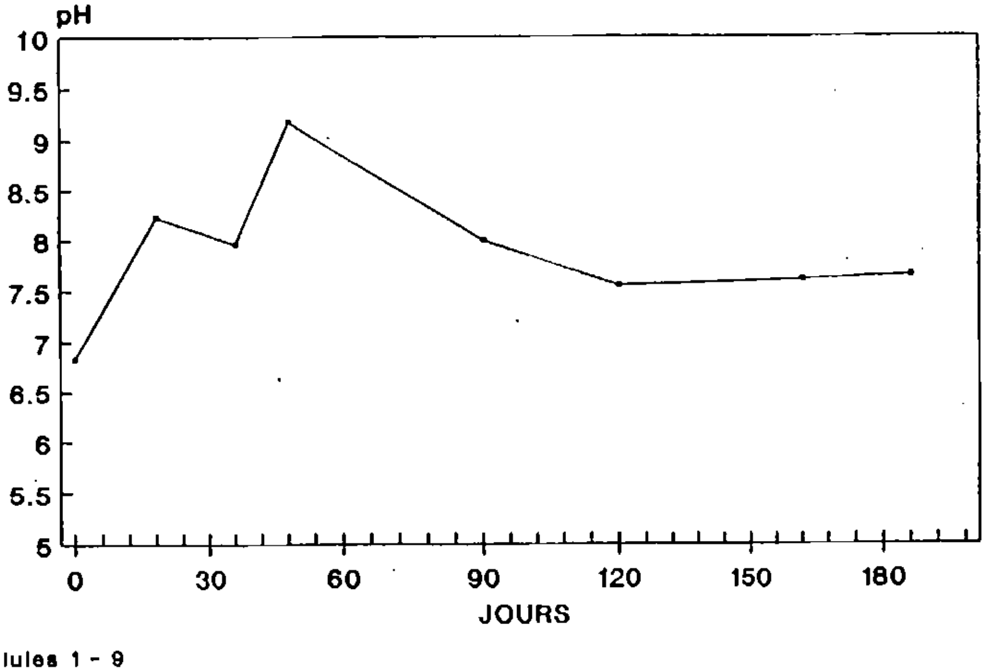
La composition de la lignine varie selon le bois, cependant, les valeurs moyennes des composantes peuvent être estimées comme suit: 60% de carbone, 5% d'hydrogène, 15% de OCH_3 (de différente origine), 20% de vanilline, les valeurs mineurs de certaines autres composantes surtout les produits d'oxydation (siringaldéhyde, p-hydroxybenzaldéhyde, etc).

Le taux élevé de carbone dans la sciure change la proportion entre le carbone et les substances nutritives. Par conséquent, l'évaluation des paramètres technologiques du procédé on-site doit prendre en considération la croissance du carbone afin d'éliminer son influence négative sur l'efficacité de la biodégradation d'hydrocarbures.

A certaines étapes de la dégradation, la vanilline est le résultat de l'hydrolyse alcaline de l'acide lignosulfonique (Buckland, 1987), ainsi que (reconnu plus tard par Kratzl and Hofbauer, 1957) le résultat du hydroxydihydroconifèraldéhyde libéré de la structure confièraldéhyde hydrosulfonique. Cette transformation produit la vanilline et l'acetaldéhyde. La biodégradation de la sciure provoque la perte des groupes méthoxyles concomitants avec formation des hydroxyles, phénoliques. En présence de l'air, la quantité d'hydroxyles, de groupes phénoliques, de carboxyles et de carbonyles augmente alors que la quantité de vanilline diminue (Schubert, 1965).

Fig.3 TRAITEMENT DE SOL PAR AERATION

changement du pH



cellules 1 - 9
melange du sol avec sciure

La formation des amines de l'azote ammoniacale ainsi que le fixation de l'azote sont possibles. Ces conditions peuvent influencer la valeur du pH. Au cours des études menées sur le sol mêlé à la sciure, une croissance du pH a été observée dans la période initiale du traitement. La valeur initiale du pH dans le mélange était de 6,8, cependant, après 50 jours de traitement, la valeur du pH a atteint 9,2 (Elektorowicz, 1991). La moyenne du pH dans le sol (séparé du mélange) a varié autour de la valeur 8.1; simultanément, le pH moyen de la sciure séparée était de 10,2 (fig.3).

CONCLUSIONS

Le processus de dégradation des hydrocarbures dans le sol offre un grand potentiel dans le domaine de la restauration des sites contaminés. Le succès de cette technique dépend de la connaissance des plusieurs processus physiques, chimiques et biologiques. Cependant, la connaissance dans ce domaine n'est pas encore suffisante pour estimer à priori le rendement de la technique sur le site. Il est nécessaire dans chaque cas particulier d'effectuer les études de faisabilité à petite échelle ou en laboratoire afin d'éliminer plusieurs interactions négatives du milieu sur le rendement de biodégradation. La température, l'humidité (le pF) et le pH doivent être strictement contrôlés. Chaque innovation dans le traitement et dans l'ajout des additifs doit être étudiée et vérifiée en tenant compte de son impact sur l'activité microbienne. La distribution des nutriments doit être bien pensée pour donner la disponibilité suffisante des nutriment par rapport au carbone.

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L'UTILISATION DU LABORATOIRE POUR L'ÉTUDE, L'ÉVALUATION ET LE DESIGN DE PROJETS DE RÉHABILITATION DES SOLS CONTAMINÉS: LE CAS DU PORT DE TORONTO

USING THE LABORATORY TO STUDY, EVALUATE AND DESIGN SOIL REMEDIATION PROJECTS: THE TORONTO HARBOUR EXPERIENCE

RÉSUMÉ

La restauration environnementale des terres adjacentes aux ports représente un souci majeur pour les autorités administratives qui visent un développement immobilier de ces lieux ayant un grand potentiel commercial. La Commission du Port de Toronto a alloué 5 millions de dollars pour le nettoyage de son territoire hautement contaminé par des hydrocarbures. Une usine des plus moderne a été construite par la compagnie SNC-Lavalin. Trois procédés s'intègrent: lavage de sol (extraction chimique des métaux lourds), pré-conditionnement et biodégradation des contaminants organiques. Le CRG a été mandaté par SNC-Lavalin pour diriger un étude de traitabilité qui comprenait l'évaluation technique des procédés, ainsi que les nouvelles informations qui puissent améliorer ou ajuster le procédé. La méthodologie et les résultats de cet exercice sont présentés dans cette communication.

ABSTRACT

Environmental clean-up of waterfront lands are of critical concern to administrative authorities aiming at a real state development of port areas with great commercial potential. The Toronto Harbour Commisioners committed 5 million dollars in order to decontaminate its territory highly contaminated with hydrocarbons. The clean-up facility was proposed by SNC-Lavalin in here three processes were integrated: soil washing (chemical extraction of heavy metals), pre-conditionning and biodegradation of organic contaminants. The GRC was mandated by SNC-Lavalin to conduct a treatability study which included the technical evaluation of the processes as well and gathering any new information that could adjust or improve the remediation process. The methodology and results of this exercise are presented in this communication.

