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# A study of the retention of heavy metals by amorphous iron-aluminium oxides and kaolinite

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# October 1999

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of Doctor of Philosophy

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## ABSTRACT

Amorphous iron-aluminium oxides are ubiquitous in the environment and control the availability of heavy metals (Pb, Cu). Oxide physicochemical properties are affected by the proportion of Fe and AI, the Fe/AI ratio. Five amorphous oxides containing Fe and/or AI were synthesised: "Fe" (only Fe); "3FeAI" (3 moles Fe per mole AI, Fe/AI = 3); "FeAI" (Fe/AI = 1); "Fe3AI" (Fe/AI = 0.3); "AI" (only AI). Kaolinite clay was also investigated along with kaolinite to which Fe-AI oxides had been added.

The effect of Fe/Al ratio on these physicochemical properties was studied:

- Specific surface area EGME retention
- pH-dependent cation and anion exchange capacity Ca(NO<sub>3</sub>)<sub>2</sub> saturation
- Particle size density sieving, pipette methods
- Surface charge density potentiometric titrations

The Fe/AI ratio influenced the specific surface area: Fe and 3FeAI had significantly greater surface areas than Fe3AI and AI; FeAI exhibited the maximum surface area. The cation exchange capacity increased rapidly above pH 5, with Fe > 3FeAI > AI > Fe3AI > FeAI at pH 6 to 7. Surface charge density of low Fe/AI oxides was more sensitive to pH changes implying =AIOH surface hydroxyl groups are more easily protonated and de-protonated than =FeOH species. An open (porous) structure of loosely linked small particles was proposed with SO<sub>4</sub><sup>2-</sup> anions forming bridges between AI<sup>3+</sup> and Fe<sup>3+</sup> ions during oxide precipitation while inhibiting extensive crystal growth.

Pb and Cu retention was measured using 24 hour batch suspension tests with varying pH and contaminant concentrations (0.5 to 25 mmol /L). Higher Fe/Al ratio oxides retained more Cu and Pb at all pH values. Cu retention (0.5 to 5 mmol /L) and Pb retention (all concentrations) followed Fe > 3FeAl > FeAl > Fe3Al > Al but at 25 mmol Cu /L, only Fe accumulated more Cu. However, low Fe/Al ratio oxides preferentially sorbed Cu over Pb from multi-contaminant solutions. Adsorption rather than bulk precipitation was the dominant

accumulation mechanism. Geochemical modelling suggested surface precipitation occurred at higher contaminant concentrations.

Adding oxides to kaolinite significantly increased the clay's specific surface area, surface charge density and contaminant retention capacity; higher Fe/Al ratio oxide-amended clays retained more Pb and Cu.

Amorphous Fe-AI oxides substantially enhance heavy metal accumulation by soils with higher Fe/AI ratio oxides being particularly effective.

## RESUME

Les oxydes de fer-aluminium amorphes sont omniprésents dans l'environnement et contrôlent la disponibilité des métaux lourds (Pb, Cu). Les propriétés physicochimiques des oxydes sont affectées par la proportion de fer et d'aluminium (le rapport Fe/AI). Cinq oxydes amorphes ont été synthésisés: "Fe" (Fe seulement); "3FeAI" (3 moles de Fe par mole d'AI, Fe/AI = 3); "FeAI" (Fe/AI = 1); "Fe3AI" (Fe/AI = 0.3); et "AI" (Al seulement). L'argile kaolinite a également été étudié ainsi que le kaolinite auquel des oxydes Fe-AI ont été ajoutés.

L'effet du rapport Fe/Al sur les propriétés physicochimiques a été examiné:

- superficie particulaire spécifique rétention EGME
- capacité d'échange cationique et anionique dépendant du pH saturation par Ca(NO<sub>3</sub>)<sub>2</sub>
- densité de la taille des particules tamissage, méthodes avec pipette
- densité de la charge superficielle titrations potentiométriques

Le rapport Fe/Al influence la superficie particulaire spécifique: Fe et 3FeAl avaient des superficies significativement plus élevées que Fe3Al et Al; FeAl avait la plus grande superficie particulaire. La capacité d'échange cationique augmentait rapidement au dessus de pH 5, et Fe > 3FeAl > Al > Fe3Al > FeAl entre pH 6 et 7. La densité de la charge superficielle des bas oxydes Fe/Al était plus sensible au variations de pH, suggèrant que les groupes hydoxyl superficiels =AlOH sont plus facilement protonés et déprotonés que les espèces =FeOH. Une structure ouverte (poreuse) de petites particules liées lâchement est proposé avec anions SO<sub>4</sub><sup>2</sup> liant les ions Al<sup>3+</sup> and Fe<sup>3+</sup> durant la précipitation des oxydes en empêchant la croissance de crystaux.

La rétention du Pb et Cu a été mesuré en utilisant des tests de suspension en lots de durée de 24 heures en variant le pH et les concentrations de contaminants (0.5 à 25 mmol /L). Les oxydes avec rapport Fe/Al plus élevés retenait plus de Cu et de Pb pour toutes valeurs de pH. La rétention du Cu (0.5 à 5 mmol /L) et du Pb (toutes concentrations) suivaient la série Fe > 3FeAl > FeAl > Fe3Al > Al, mais à 25 mmol Cu /L, seulement le Fe accumulait plus de Cu.

Cependant, les oxydes à bas rapport Fe/Al accumulaient le Cu de facon préférentielle sur le Pb dans les solutions à contaminants multiples. L'adsorption était le mécanisme dominant versus la précipitation. La modelisation géochimique suggère qu'une précipitation superficielle se produisait aux concentrations élevées de contaminants.

L'ajout des oxydes au kaolinite a augmenté significativement la superficie particulaire de l'argile, ainsi que la densité de la charge superficielle et la capacité pour la rétention des contaminants; les argiles enrichies d'oxydes à rapport élevé Fe/Al ont retenu plus de Pb et de Cu.

Les oxydes amorphes de Fe-Al font accroître l'accumulation des métaux lourds par les sols, les oxydes avec rapports élevés de Fe/Al étant spécialement efficaces.