INTRODUCTION

Les projets de décontamination des terrains contaminés posent des problèmes tant sur le plan technique que financier. Le but final des professionnels impliqués dans ce type de projet est d'en arriver à une stratégie de nettoyage efficace, moins coûteux, qui protège la santé des citoyens et qui minimise les impacts sur l'environnement.

Les études de traitabilité en laboratoire procurent des informations critiques qui améliorent le choix de stratégies sur le plan technique et donnent un indicatif sur les coûts. Plus spécifiquement, ils procurent des informations sur les variables physico-chimiques et biologiques d'une technologie de traitement dans des conditions très différentes et sur des conditions contrôlés simulant le terrain. Il est très important de comprendre que lorsqu'on applique une technologie dans un site particulier il est impossible d'avoir toutes les réponses à partir d'un seul protocole d'essais et que, par contre, plusieurs essais doivent être effectués à partir des objectifs recherchés.

Le procédé de traitement utilisé à Toronto fonctionne à l'aide de réacteurs séquentiels à flux continu de boues avec une capacité totale de 50 tonnes/jour. Le procédé est décrit brièvement comme suit: une usine de lavage qui transforme le sol en boues où les métaux sont extraits par frotation, ce procédé est suivi par l'oxydation chimique des hydrocarbures dans des réacteurs; la contamination organique résiduelle est traitée en bio-réacteurs.

Le premier traitement mécanique de lavage et de séparation enlève la fraction grossière, laquelle est nettoyée facilement. Les écumes sont ramassées et le matériel propre est recyclé. Étant hautement contaminées, les particules fines sont les plus problématiques; cette fraction est dirigée vers les procédés de pré-oxydation et de biodégradation.

L'application d'un procédé mixte de pré-oxydation/biodégradation cherche à purifier un sol avec une granulométrie fine (limons-argile) hautement contaminé par des hydrocarbures lourds (>20% huiles et graisses). Ce projet avait pour but de faire la lumière sur le potentiel d'utilisation de cette technique.

DÉFINITION DU PROBLÈME ET OBJECTIFS

Ce projet de recherche appliqué comprenait la simulation en laboratoire de l'application séquentielle d'un procédé d'oxydation chimique suivi par un procédé de biodégradation dans quatre différentes conditions (4 phases). Les objectifs principaux de chaque phase ont été:

-L'évaluation de la capacité d'oxydation de plusieurs produits chimiques oxydants en application individuelle avec ou sans additifs pour la détermination de leur pouvoir oxidatif de substances récalcitrantes telles que certains composés polycycliques aromatiques (benzo (a) pyrène, benzo (b) fluorenthène, dibenzo (a,h) anthracène, indène et chrysène).

-La détermination des facteurs influençant l'efficacité de l'oxydation chimique: dosage, forme d'injection, degré de mélange et temps de rétention.

-L'évaluation de l'influence du taux huile/sol dans le processus de biodégradation. La faisabilité de biodégradation des substances récalcitrantes fractionnées préalablement dans l'étape de pré-oxydation chimique.

-L'évaluation de la toxicité des produits chimiques utilisés dans la pré-oxydation dans la croissance de la population microbienne pendant la biodégradation. L'évaluation des patrons de biodégradation.

MÉTHODOLOGIE ET MATÉRIELS

Tous les essais ont eu lieu dans des réacteurs batch de 500 mL de volume contenant de la boue huileuse (avec une concentration constante/variable en huiles et graisses). Les réacteurs sont scellés avec deux orifices d'entrée, un pour l'insertion d'un agitateur mécanique et un pour l'insertion d'un tuyau d'alimentation pour l'injection d'air et/ou des nutriments et un orifice de sortie pour la collecte de gaz. L'installation est présentée à la figure 1.

Tel qu'indiqué antérieurement le projet comprenait 4 phases, lesquelles sont décrites comme suit:

Phase I

Quatre produits oxydants ont été testés: la chaux, le peroxide, le permanganate de potassium et l'aération; le peroxide a été essayé en plusieurs concentrations avec l'ajout du réactif Fenton. L'efficacité d'oxydation a été mesurée à partir des variations des paramètres de COD, Huiles et graisses totales, et la liste de l'EPA des 16 HAP. Des concentrations différentes en teneur en huiles et graisses totales ont été testées.

Phase II

Après une analyse des résultats de la phase I en termes d'efficacité/coûts, deux produits oxydants ont été retenus. En utilisant ces deux produits, une deuxième batterie de tests a été effectuée pour la détermination des conditions optimales d'application. L'influence du dosage, la forme d'application du réactif, le degré de mélange optimal et le temps de rétention ont été étudiés dans cette phase.

Phase III

La biodégradation a été testée dans des conditions différentes de concentration de solides en ayant une quantité constante d'huiles et graisses. Dix différentes concentrations ont été essayées. La biodégradation a été démarré par l'inoculation des réacteurs avec des bactéries indigènes. La biodégradation a été suivi selon les paramètres de nombre total d'organismes, temps de croissance, HAP individuellement et totaux et la concentration totale des huiles et graisses.

Phase IV

Les conditions de pré-conditionnement entre l'étape de pré-oxydation et l'étape de biodégradation ont été testés pendant la phase IV. Le protocole d'essai a été élaboré sur le bases des résultats trouvés à la fin des phases II et III. Les manoeuvres pour l'ajustement de la température, le pH et le potentiel redox de telle manière à démarrer la biodégradation furent évalués a long de cet essais.

RÉSULTATS ET DISCUSSION

Les résumés des résultats sont présentés dans les figures 2-7.

Les dosages en chaque réactif requis pour l'oxydation d'un gramme de COD initiale fut calculé, ces mêmes dosages ont été exprimés en termes de leur coûts. Le meilleur oxydant a montré un coût 25 fois plus cher que l'oxydant le moins cher. Trois oxydants ont montré une efficacité semblable avec des coûts très variables et plus élevés. L'oxydant avec une efficacité moyenne et un coût bas fut choisi.

Il a été démontré que l'efficacité d'oxydation augmente quand le temps de rétention augmente, à cause de l'agrandissement du contact entre les hydrocarbures et le réactif, de la même façon le rendement est haut quand le réactif est appliqué en forme liquide.

Le pouvoir oxydative du réactif pour chaque HAP fut mesuré. Les patrons d'oxydation pour chaque HAP indiquent que les HAP légères sont facilement oxydables et dans le mêmes proportions, le patron de dégradation des HAP avec un demi-vie plus longue (>420 jours) est plus variable.

Quand à la biodégradation, on a pu observer qu'il existe un temps initial de accoutumance où la population microbienne tombe en dessous de la valeur d'inoculation pour ensuite remonter avec le temps. Même s'il s'agissait du même sol, et les bactéries inoculées sont indigènes au site, il est évident que les produits de pré-oxydation montrent une certain toxicité sur la population microbienne.

Les résultats montrent que la capacité de traitement est optimale pour des sols fines contenant 30 - 40% de huile et graisse. Les microbes montrent une préférence pour les boues de consistance plus épaisse (> 20% solides), des matrices trop liquides semblent avoir une effet négative dans la reproduction de la population des microorganismes, probablement cet effet est causé par la manque des sites de attachement ou les colonies se développent.

De trois paramètres de contrôle le COD et le PAH furent les plus descriptives, COD et HAP totaux se relient directement, étant COD le moins coûteux. le test de huiles et grasisses par extraction soxhlet montre beaucoup des interférences (i.e. la biomasse).

CONCLUSION

L'application des procédés mixtes (physico-chimique-biologique) dans le nettoyage des sols est très récent mais prometteur. Les problèmes rencontrés sont au niveau de la conjoncture des procédés: l'efficacité de la biodégradation est menacée lorsque le traitement chimique appliqué préalablement pose des problèmes de toxicité aux bactéries dégradatrices de contaminants. Par contre, avec un contrôle et la connaissance des facteurs influençant le processus, l'efficacité de dégradation peut être augmentée et/ou manipulée. La grande nouveauté des techniques combinées fait que plusieurs problèmes scientifiques et techniques ne soient pas encore résolus. Les premièrs essais montrent qu'il s'agit d'un une technique très prometteuse surtout du point de vue de l'application à des matrices hautement contaminées par une contamination mixte.