## ACKNOWLEDGEMENTS

I would like to thank the following without whom I would not have completed this Ph.D. thesis:

Professor Raymond Yong (formerly William Scott Professor of Civil Engineering & Applied Mechanics, McGill University; currently Distinguished Research Professor & Senior Scientific Director, Geoenvironmental Engineering Research Centre, School of Engineering, University of Wales, Cardiff) provided critical inspiration when I started graduate school, and financial and intellectual support during my Ph.D. as my thesis supervisor.

Elaine Macdonald, fellow graduate student and dear friend, who kept me sane through many long years in the laboratory and whose friendship and humour during my Montréal experience gave me the strength to survive and flourish despite the trials and tribulations of a Ph.D. at McGill.

I was financially supported during my Ph.D. by a **Canadian Commonwealth Scholarship** for which I am very grateful. I came originally to Montréal as a recipient of the first **Canada Memorial Foundation Scholarship** which was created in memory of the 900,000 Canadians who served with Great Britain during the First and Second World Wars; I hope I have been a fitting living tribute to their memory.

Colleagues and staff in the Geotechnical Research Centre at McGill who were very helpful in planning and implementing my experimental program; friends at AGSEM - McGill's TA union and McGill Nightline who helped me find the world outside the lab; & the Groundwater Section of the Environment Agency in Leeds.

Finally I would like to thank Kate (you know why !), Matt & Diane, Nige & Lucy, Pamela, M-C, Mick & Kate, Liz (especially for translating my abstract !), Natalie and of course, Houdini, along with all my other friends, both in Canada and England, for tremendous personal and emotional support throughout the long process of my Ph.D. - you're the best !

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## CHAPTER 1 INTRODUCTION

#### 1. Contaminated soils and sediments

Contaminated land is a problem throughout the industrialised world with over 100,000 sites covering 50,000 to 200,000 hectares thought to exist in the UK (RCEP, 1996) and at least 4,000 in the Netherlands (Pearce, 1992), while the US Superfund Program has spent over \$10 billion cleaning up many contaminated sites since its inception in 1980 (US EPA Superfund Program Web Site, 1999). Early remediation projects involved simple excavation of soil and disposal in landfill sites, however more progressive countries (e.g. Germany, Netherlands, USA) increasingly require treatment prior to landfilling (Elliott & Brown, 1989; RCEP, 1996). While a multitude of treatment techniques are available depending on the type of contamination, effective and efficient clean up is only possible when the nature of the contaminant-soil association is understood. This is particularly the case for the more innovative *in-situ* and *ex-situ* treatments which aim to remove or immobilise contaminants and thereby produce clean, or at least safe, soils in contrast to the "dig-and-dump" approach which simply transfers contaminants and soils to landfill sites.

As the pressure for new housing and business sites within urban areas grows, and resistance to new green belt development rises (Begley, 1997; RCEP, 1996), governments are increasing looking to the regeneration of *brownfields* in inner-cities and elsewhere with President Bill Clinton recently stating "we should restore contaminated urban land and buildings to productive use" (US EPA Brownfields Web Site, 1998). This pressure has renewed interest in cleaning contaminated land *in-situ* so that it may be returned to productive use.

Industrial effluents have caused contamination of sediments in rivers, lakes, and harbours (Lum et al, 1991; Adams et al, 1992). The impact of such pollution on aquatic life is becoming increasingly recognised as a result of public attention being drawn to specific situations such as the plight of the Beluga whales in the St. Lawrence River, whilst the US Environmental Protection Agency recently identified contaminated sediments as "a significant problem in many watersheds"

around the country" (US EPA, 1997). The regulatory reaction to such incidents of aquatic pollution in the Great Lakes/St. Lawrence River area and elsewhere has been the introduction of legislation restricting the discharge of effluents into these surface waters (Nichols et al, 1991; Power et al, 1991; Armitage, 1993; Lee & Jones-Lee, 1993). Whilst this is a necessary first step in solving these pollution problems, historic discharges have left a legacy of contaminated sediments on the bottom of many watercourses which have been described by researchers and the US EPA as a "significant reservoir...that contributes to the poisoning of the food-web" (Champoux & Sloterdijk, 1988; Champoux et al, 1988; Rose, 1993; Stigliani & Salomons, 1993; US EPA, 1997).

Heavy metals are accumulated by agricultural soils as a result of the application of sewage sludge; in the UK, an increasing proportion of sludge will be disposed of to land as a result of the implementation of the 1991 EU *Directive on Urban Wastewater Treatment* and the phase-out of dumping at sea (ENDS Report 279, 1998). Questions have been raised about the long-term safety of such disposal practices given the known ability of some plants to accumulate metals and pathogens (ENDS Report 275, 1997; RCEP, 1996). The need exists for non-destructive remediation of metal-contaminated soils in which the fertility and health of the soil is maintained if the introduction of sewage sludge to farmland is to be considered a *sustainable* activity.

Historic and current mining activities are another major source of heavy metals in the environment and have caused pollution of surface waters and sediments in watercourses draining mining areas (Fuge et al, 1994; Webster et al, 1998). In addition to the "authorised" contamination of soils, accidents can cause devastating pollution to the environment. The recent release of several thousand tons of highly contaminated mine tailings after a dam failed in Spain resulted in the deposition of heavy metals on previously pristine agricultural land as well as polluting one of the most important wetlands for migrating birds in Europe (IPS, 1998). Initial remedial measures are likely to involve excavation of these tailings but there is concern that heavy metals will have leached down into the underlying ground. Clean-up of this type of accident would be considerably more effective if

the behaviour and fate of contaminants in soils were more completely understood.

#### 2. Heavy metal contaminants

Lead and copper are defined as List II substances in the EU Directive on the Protection of Groundwater against Pollution caused by Certain Dangerous Substances (EU, 1980) signifying that they could have a harmful effect on groundwater. Their use must therefore be monitored so as to limit their introduction to groundwater since this could cause pollution. Rampley & Ogden (1998) reported that lead is the most frequently found metal at hazardous waste sites in the United States, appearing at one third of sites on the National Priorities List, while heavy metals constitute five of the six most cited hazardous materials at Army sites (Neale et al, 1997). Although debate continues over acceptable lead levels in the environment from a health perspective (Wixson & Davies, 1994), there is general agreement that lead in soils represents a definite health risk to young children since they tend to ingest soil while playing (Renner, 1995). Copper is another common contaminant, particularly in watercourses impacted by mining activities and from agricultural sources such as fungicides (Yong et al, 1992b). While copper is an essential nutrient for many animals and plants, high concentrations may be toxic, especially when occurring as the free ion, Cu<sup>2+</sup> (Grossl et al, 1994).