REMERCIEMENTS

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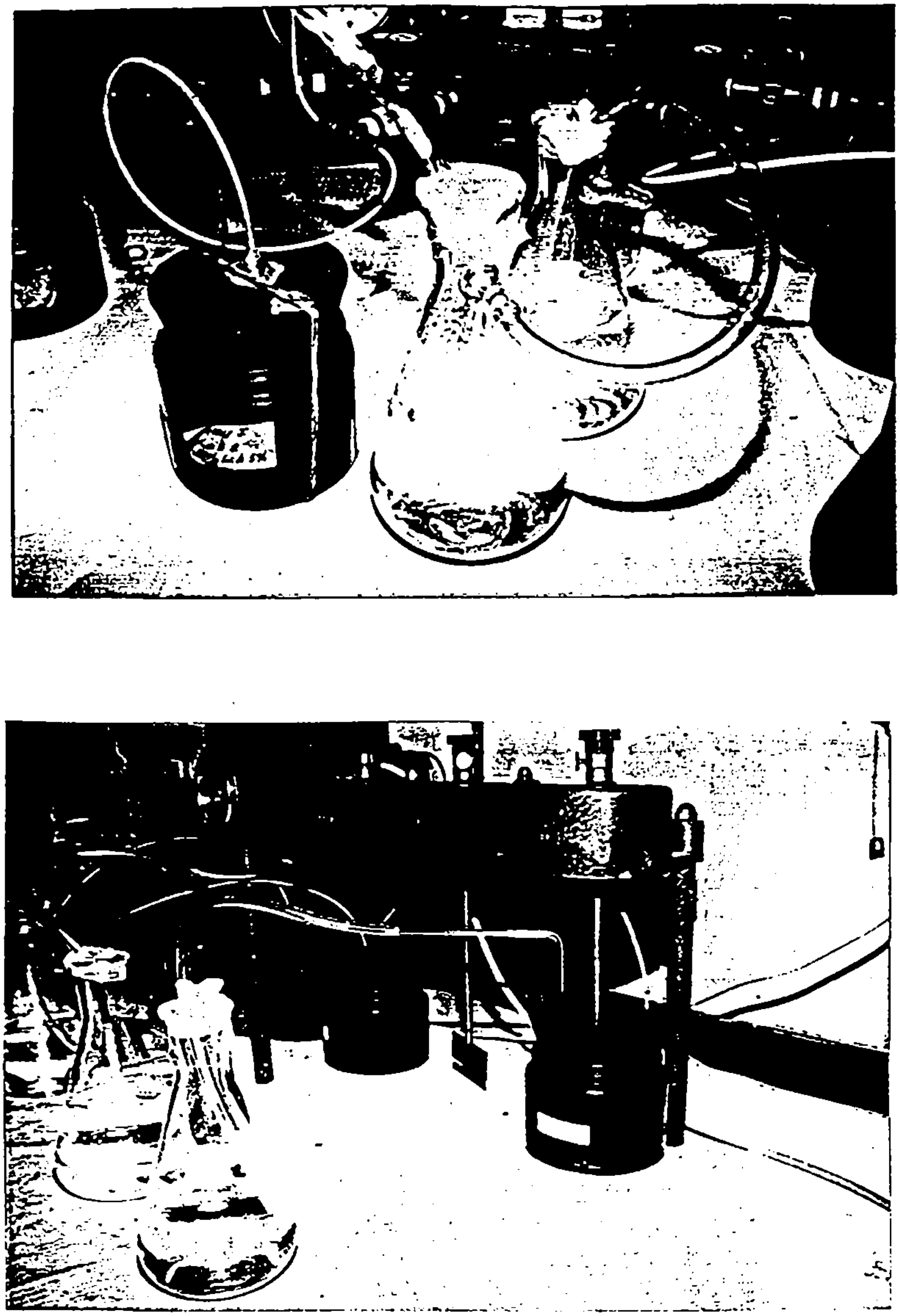
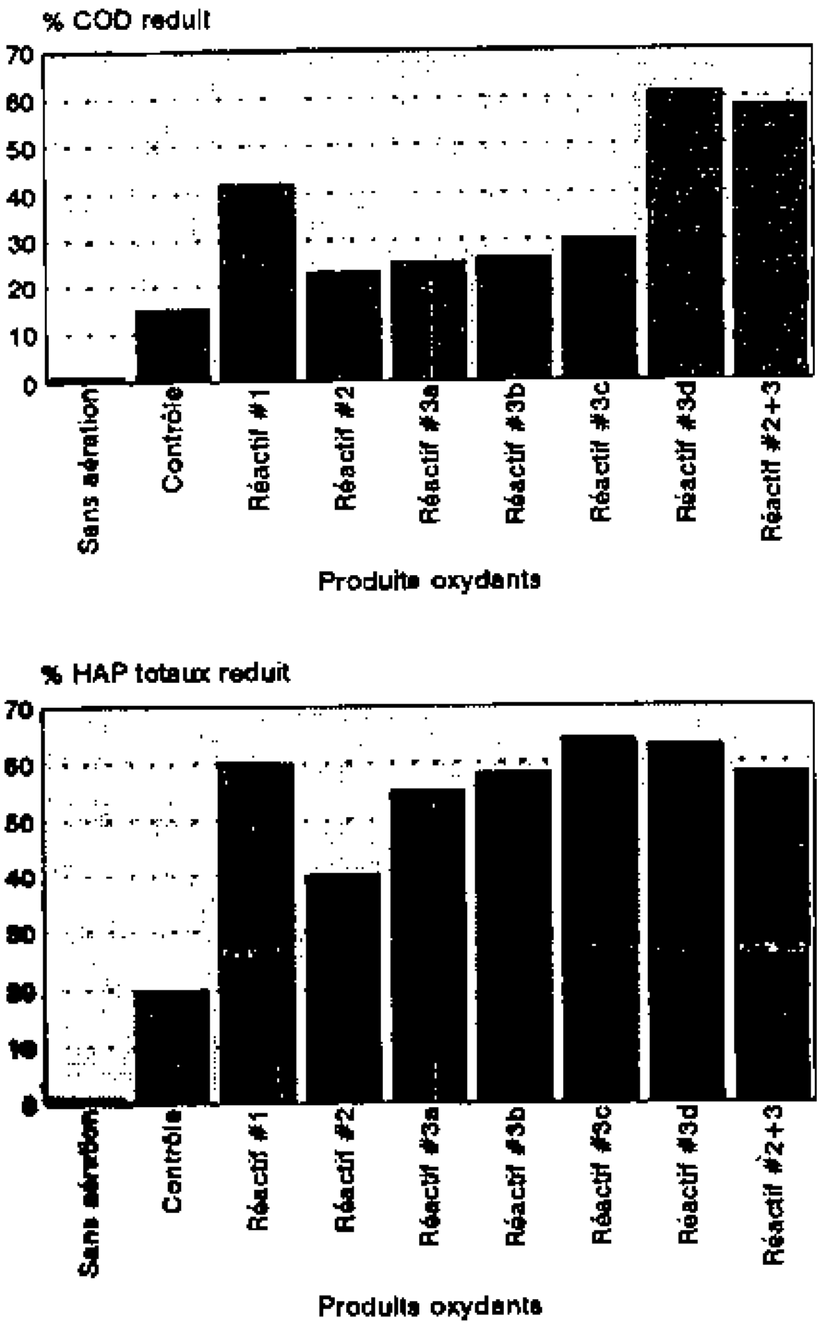
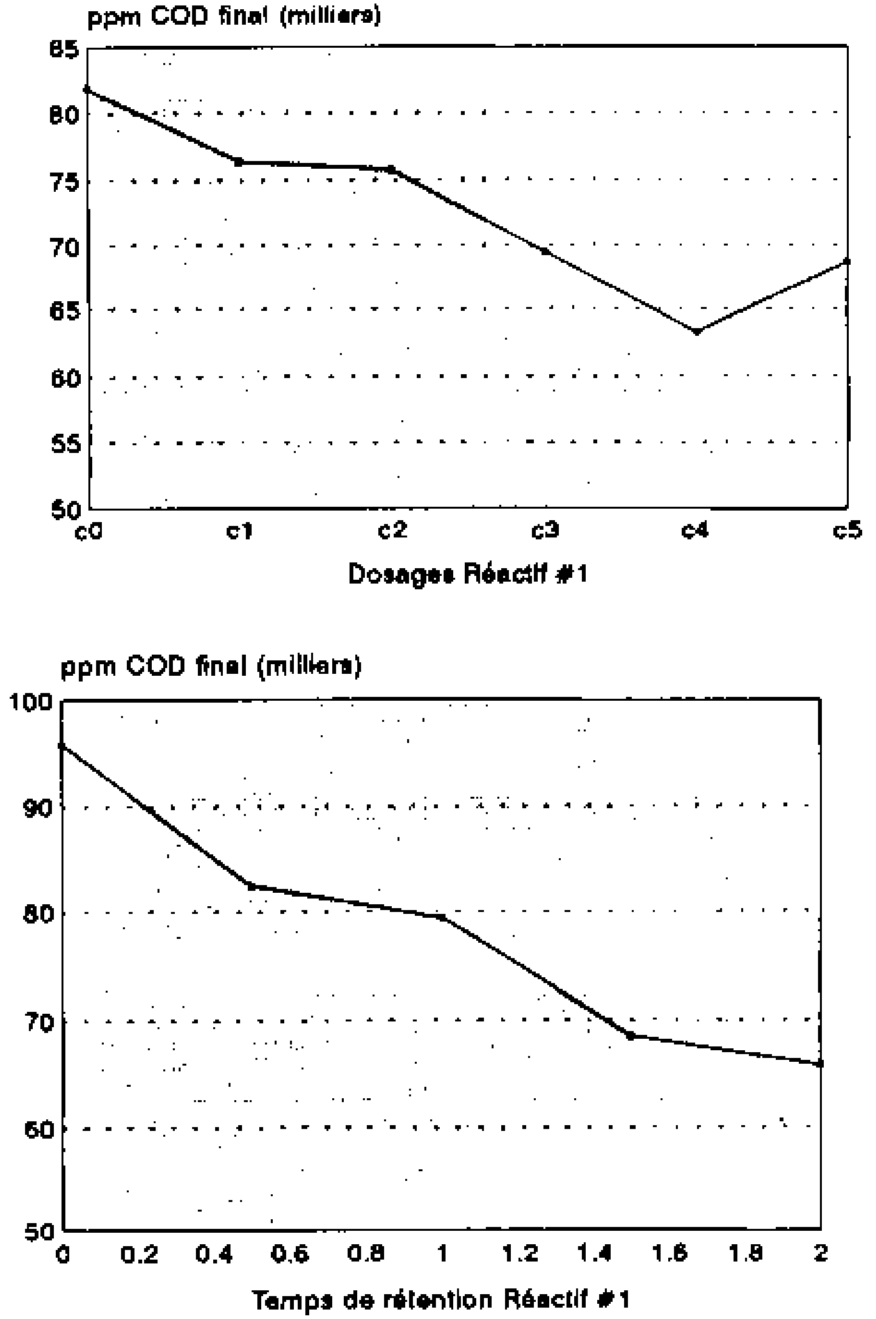


Figure No 1

Effic .tés d'oxydation des produits chimiques

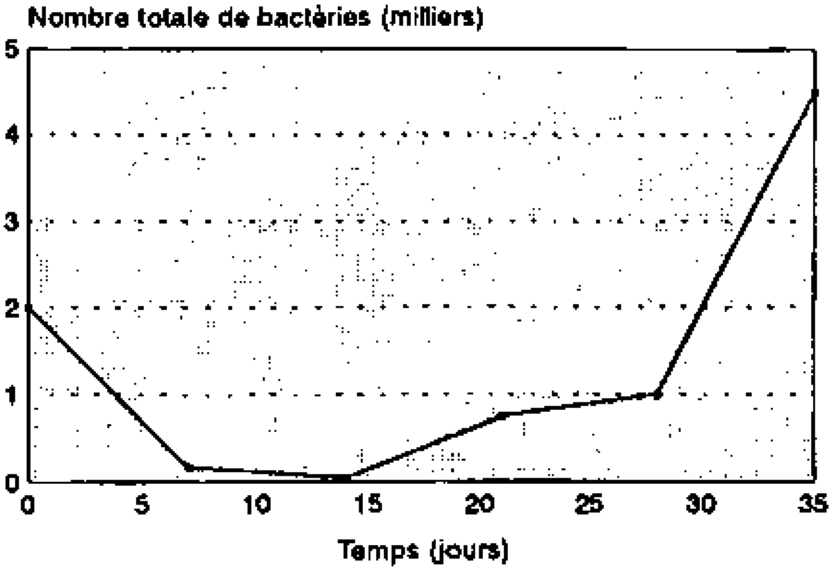


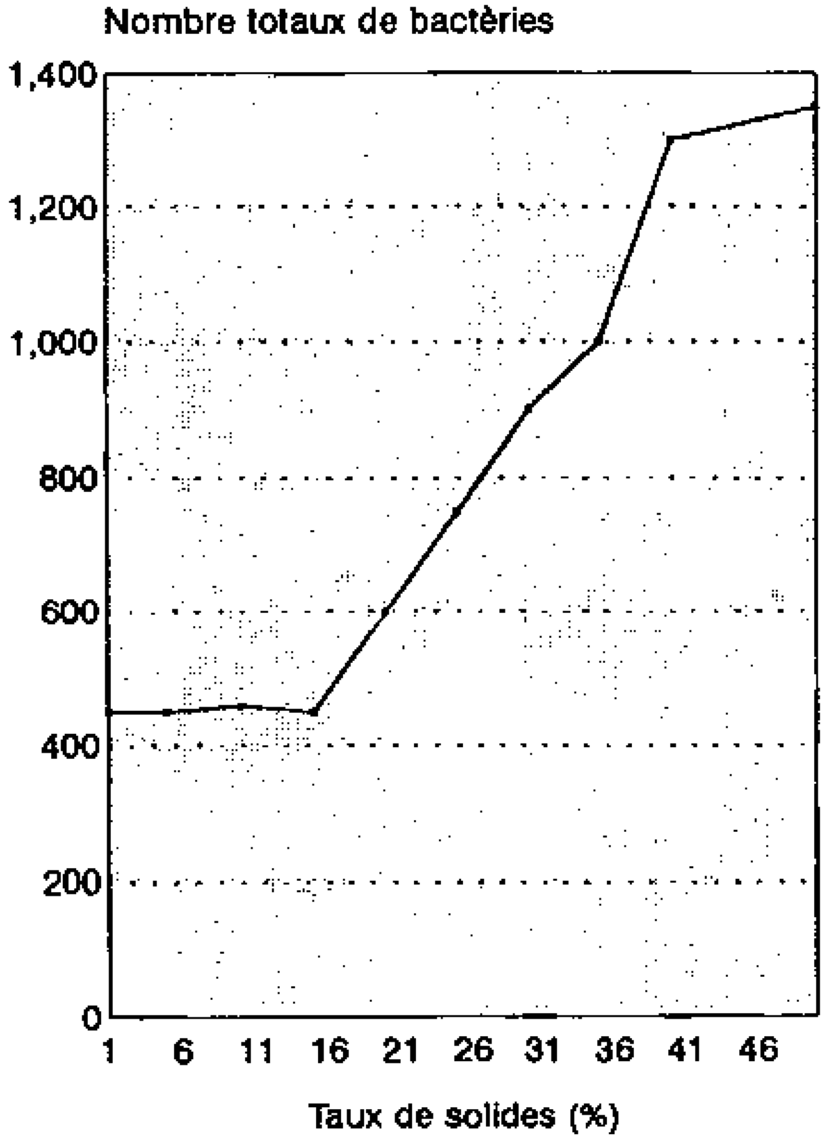
Dosage et temps de rétention optimal Reacti



Figures 2,3,4,5

Effets d'accoutumance et taux de solides dans la croissance de la population microbiènne





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ÉVALUATION DU COMPORTEMENT DE LA COUVERTURE ARGILEUSE SOUMISE AUX DIFFÉRENTES CONDITIONS ENVIRONNEMENTALES

PERFORMANCE EVALUATION OF ENGINEERED CLAY COVER SUBJECTED TO DIFFERENT ENVIRONMENTAL CONDITIONS

RÉSUMÉ

Cette étude est désignée pour étudier expérimentalement l'effet de la distribution de température sur la migration des contaminants dans une couverture argileuse gelée. Le sol argileux a été soumis à différents cycles de gel/dégel. L'eau distillée (pH 5.8) a été la source de liquide capté durant le gel. Après chaque cycle de gel, le contenu de l'eau non gelée et la concentration des différents ions des métaux ont été déterminé expérimentalement en fonction de la distance. La conductivité hydraulique a été calculée après le gel/dégel cyclique.

Les résultats ont démontré que durant le gel, la redistribution de l'humidité est contrôlée par le gradient de température, et la durée de l'essai. La redistribution des cations en fonction de la distance de la source des liquides et des cycles de gel/dégel, est contrôlée par le contenu de l'eau non gelée, et la capacité d'échange cationique. La conductivité hydraulique a augmenté presque 1.5 fois de sa valeur initiale à cause de l'effet de gel et dégel, de la redistribution de l'humidité et l'effet électro-osmotique.

ABSTRACT

This study was designed to experimentally investigate the effect of temperature distribution on contaminant migration in frozen clay cover. Soil specimens were subjected to various freeze/thaw cycles. The fluid intake during freezing was distilled water (pH = 5.8). After each freezing cycle, unfrozen water content, and concentration of various metal ions were experimentally determined as a function of distance. Hydraulic conductivity was calculated after cyclic freeze/thaw.

The experimental results have shown that during freezing, moisture redistribution is controlled by temperature gradient, and test durations. Cation redistributions as a function of distance from the fluid intake and cyclic freeze/thaw are controlled by unfrozen water content and cation exchange capacity. The hydraulic conductivity increased by about 1.5 times form its initial value due to the effect of cyclic freeze/thaw, redistribution of moisture, and electro-osmotic effects.

INTRODUCTION

In recent years, the proper treatment and disposal of hazardous waste became the very important issue. Inappropriate design of waste disposal sites can cause severe degradation of water quality in both subsurface and surface systems and have harmful impact on humans, animals and plants. For correctly operated landfill, the side clay barriers and the clay cover system have to be designed to account for: (1) the effect of freezing and thawing; (2) the effect of ion migration from the waste piles during freezing period, and (3) the effect of chemical interactions on the integrity of the clay barrier system and the resultant effect on changes in clay permeability.