The extent to which contaminated soils need to be cleaned up varies from country to country and while absolute levels are still used in some parts of the USA (Nedwed & Clifford, 1997), many regulatory regimes (e.g. UK, Netherlands) are moving towards remediation based on risk-assessments with acceptable levels depending on the projected end use (Quint, 1997). For these risk-oriented remediation regimes to attain public acceptance, there must be confidence in the underlying science; this can only be achieved if there is a complete understanding of the nature and stability of contaminant-soil retention mechanisms.

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#### 3. The role of particulate matter

The fate of contaminants in soils and sediments is not fully understood although it has been established that many pollutants will preferentially partition onto particulate matter (Lion et al, 1982; Davies-Colley et al, 1984; Allan, 1986; Chapman, 1989). This partitioning is a significant means for removing contaminants from the soil solution which is the most bioavailable soil compartment, at least temporarily, and is very important for heavy metals (e.g. lead, copper, zinc, cadmium) and hydrophobic organic chemicals (e.g. polychlorinated biphenyls) (Oakley et al, 1981; Karickhoff & Morris, 1985; Förstner, 1987; Burton, 1992).

Soils and sediments are composed of a complex mixture of both inorganic and organic material (Yong, 1994). The inorganic fraction includes crystalline clay, oxide and carbonate minerals, quartz, and feldspars in addition to amorphous materials such as oxides, hydrous oxides, hydroxides, and oxyhydroxides (collectively referred to as "oxides" in this thesis) of iron, silicon, aluminium and manganese, and under anoxic conditions, metal sulphides (Kersten & Förstner, 1989; DeVitre et al, 1989; Fu & Allen, 1992; Howard & Evans, 1993). Natural organic matter may be living (e.g. plants, algae) or non-living (e.g. humic and fulvic acids, humin and dead organisms), and is composed of complex surface-active molecules (Fu et al, 1992; Yong et al, 1992b).

Organic detritus and fine-grained inorganic particles are consumed by many aquatic organisms, especially at the bottom of the aquatic food-chain (Rao & Mudroch, 1986; Swartz et al, 1988; Sloterdijk et al, 1989; Sadiq et al, 1991), and the particulate associated contaminants may therefore be assimilated into the tissues of these organisms (Tessier et al, 1984; Landrum & Faust, 1991; Burton & Scott, 1992; Soster et al, 1992). Predation on the detritus feeding organisms can subsequently lead to bio-accumulation in higher forms of aquatic life and this can then impact on animals at the top of the food chain such as Beluga whales and humans (Langevin et al, 1992). Similarly, contaminants in soils may be accumulated by animals or plants and hence be introduced to the food-chain.

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Figure 1.1. "Typical" soil or sediment sample at the particle scale. Amorphous oxides, carbonates and sulphides may be discrete particles or coatings on other grains.

Sediments and soils have been recognised as an important "sink" for pollutants due to the presence of surface-active constituents and the scavenging behaviour that these constituents exhibit (Koelmans & Lijklema, 1992). The role of lakes, canals and other low-flow waters in the deposition of suspended particles is well known, however the impact of re-suspension of these sediments by natural (e.g. storms) or artificial (e.g. dredging) events on any associated contaminants is less well understood (Lee et al, 1987; Ludwig & Sherrard, 1989). While contaminants are often tightly bound to particulate matter, contaminated land may be an important "source" of pollutants if, for example, there is an influx of clean water which disrupts the existing chemical equilibrium and causes the release of additional contaminants to groundwater or surface waters (Luoma, 1989; Salomons et al, 1987; Thomann et al, 1993). The ability to predict and control this type of change is necessary if the negative impact of contaminated land is to be minimised.

#### 4. Statement of the problem

A considerable body of work exists on the adsorption of heavy metals and anions by oxides of iron, manganese, silicon and aluminium under a variety of environmental conditions. This has included the effects of pH (Posselt et al, 1968; Kinniburgh et al, 1975, 1976; Stumm et al, 1976; Elliott et al, 1986; Courchesne & Hendershot, 1989; Schulthess & Huang, 1990; Hendershot et al, 1992), ionic strength (Swallow et, 1980; Kooner, 1993), surface area (O'Connor & Kester, 1975; Kooner, 1993), and the degree of crystallinity (Swallow et, 1980). Recently, there has been an increased focus on the heavy metal retention behaviour of soils and sediments under changing environmental conditions (e.g. pH and redox potential) for the purposes of predicting the release of contaminants during the dredging and disposal of contaminated sediments, and as a result of efforts to assess the risk associated with contaminated soils (Gambrell et al, 1991; Calmano et al, 1988, 1992, 1993; Saeki et al, 1993).

Most previous studies have been performed on oxides containing only Fe or AI (Calmano et al, 1988) but this does not allow consideration of particle-particle interactions (e.g. particle coatings, multi-component aggregation etc.). Honeyman (1984) investigated mechanically combined mixtures containing two oxide components (e.g. Fe and Al) whereas natural oxides are typically coprecipitated solids (Norrish & Taylor, 1961; Lewis & Schwertmann, 1979). The reactivity of Fe oxides may be increased by the isomorphous substitution of AI (Postma, 1993) and the crystalline Fe oxide, goethite, commonly contains up to 35 mole % Al in the natural environment (Ainsworth et al, 1989). However, few studies have been reported for mixed Fe-AI oxides (Davis & Kent, 1990; Zachara et al. 1989), particularly amorphous forms (Anderson & Benjamin, 1990a, b) despite studies showing that the majority of natural particle surfaces are enriched with AI (Schulthess & Huang, 1990). Previous research suggests that AI oxides may exhibit a higher contaminant binding intensity for some heavy metals than Fe oxides (Kinniburgh et al, 1976) although these results have been disputed (Karthikeyan et al, 1997).

Questions that remain to be fully answered include whether metals are specifically adsorbed (chemisorption) onto particle surfaces as inner sphere

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complexes or if electrostatic bonding (outer-sphere complexes) are more important. Inner-sphere complexes are more stable since the metal ion bonds directly with the surface functional group (e.g.  $\equiv$ AlOH) and may be either covalent or ionic. Conversely in outer-sphere complexes, the metal ions are separated from the surface by at least one water molecule from the hydration shell of the metal and are held by weaker coulombic bonds (Sposito, 1984).

While many studies have been conducted at low metal concentrations, contaminated land often contains very high levels of metals and it is essential that research be conducted to determine whether mechanisms and binding constants derived at low metal loadings can be applied to these more extreme conditions. Similarly most previous studies have utilised non-interacting salts such as nitrate, however acetate and other low molecular weight organic molecules which form stable soluble complexes with metals are common in ground and surface waters; this thesis will investigate whether acetate interferes with the retention of heavy metals.

The acid-base surface properties of oxides strongly influence their contaminant retention behaviour yet most previous studies have focussed on simple nitrate containing oxides despite the prevalence of oxides precipitated from sulphate-rich waters in natural environments, particularly in areas impacted by mining.

One approach that has improved the understanding of the distribution of metals among soil and sediment components has been to add progressively harsher reagents to selectively dissolve individual components (Tessier et al, 1979; Lion et al, 1982; Elliott et al, 1986; Yong et al, 1993; Macdonald & Yong, 1997) although concerns have been raised over the selectivity of these *sequential chemical extraction* techniques (Nirel & Morel, 1990) and the possibility that the reagents may alter the surface chemical characteristics of the material (Fu & Allen, 1992). An alternative approach has been to combine well-defined sediment phases into a more complex mixture (Oakley et al, 1981; Davies-Colley et al, 1984), and while such synthetic materials cannot fully represent natural environments, they can provide some insight into the effect of particle-particle interactions on the contaminant retention behaviour and other physicochemical

properties of particles. Luoma & Davis (1983) concluded that understanding the influence of particle coatings and multi-component aggregation on the metal binding capacity of sediments was one of the most important requirements for accurate modelling of the distribution of heavy metals in the environment, however there remains considerable scope for further investigations in this area. The recent interest in enhancing the accumulation capacity of natural soils without destroying their ability to support vegetation also requires additional research. This thesis will investigate the effects of adding amorphous oxides to kaolinite clay on the physicochemical and contaminant retention properties of oxide-amended clays.

#### 5. Objectives of the thesis

This thesis will evaluate the relative accumulation capabilities of amorphous Fe, AI, mixed Fe-AI oxides and oxide-amended kaolinite clays for lead and copper as a function of pH and metal concentration; contaminant solutions will contain acetate to investigate possible interference due to the formation of soluble metalacetate complexes. Clarification of the role of mixed Fe-AI oxides will improve prediction of the behaviour of heavy metals as a result of different remedial activities (e.g. "no-action", soil washing, dredging etc.). By adding oxides to kaolinite clay and investigating the consequent effects on the physicochemical characteristics of the particle surface, insight should be gained into the effect of particle coatings on the distribution of heavy metals in natural soils and sediments.

The objectives of this thesis may therefore be summarised as follows:

- 1. Assessment of the role of amorphous Fe, Al, mixed Fe-Al oxides and oxide-amended kaolinite clays in retaining heavy metals (Pb and Cu) as a function of pH and contaminant concentration.
- Elucidation of the competition between Pb and Cu for oxides and oxideamended kaolinite clays, and the influence of Fe/Al ratio on this competition.

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 Evaluation of the effect of Fe/AI ratio on the physicochemical properties and contaminant retention capacity of amorphous oxides containing Fe and/or AI, and on oxide-amended kaolinite clays.

#### 6. Experimental Program

The experimental programme has been designed to elucidate the mechanisms by which Pb and Cu are accumulated by amorphous oxides containing Al and/or Fe, as well as by kaolinite to which amorphous oxides have been added. Clarification of these mechanisms will provide insight into the strength and stability of the contaminant-particle association ("bond"), and the conditions under which the different heavy metals would be released. Batch suspension tests lasting 24 hours will be conducted to assess the equilibrium distribution of heavy metals between the oxides or clays and the solution phase. The variation in the physico-chemical properties of the amorphous iron-aluminium oxides will be evaluated as a function of the Fe/AI ratio. These properties will include the oxide composition, specific surface area, cation exchange capacity, surface charge density, specific gravity and particles size distribution. The results should aid in assessing the risk associated with contaminated soils and also in choosing appropriate remediation and containment systems such as dredging, controlled mobilisation of contaminants from materials (e.g. soil washing), immobilisation or encapsulation.

#### 7. Organisation of the thesis

The thesis is organised in the following manner:

#### Chapter 1. Introduction:

States the problem being investigated in this thesis and explains the objectives and experimental approach.

Chapter 2. Literature Review.

**Chapter 3. Materials and Methods** 

Details the materials used and experiments conducted in support of the thesis objectives.

Chapter 4. Physicochemical properties of oxides and synthetic clays Results and discussion of the physicochemical experiments.

Chapter 5. Contaminant retention behaviour of oxides Results and discussion of the Pb and Cu retention tests.

Chapter 6 - Contaminant retention behaviour of synthetic clays Results and discussion of the Pb and Cu retention tests.

Chapter 7 - Modelling - contaminant retention Application of surface complexation model to contaminant retention results.

Chapter 8 - Conclusions Conclusions, contribution to knowledge and recommendations for future research.

References

## CHAPTER 2 LITERATURE REVIEW

#### 1. Amorphous oxides and heavy metals

Previous experience shows that the fate of heavy metals in contaminated soils and sediments is significantly influenced by the pH of the local environment (Harter, 1983; Yong et al, 1993). Precipitation as a mechanism of heavy metal accumulation in soils occurs when the pH of the system is raised above the precipitation pH of heavy metal minerals (e.g. Pb(OH)<sub>2</sub>). Another critical factor in assessing the fate of heavy metals is the quantity and nature of amorphous iron and aluminium oxides, hydrous oxides, hydroxides and oxyhydroxides (collectively referred to as "oxides" in this thesis). These oxides are ubiquitous in soils and sediments as coatings on other particles (Coston et al, 1995) or as discrete solids and are very effective at removing heavy metal contaminants due to their high specific surface areas and reactive surface functional groups (Kinniburgh et al, 1976; McLaughlin et al, 1981; Elliott at al, 1986; Schulthess & Huang, 1990).