In a partially saturated soil such as that represented by the cover, temperature gradient induced by freeze and thaw results in the development of coupled heat and water flow. Water movement in unsaturated soil takes place in both, the liquid and vapour phases. In the vapour phase water molecules diffuse in direction of decreasing temperature. Apart of the vapour diffusion process, water translocation under thermal gradient is associated with the movement in the moisture films surrounding the soil particles and through the soil pores when the water content is high enough.

The migration of various kinds of solutes through unfrozen clay barriers has been extensively investigated (Yong, Mohamed and Warkentin, 1992). However, little is known about the solute migrations in freezing and frozen clay barriers. In the case of water transport, ion movements can take place by: (1) diffusion when the moisture content is low enough to allow transport by vapour convection actions; (2) movement through the unfrozen water films around the particles in frozen soil, and (3) mass transport in freezing and thawing clay barriers. The magnitude and direction of ion migration will depend upon rate of freezing, initial water content, phase boundary transport process and type of ions in soil solution (Mohamed et al. 1993). In a highly complicated soil system, where input of chemicals causes exchangeable ions, it is difficult to predict the direction and rate of ion movements. Furthermore, under subfreezing temperatures water in the soil pores freezes and ions excluded from ice crystals concentrate in the remaining soil solution either in pocket or in the thin liquid films around the particles. The temperature and concentration of this solution could affect chemical reactions.

Repeated freeze/thaw cycles are known as a factor which changes the physical properties of soil (Yong et al. 1985; Yong and Mohamed, 1992). They may affect soil aggregation, soil structure and hence soil permeability. The effect of freeze/thaw cycles on soil aggregates depends not only on the conditions of freezing and thawing, but also on initial conditions such as water content.

All these interactive processes produce multi-relationships which control the distribution of heat, moisture and solution concentration so, they must be taken into considerations for a proper clay cover design. This study was designed to investigate the effect of temperature distribution on the water content and ion concentration distributions in a soil column test subjected to cyclic freeze/thaw. Fluid intake during freezing was distilled water (pH = 5.8).

Table 1 Selected Properties and Compositions of Illitic Soil

Geotechnical Properties		Chemical Properties	
Consistency Limit		Soil pH	
• Liquid Limit %	33.5	(1:10 soil:water)	8.4
• Plastic Limit %	20.8		
• Plasticity Index %	12.5	C.E.C.	
		(cmol (+) kg^{-1})	40
Compaction properties:		(cmol (++) kg^{-1})	20
• Maximum dry density Mg/m^3	1.84		
• Optimum moisture content %	16.5	surface area ($m^2 Kg^{-1}$ x 10^{-3})	92
Grain Size Analysis		organic content (% w/w)	0.9
D_{50} µm			
	5.0	carbonate content (% w/w)	14.7
D_{10} µm	0.4		
C_u	20.3	amorphous content	
Cc	3.1	S_iO_2	2.1
		Fe_2O_3	3.6
Mineralogical composition (given in a decreasing order)		Al_2O_3	1.1
(Illite, chlorite, quartz, feldspar, calcite)		Total	6.8

MATERIALS AND METHODS

A single type of soil - silty clay called Domtar Sealbond was used throughout this study. This soil, which obtained from the pulverized Canadian old marine shale, is expected to have mineralogical characteristics similar to natural clay (Quigley, 1983). It is commercially available in a form of powder, so it is easy to obtain and can be well prepared for laboratory tests.

Before freezing, soil was subjected to many physical and chemical tests such as consistency limits, grain size analysis, cation exchange capacity, surface area measurement, pH measurement and initial cation concentrations in soil solution. The obtained results are listed in Table 1. During freezing tests, specimens were allowed to uptake distilled water (pH = 5.8).

Test Apparatus

The soil samples were subjected to freeze/thaw cycles in four plexiglass cylinders. Each cylinder, measuring 50 mm in diameter and 200 mm in height, was connected by a plastic tubing to a burette filled with distilled water. To control the temperature gradients along the soil column during freezing, three thermocouples were installed which are located at 5 mm from the source of water intake, the middle, and 5 mm below the cooling cap which is located at the top of the soil column. Schematic diagram of the test apparatus is shown in Fig. 1.

Test procedure

The illitic soil was mixed with distilled water to its approximate optimum water content and then allowed to equilibrate in a humid room for at least 24 hours. The prepared soil was compacted in plexiglass cells to its maximum dry density and optimum moisture content. Next, the themocouples were inserted. The cylinders were wrapped with plastic seal and insulated by two layers of fibreglass. Cooling caps were placed on the top of the soil sample in each cylinder. They were connected to a cold bath, which temperature was kept between -14 and -18 °C. Cold room temperature, where specimens were freezed, varied from 3 to 5.5 ° C. When specimens were frozen, the cells together with their connected burettes were removed from the cold room. The insulation was then taken off and the soil specimen were let to thaw during overnight at about 22°C. Before next freezing, liquid from each burette was taken for chemical tests. Once again, soil columns were placed in the cold room and freezing starts. After each cycle, one soil specimen was removed and cut into 11 sections for fluid content determination and chemical analysis. It should be mentioned that each time soil was removed in its frozen state, e.g., after first freezing, freeze/thaw cycle + freezing, second freeze/thaw cycle + freezing, etc.

Identical prepared specimens were used for permeability tests. After a respective cycle, one cell was disconnected and permeability test was performed by falling head method. Permeability of illitic soil was checked after 1, 2, and 4 freeze/thaw cycles.

Methods of chemical analysis

After fluid content measurements were conducted, dry soils were ground and subjected to chemical examination. The powered soils were mixed with distilled water in a ratio of 1:10 then, shaken in a mechanical shaker for a period of 18 hours. Soil solutions were centrifuged and the supernatant was checked for pH value, and metal ion concentrations.

Unfrozen fluid content measurement

The differential scanning calorimetry technique (DSC), describeα by Mohamed et al. (1993), was used to calculate the unfrozen fluid content and to estimate the associated energies of the specimens tested. The measured ion concentrations were then expressed in terms of the unfrozen fluid content as a function of distance along the soil column.

RESULTS AND DISCUSSIONS

Temperature Distribution:

As shown in Table 2, a number of tests were conducted. The initial and boundary conditions of each test are shown in Table 2. Temperature distributions at steady state conditions are shown in Fig. 2. It can be seen that the temperature distributions are different from a specific freeze/thaw cycle to another. This is attributed to the difficulties in controlling the exact boundary temperature during cyclic freeze/thaw. However, the temperature gradients across the frozen soil column were more or less within the same range as shown in Table 2.