#### 2. Iron and aluminium oxides

Iron and aluminium minerals occur with a variety of chemical and physical structures in soils and sediments; the main forms are *oxides*, *hydroxides* and/or *oxyhydroxides*. The difference between these forms is illustrated by the chemical formulae in Table 2.1; in addition to the metal ion (Fe or AI), *oxides* contain O, *hydroxides* are comprised of OH ions, and *oxyhydroxides* consist of O and OH ions. For simplicity, many authors include all of these possible minerals within the general term *hydrous oxides*.

The basic structural unit for Fe oxides is for each Fe<sup>3+</sup> ion to be surrounded in an octahedral pattern by six oxygen ions or a mixture of oxygen (O<sup>2-</sup>) and hydroxyl (OH<sup>-</sup>) ions (Schwertmann & Cornell, 1991). Isomorphous substitution, in which Al and other similarly sized trivalent cations replace Fe, is common, without significantly distorting the structure of the oxide. Oxides in which Al<sup>3+</sup> is the central metal ion have a similar octahedral structure. The exact arrangement of

the Al or Fe(O,OH)<sub>6</sub> octahedra determines the structure of the individual Al or Fe oxide (Schwertmann & Cornell, 1991). The  $\alpha$ -phases listed in Table 2.1 are generally more stable than their corresponding  $\gamma$ -phases; the O<sup>2-</sup> and OH<sup>-</sup> ions in  $\alpha$ -phase minerals form layers that are primarily hexagonally close-packed (hcp) while in  $\gamma$ -phases, these counter-ions are predominantly cubic close-packed (ccp). In both  $\alpha$ - and  $\gamma$ -phase structures, tetrahedral interstices exist between the three anions in one plane and the O<sup>2-</sup> or OH<sup>-</sup> in the plane above.

Oxides		Hydroxides	· · · · · · · · · · · · · · · · · · ·
Mineral	Formula	Mineral	Formula
Hematite	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Ferrihydrite'	Fe <sub>5</sub> HO <sub>8</sub> .4H <sub>2</sub> O
Maghemite	γ- <b>Fe</b> <sub>2</sub> O <sub>3</sub>	Schwertmannite'	Fe <sub>6</sub> O <sub>6</sub> (OH) <sub>6</sub> SO <sub>4</sub>
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	Gibbsite	γ-Al(OH) <sub>3</sub>
Corundum	α-Al <sub>2</sub> O <sub>3</sub>	Aluminium hydroxide <sup>1</sup>	AI(OH) <sub>3</sub>
Oxyhydroxides			
Mineral	Formula	Mineral	Formula
Goethite	α-FeOOH	Lepidocrocite	γ-FeOOH
Akaganeite	β-FeOOH	Diaspore	α-ΑΙΟΟΗ
Boehmite	γ-ΑΙΟΟΗ		
Table 2.1. Chemical formulae of some naturally occurring oxides,hydroxides and oxyhydroxides of iron and aluminium (adapted fromBrown et al, 1978; Schwertmann & Cornell, 1991; Bigham et al,1996).Minerals in bold are common in soils. 1 signifies amorphous minerals.			

#### 2.1 Oxyhydroxide structure

The structure of the oxyhydroxides involves double bands of edge-sharing  $AlO_3(OH)_3$  (or Fe) octahedra in which only about half the octahedral interstices are filled by  $Al^{3*}$  or Fe<sup>3\*</sup>; in the  $\alpha$ -phases (e.g. goethite, diaspore), these double bands form 2 by 1 octahedra *tunnels* crossed by hydrogen bonds (OH-O) and linked by sharing the corners of adjacent octahedra (Schwertmann & Cornell, 1991). If the three dimensional structure is described by three perpendicular axes, a, b and c, (see Figure 2.1) the distance along the a-axis between adjacent double bands of octahedra is half that along the b-axis (Brown et al, 1978). The double bands of octahedra containing  $Al^{3*}$  or Fe<sup>3\*</sup> are present as strips running parallel to the c-axis which alternate with octahedra without a metal ion (tunnels);

hydrogen ions fill some of the vacant octahedra in tetrahedral co-ordination and link adjacent oxygen ions via hydrogen bonds. The variation in the identity of the central ion (e.g..  $Ai^{3+}$ ,  $Fe^{3+}$ ,  $H^+$ ) results in distortion of the octahedra; for simplicity this distortion has not been included in Figure 2.1.



Figure 2.1. Goethite ( $\alpha$ -FeOOH) structure showing packing of Fe(O,OH)<sub>6</sub> octahedra with O representing oxygen or hydroxyl groups surrounding Fe ions (•); hydrogen bonds are depicted by broken lines (adapted from Brown et al, 1978). Diaspore ( $\alpha$ -AlOOH) has a similar structure. The plane of the paper is perpendicular to the c-axis.

The  $\beta$ -phase oxyhydroxide minerals (e.g. akaganeite) consist of larger 2 by 2 tunnels bounded by double chains of FeO<sub>3</sub>(OH)<sub>3</sub> octahedra which share corners (Bigham et al, 1990). These tunnels comprise linked cavities formed by eight OH groups and are large enough to accommodate anions such as chloride (Schwertmann & Cornell, 1991). This structure is illustrated in Figure 2.2.



Figure 2.2. Akaganeite ( $\beta$ -FeOOH) structure showing packing of Fe(O,OH)<sub>6</sub> octahedra with O representing oxygen or hydroxyl groups surrounding Fe ions (•); Cl<sup>-</sup> ions are present in the tunnels. The plane of the paper is perpendicular to the c-axis.

Figure 2.3 illustrates the  $\gamma$ -structure oxyhydroxides (e.g. lepidocrocite), in which the double bands of octahedra are arranged in a zig-zag layer pattern where the edges are shared, with each layer being connected by hydrogen bonds through vacant octahedra (Brown et al, 1978). Each oxygen ion that is common to two layers is shared by four octahedra.

#### 2.2 Oxide structure

Hematite forms a compact structure without hydrogen bonding resulting in a high specific gravity mineral (5.26 g / cm<sup>3</sup>, Schwertmann & Cornell, 1991). The layers of FeO<sub>6</sub> octahedra are connected by edge and face sharing of oxygen ions with only two thirds of the octahedral interstices being filled with Fe<sup>3+</sup> (Figure 2.4). The hexagonally close-packed oxygen ions are in planes perpendicular to the c-axis and in contrast to the oxyhydroxides, iron atoms in adjacent octahedra are close enough to repel each other across face-shared octahedra which leads to a regular distortion of the structure (Brown et al, 1978); for simplicity this distortion has not been included in Figure 2.4. Corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) has the same structure as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>).



Figure 2.3. Lepidocrocite ( $\gamma$ -FeOOH) structure showing packing of Fe(O,OH)<sub>6</sub> octahedra with O representing oxygen or hydroxyl groups surrounding Fe ions (•); hydrogen bonds are depicted by broken lines (adapted from Brown et al, 1978). Boehmite ( $\gamma$ -AlOOH) is isostructural with lepidocrocite. The plane of the paper is perpendicular to the a-axis.

#### 2.3 Hydroxide structure

Gibbsite consists of two close-packed layers of hydroxyls (OH) arranged as octahedra in which two thirds of the interstices are filled with Al<sup>3+</sup> (Figure 2.5). The arrangement is such that OH groups on one layer are opposite hydroxyl groups on the adjacent layer thus encouraging the formation of hydrogen bonds between layers (Brown et al, 1978).



Figure 2.4. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) structure showing packing of FeO<sub>6</sub> octahedra with O representing oxygen ions surrounding Fe ions (•) (adapted from Brown et al, 1978). Corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) is isostructural with hematite. The plane of the paper is perpendicular to the b-axis.



Figure 2.5. Gibbsite  $(\gamma$ -Al(OH)<sub>3</sub>) structure showing packing of Al(OH)<sub>6</sub> octahedra with O representing hydroxyl groups surrounding Al ions (•); hydrogen bonds are depicted by broken lines (adapted from Brown et al, 1978). The plane of the paper is perpendicular to the a-axis.

#### 2.4 Amorphous minerals

The structure of ferrihydrite is not well understood since it is, by definition, amorphous to X-ray diffraction techniques, however it is generally considered to consist of hexagonally close-packed oxygen planes with Fe ions in the octahedral interstices in a similar manner to hematite (Schwertmann & Cornell, 1991). Although the lack of three dimensional regularity limits characterisation, it is thought that the amorphous structure is due to many vacant Fe octahedral sites and the replacement of some oxygen by H<sub>2</sub>O and/or OH groups. Ferrihydrite is converted into hematite if stored as a suspension between pH 7 and 8 whilst goethite forms at pH 4 and above pH 12 (Schwertmann & Murad, 1983). These researchers concluded that the low and high pH conditions promoted some dissolution of Fe(III) ions from the ferrihydrite which subsequently crystallised as goethite; conversely, hematite crystals formed as a result of internal dehydration and rearrangement within the ferrihydrite aggregates.

The sulphate rich amorphous mineral, schwertmannite, is thought to have a tunnel structure similar to akaganeite in which vacant octahedra (no Fe<sup>3+</sup> present) provide linked cavities (Bigham et al, 1996). Since sulphate has a larger ionic radius than chloride (SO<sub>4</sub><sup>2+</sup> = 0.50 nm; Cl<sup>-</sup> = 0.36 nm; Bigham et al, 1990), it can only be accommodated in these cavities by sharing oxygen ions with adjacent Fe<sup>3+</sup> ions to form a bridged bidentate complex, e.g. -Fe-O-SO<sub>2</sub>-O-Fe-. The space available in the tunnels requires the S and two of the sulphate O ions to occupy two neighbouring cavities parallel to the tunnel axis. Incorporation of SO<sub>4</sub><sup>2-</sup> within the octahedra would lead to some structural distortion; this is consistent with the low crystallinity of schwertmannite (Bigham et al, 1990). Bigham and co-researchers (Bigham et al, 1990, 1996) used Mössbauer spectra and infrared spectroscopy to conclude that sulphate ions were present as both structural ions and as complexes adsorbed by Fe sites at the particle surface. These researchers invoked two types of Fe octahedral sites; a minority in which Fe<sup>3+</sup> is in the normal octahedral position surrounded by O and OH groups (i.e.

 $FeO_3(OH)_3$ ; and a larger number of octahedra in which one OH group is replaced by  $SO_4^{2-}$  to give  $FeO_3(OH)_2O-SO_3$ .

#### 3. Choice of contaminants and levels

Studies have shown that lead and copper can cause deleterious effects to vegetation, aquatic and soil organisms (Alloway, 1995) and these heavy metals are listed as dangerous substances in Europe and the USA (EU, 1980; Rampley & Ogden, 1998). While the bioavailability of heavy metals cannot be directly predicted from the total concentration of metals in soils or sediments (Stumm & Morgan, 1996), recent investigations have confirmed that the concentration of free metal in solution (e.g. Pb<sup>2+</sup>, Cu<sup>2+</sup>) can be used to predict toxic effects on vegetation and soil organisms (Sauvé et al, 1998). The free metal activity is influenced by many factors including pH, total metal concentration, the presence of complexing ligands and the reactivity of the solid particles (Stumm & Morgan, 1996); there remains scope for additional research into the importance of amorphous oxides in controlling the concentration of soluble metals.

Soils and sediments have a finite capacity to accumulate contaminants (Yong et al, 1992b). Clay landfill liners, land impacted by mining and other industrial activities, or agricultural soils subject to applications of sewage sludge may receive repeated loading of heavy metals over periods of years or even decades. In order to assess the ability of such systems to continue to retain contaminants over time, it is necessary to investigate the maximum soil retention capacity, and how the affinity of heavy metals for soils is affected by changing environmental conditions such as pH.