Moisture Redistribution:

The relative changes in fluid content, which represent the ratio of fluid content in the freezing state after each specific cycle over the initial fluid content after specimens preparations, are shown in Fig. 3. The fluid content at each position along the soil column increases as function of cyclic freeze/thaw. The increase in fluid content for a specific freeze/thaw cycle is greater than the initial fluid content for all sampling positions except at 5 mm location which could be attributed to: (1) upward movement due to temperature gradient, and (2) downward movement due osmotic flow between soil water in this section and pure distilled water in the burette. As the concentration of cations in the water increases, the chemical potential between soil solution and water decreases; hence, forces caused water movement in the upward direction are predominant. Furthermore, the marked increase in the fluid content at both 85 and 105 mm distances from the source of fluid intake could be attributed to: (1) fluid movement from higher to lower temperature zones; (2) ice nucleation in lower temperature zones, and (3) creation of high osmotic potential caused by high concentration of cations in the lower temperature zones (Mohamed et al. 1993).

Table 2 Initial and Boundary Conditons for Various Tests Conducted in this Study

Freeze/thaw cylces	Test #	Cell #	Average w.c. [%]	Average temp. of cold bath [°C]	Water intake [ml]	Time of freezing [h]	Temp. gradient	
							During freezing	Frozen soil
0	I	4(a)	17.3	-13.6	3.8	13.5	1.10	0.65
		3(b)	17.3		4.0	19.0	1.01	0.59
		2(c)	17.3		4.6	18.5	1.04	0.60
		1(d)	17.3		3.8	14.5	1.17	0.75
1	Ia	4(a)	18.7	-14.5	3.3	12.0	1.16	0.57
		3(b)			3.8	11.5	1.13	0.54
		2(c)			4.0	13.0	1.00	0.62
		1(d)			3.0	11.0	1.14	0.64
2	Ib	3(b)	20.0	-14.0	3.2	12.0	1.31	0.57
		2(c)			3.4	15.0	1.12	0.57
		1(d)			2.8	12.5	1.20	0.67
3	Ic	2(c)	20.1	-17.8	2.4	10.5	1.44	0.65
		1(d)			1.2	8.5	1.45	0.73
4	Id	1(d)	21.2	-18.1	0.6	8.0	1.27	0.72

Generally, it is known that due to cyclic freeze/thaw, soils form aggregates (Yong et al. 1985), hence liquid limit, specific surface area and soil water potential decreased (Yong and Mohamed, 1992). Accordingly, in a no volume change set of experiments, pore sizes within the soil column increased. During subsequent freezing condition, larger ice crystals could be formed within the larger pores, hence higher fluid content is obtained, as shown in Fig. 3, with the increase in freeze/thaw cycles.

Cation Redistribution:

As previously mentioned, concentration of cations was determined relative to the unfrozen fluid content, which calculated by using the differential scanning calorimetry technique. The following relationship (Mohamed et al. 1993) is used to calculate the amount of unfrozen fluid content as a function of temperature.

$$W_{uf} = a + b \ \exp\left[-0.5\left(\frac{T-C}{d}\right)^2\right] \qquad (1)$$

where W_{uf} is the unfrozen water content (%); T, temperature in deg. C, and a, b, and c are material parameters which determined by fitting the experimental data obtained from the differential scanning calorimetry technique.

The relative change in concentrations, which represents the ratio between the concentration as a function of distance and time relative to the initial concentration before freezing, is shown in Figs. 4a to 4d. Each figure depicts the relationship between the relative change in concentration of a specific cation versus the number of freeze/thaw cycles at different positions along the frozen soil column. The concentration of cations increases at lower temperature zones after each cyclic freeze/thaw due to: (1) decrease in the amount of unfrozen fluid content, and (2) increase in the mobility of cations due to electro-osmotic effect. The sodium concentration at 5 mm distance from the source of distilled water intake (Fig. 4a) is close to or slightly lower than initial fore fluid concentration, which is attributed to electro-osmotic effect between the soil pore fluid and the distilled water in the burette. With increasing number of freeze/thaw cycles, the concentration of cations in the burette increased, which remained below the initial concentration of soil pore fluid. This indicates that the downward movements of cation may not influence the overall cation redistribution along the frozen soil column.

Both divalent cations (Figs. 4c and 4d), calcium and magnesium, showed similar behaviour during freeze/thaw conditions. As it was in the case of monovalent cations, the divalent cation redistributions were highly dependent on fluid content distribution. However, the decrease in concentrations, close to fluid source, is most likely a result of not only water migration but also cation exchange which is attributed to the reduction in concentration of calcium and magnesium in solution. Cation replaceability may also explain the low concentrations after first freezing cycle.

Hydraulic conductivity.

Previous studies (Chambelain and Gow 1979, and Yong et al. 1985, Yong and Mohamed, 1992) on the effect of cyclic freeze/thaw on the physical and mechanical properties of clay soils showed significant changes in original soil structure and its properties. The increase in hydraulic conductivity was found to be higher for soils with large plasticity index and high moisture content which is attributed to the formation of vertical cracks during freezing as well as rearrangement and aggregation of soil particles. The changes in hydraulic conductivity as a function of number of freeze/thaw cycles are shown in Fig. 5. The hydraulic conductivity increased by about 1.5 times from its initial value before freezing. No distinct vertical cracks or ice lenses were found in the frozen soil column. Apparently, the grain size (relatively high content of silt-size particles) and low initial fluid content influenced such behaviour. The slight difference might occur as a result of reducing interparticle spaces due to ice pressure and/or migration of adsorbed water (Yong et al. 1985).

CONCLUSION

The experimental results have shown that during freezing moisture redistribution is controlled by: (1) temperature gradient; (2) soil water potential which directly controls the diffuse double layer thickness, and (3) duration of the test. Cation redistributions during freezing are ruled by two basic phenomena: (1) unfrozen water content, and (2) cation exchange. Changes in the hydraulic conductivity could be obtained due to both cyclic freeze/thaw and osmotic flow.

The changes in both physical and chemical characteristics of a specific designed clay cover are of importance in order to control the migration of metal ions from the lower part of the clay cover to the surface and to transport routes, i.e., surface water, atmospheric and biotic. Hence, a designed clay cover should account for the following: (1) the effect of freezing and thawing; (2) the effect of ion migration during freezing period, and (3) the effect of chemical interactions on the integrity of the clay cover and the resultant effect on changes in hydraulic conductivity.