Most laboratory studies have used low metal concentrations (<10<sup>-4</sup> M) to avoid problems of precipitation and to investigate adsorption mechanisms (e.g. Benjamin & Leckie, 1981). Certain environments have been contaminated by very high levels of metals and it is important to clarify whether retention mechanisms and binding constants obtained at lower concentrations are applicable to these more extreme situations. High levels of Cu and Pb contamination have been reported in stream sediments draining mining areas
(e.g. Pb = 80.300 mg/kg, Cu = 1910 mg/kg, Fuge et al, 1994), in soils under wood treatment facilities (e.g. Cu = 104,000 mg/kg, Turner & Foerst, 1993), Pbbattery reclamation sites (e.g. 1 - 5% Pb, Turner et al, 1994; 30% Pb, Nedwed & Clifford, 1997), and small-arms firing ranges (e.g. Pb = 30,000 mg/kg, Johnson et al, 1994), while in UK sites, soils have been found to contain up to 12% Pb (Alloway, 1995) and 10% Cu (Environment Agency, personal communication). Merrington & Alloway (1997) compared the metal accumulation capacity of natural soils contaminated with Pb at levels up to 62,080 mg /kg by mining. sewage sludge application and clay-pigeon shooting, smeltina. with uncontaminated soils from adjacent locations. They found that pre-existing contamination lowered the metal-soil affinity and limited the ability of soils to retain additional Pb. These results are not unexpected if the current knowledge of contaminant retention mechanisms is considered, however such considerations appear to be rarely included when the repeated application of sewage sludge is being proposed.

#### 4. Remediation techniques and assessing their likely success

There are two main approaches for the management of metal contaminated soils: technologies that leave the metal in the soil. e.q. capping/stabilisation/excavation; and those that remove the metal from the soil, e.g. soil washing with acids or chelating agents (Berti & Cunningham, 1997). As noted in Chapter 1, the former is cheaper, easier but cannot be considered sustainable since it requires the final disposal site to be monitored in perpetuity to avoid leaching, while in-situ immobilisation with cementing agents can render the soil unsuitable for vegetation (Neale et al, 1997). Contaminant extraction technologies are therefore becoming increasingly popular.

Various acids and chelating agents have been used to extract heavy metals such as Pb from contaminated soils (Nedwed & Clifford, 1997). Acids are effective at solubilising metals by enhancing ion exchange, and by dissolving some soil components (e.g. carbonates, oxides) while chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) compete with particle surface functional groups for sorbed metals (Brown & Elliott, 1992;

Peters & Shem, 1992; Neale et al, 1997). Since acids may cause irreparable and undesirable damage to soil components and hence inhibit plant growth, chelating agents have become increasingly popular soil washing additives. Elliott & Brown (1989) found that EDTA was able to extract up to 90% of Pb from a highly contaminated soil at a battery recycling facility (Total Pb = 21% or 210,000 mg/kg) and concluded that the non-extractable fraction was bound within the silicate matrix. However concerns have been raised over the possibility that the substitution of EDTA and NTA for phosphates in detergents may lead to their uncontrolled discharge and hence mobilise metals from river sediments (Banat et al, 1974; Samanidou & Fytianos, 1990).

In order to predict their success in remediation projects or in reducing the risk associated with their discharge in sewage effluents, the ability of chelating agents to out-compete soil components for metals must be assessed. If the stability constant for the formation of the chelate-metal complex is larger than that for the soil-metal surface complex, then the metal should be extracted from the soil, although kinetic considerations may interfere with predictions based on equilibrium constants. Another complicating factor is the degree to which the metal-chelate complex is adsorbed by soils since this may significantly reduce the extraction of metals (Nowack et al. 1996). While chelate-metal stability constants in solution are well known (e.g. Martell & Smith, 1974), additional research is required to obtain such constants for individual soil components (e.g. oxides, clays) and for composite soils. Smith & Jenne (1991) compiled surface complexation constants for several metals onto iron and manganese oxides while Dzombak & Morel (1990) have published an exhaustive review of binding constants for metals and anions onto amorphous iron oxides. However, these constants were all derived from experiments using pure oxides containing only Fe or Mn that were precipitated from nitrate salts whereas natural oxides tend to be mixtures of Fe, Al, Si and/or Mn. The surface acidity constants, Ka1 and Ka2 (see Chapter 4), have been identified as the most significant source of variation among calculated values of metal binding constants due to their influence on the estimated site density (Smith & Jenne, 1991), but little consideration is given to the effect on these parameters of adsorbed anions and structural impurities (e.g. sulphate) that are often present in natural oxides (Webster et al, 1998).

Another important variable is the initial metal concentration in the soil since a greater proportion of total Pb is removed by extractants as the initial contaminant level increases (Neale et al, 1997). This can be explained if the nature of the retention mechanism varies with metal concentration; possible mechanisms are surface complexation which may involve multiple sites each with a different metal affinity, surface precipitation, bulk precipitation and ion exchange (Farley et al. 1985; Yong et al. 1992b). At lower metal concentrations, high affinity sites (mechanisms) are dominant and it is consequently more difficult to re-mobilise these metals. Rampley & Ogden (1998) used a chelating agent, Metaset-Z, to extract Pb from artificial and real contaminated soils. While extraction from artificial soils could be described by a one-site model, the more complicated mixture of possible binding sites found in the natural soil caused Pb-extraction at two reaction rates and thus required two discrete site types: one from which Pb is easily removed and a second from which removal is more difficult. The system pH affects the degree to which metal chelation occurs since increasing competition from hydroxyl ions as the pH rises inhibits metal-chelate complex formation (Elliott & Brown, 1989).

Immobilisation of contaminants within the soil remains an attractive alternative to extraction techniques since it avoids the need to dispose of the concentrated metal-bearing wastewater generated by soil washing methods. Berti & Cunningham (1997) promoted "in-place inactivation" using soil amendments as a cheap and long-lasting alternative to simple capping or chemical stabilisation (e.g. with Portland cement). Their method involves the addition of soil amendments that effectively change the soil chemistry and speciation of contaminants (e.g. Pb) while having a neutral to positive effect on plant growth; the effectiveness of various amendments in immobilising contaminants was measured for soil Pb levels of up to 3500 mg/kg using a leaching technique that mimics mammalian gastric-intestinal tract solutions. Lothenbach et al (1997) investigated the addition of the polynuclear aluminium complex,  $[A|Q_4A|_{12}(OH)_{24}(H_2O)_{12}]^{7+}$  (often referred to as  $A|_{13}$  for simplicity) to montmorillonite clay and found that it significantly enhanced the immobilisation of metals, thus reducing their availability to plants. This technique should not

significantly alter the existing pH of the soil nor interfere with normal plant growth, as compared with more aggressive soil additives such as cementing agents. While the addition of oxides could lower soluble metal levels, a full understanding of the long-term stability of these oxides is necessary for confidence in remedial measures and hazard assessment, particularly for Fe oxides. Concerns have been raised that the microbial reduction of Fe (III) to Fe (II) under anoxic conditions (e.g. in sediments or beneath landfill sites) with a consequent dissolution of Fe (III) oxides could be accompanied by the release of any sorbed metals (Markwiese et al, 1998).