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Fig. 1 Schematic Diagram of Test Apparatus

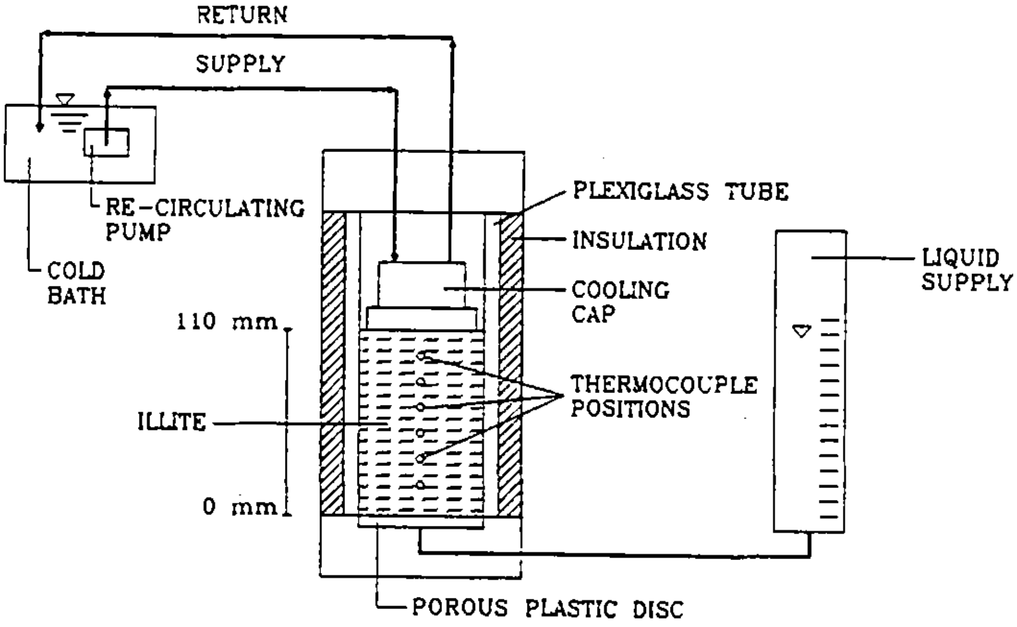
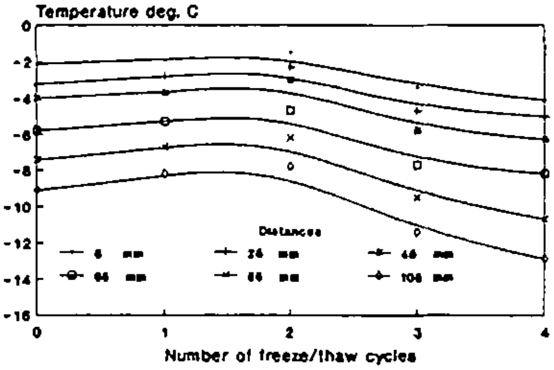
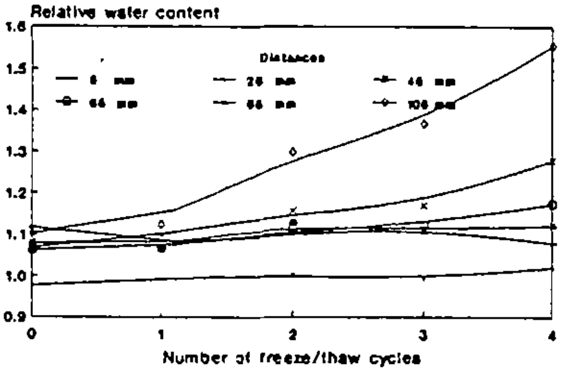


Fig. 2 Steady state temperature distributions; distilled water.



Distances are measured from fluid intake

Fig. 3 Relative change in water content with freeze/thaw cycles; distilled water



Distances are measured from fluid intake

Fig. 4a Relative Change in Concentration with Freeze/ Thaw Cycles for Sodium.

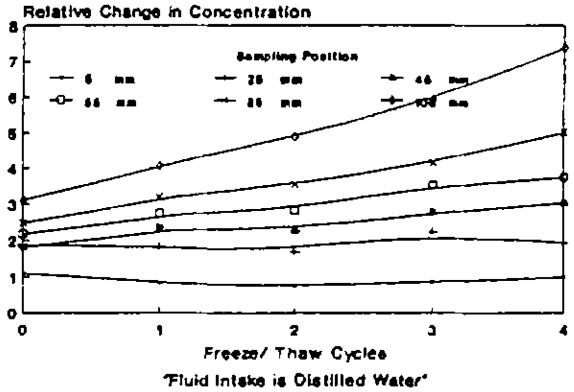


Fig. 4b Relative Change in Concentration with Freeze/ Thaw Cycles for Potassium.

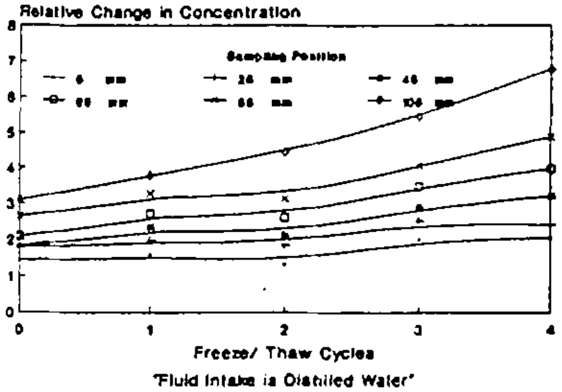


Fig. 4c Relative Change in Concentration with Freeze/ Thaw Cycles for Calcium.

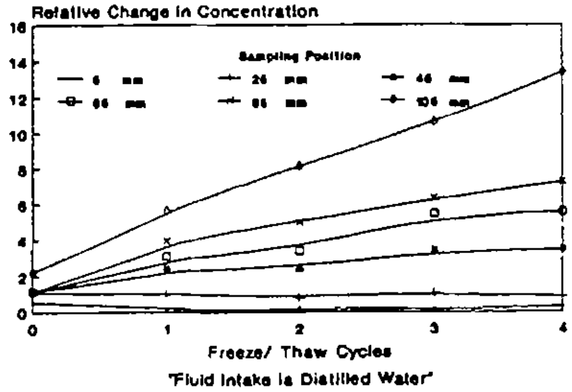


Fig. 4d Relative Change in Concentration with Freeze/ Thaw Cycles for Magnesium.

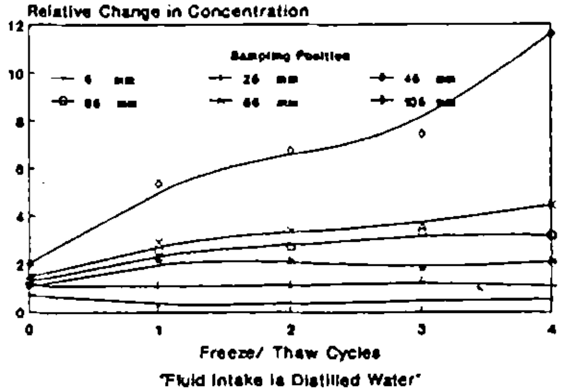


Fig. 5 Hydraulic conductivity variations with freeze/thaw cycles.