Recent research has promoted the use of *permeable reactive walls* for treating groundwater contaminated with both organic chemicals (e.g. DDT, Sayles et al, 1997) and metals (Blowes et al, 1997; Waybrant et al, 1998). This approach uses the redox sensitivity of the contaminants to transform or immobilise them; organic chemicals are typically *oxidised* by contact with zero-valent iron, while metals are *reduced* to a less hazardous or toxic form (e.g.  $Cr(VI) \rightarrow Cr(III)$ ;  $Cu^{2*}(aq) + SO_4^{2*} + 8H^* \rightarrow CuS(s) + 4H_2O)$  by either biotic or abiotic mechanisms (Waybrant et al, 1998). The reduction of Cr(VI) to the less mobile Cr(III) is often designed to be accompanied by the oxidation of Fe(0) and the subsequent precipitation of sparingly soluble Fe(III)-Cr(III) (oxy)hydroxides (Blowes et al, 1997) which in turn may sorb other heavy metals.

Phytoremediation is an alternative method of remediation that has recently received considerable interest, particularly for metals such as Pb (Watanabe, 1997). Certain plants known as hyperaccumulators are able to absorb high levels of contaminants from soil solutions through their roots and then concentrate them within their biomass (e.g. roots, shoots and leaves). Metal hyperaccumulators have been defined as plants which contain more than 1,000 milligrams of metal per kilogram of dry plant matter (Baker & Brooks, 1989). Although attractive in theory, there remain concerns that phytoremediation is too slow a process, taking years or decades rather than months to lower soluble metal levels to acceptable levels (Lothenbach et al, 1997), however recent research using chelating agents and/or pH adjustments to help solubilise metals is improving remediation rates (Watanabe, 1997). Obviously an improved understanding of the mechanisms by

which metals are bound to soils will enhance efforts to optimise the transfer of metals from soils to plants.

#### 5. Metal retention by oxides

Possible heavy metal retention mechanisms include ion exchange, adsorption of the free ion (e.g.  $Cu^{2+}$ ) or hydrolysis products (e.g. PbOH<sup>+</sup>), adsorption of polymerised species (Lothenbach et al, 1997), or the formation of a surface precipitate (Farley et al, 1985). If heavy metals are removed from solution by ion exchange onto soil surfaces, they may be easily re-mobilised if the solution composition changes (e.g. an influx of seawater), and while precipitation (e.g. as PbS) tends to result in lower dissolved contaminant concentrations (Morse, 1994; Xu et al, 1994), re-mobilisation is possible (e.g. due to a significant decrease in pH). The formation of surface complexes in which a covalent bond is created between the surface functional group and the contaminant ion will provide an even more stable bond that is less sensitive to fluctuations in the solution pH. One implication of surface precipitation, in which retention is a combination of covalent bonding and precipitation (Fendorf et al, 1992), is that contaminants sorbed in this way should not be subject to desorption unless solution conditions change significantly. Furthermore, the surface precipitate will mask the original surface to some extent thus altering the surface properties of the solid (e.g. acidbase behaviour, ability to retain other contaminants).

Amorphous Fe and AI oxides demonstrate high specific surface areas and coupled with the reactive nature of their surface functional groups (e.g. =X-OH where "=X" represents AI or Fe at the oxide surface), these components have a high capacity to retain heavy metal contaminants (Anderson & Benjamin, 1990a, b; Meng & Letterman, 1993a, b). The charge on these hydroxyl surface functional groups is controlled by pH; at low pH, protonation will encourage the formation of positively charged =X-OH<sub>2</sub><sup>+</sup> groups while at high pH de-protonation will promote negative =X-O<sup>-</sup> groups (Hohl et al, 1980):

#### **Equation 2.1**

$$\equiv X - OH; \quad \xleftarrow{H^{*}} \equiv X - OH \quad \xleftarrow{OH} \Rightarrow \equiv X - O^{*} + H_{2}O$$

The pH at which the net surface charge is zero is termed the zero point of charge or  $pH_{ZPC}$  (Parks & De Bruyn, 1962), which varies amongst the oxide minerals with silica having a  $pH_{ZPC}$  of about pH 2, Fe oxides ca. pH 7-8, and Al oxides having a  $pH_{ZPC}$  around pH 9 (Kinniburgh et al, 1976; Schulthess & Huang, 1990). The ability to exhibit both positive and negative surface charge depending upon the solution pH illustrates the amphoteric nature of these materials (Stumm et al, 1976).

At greater than  $pH_{ZPC}$ , heavy metal cations will be drawn towards the soil surface by electrostatic attraction (physical or non-specific adsorption) that can be quantified through cation exchange capacity experiments. In addition, due to the high chemical affinity that surface hydroxyl groups (e.g. =AIOH) have for certain heavy metals, oxide surface functional groups may form surface complexes (specific adsorption) with contaminants even if the surface is positively charged (Stumm & Morgan, 1996). Pb and Cu can therefore be retained below the  $pH_{ZPC}$ despite the surface carrying a net positive charge. The formation of such surface complexes can involve the replacement of protons in surface hydroxyl groups with metal cations and the formation of an "inner-sphere" covalently bonded complex (Stumm et al, 1976; Meng & Letterman, 1993b):

#### Equation 2.2

 $\equiv X - OH + Cu^{2*} \longleftrightarrow \equiv X - OCu^* + H^*$ 

The stability of such surface complexes depends on the identity of the metal in the surface functional group (Al or Fe) and the nature of the contaminant (e.g. Cu or Pb), as well as the prevailing environmental conditions (pH, ionic strength, multiple contaminants).

Charlet & Manceau (1992) studied the sorption, surface precipitation and coprecipitation of Cr(III) on Fe oxides (goethite and amorphous hydrous ferric oxide) with X-ray absorption fine structure spectroscopy (EXAFS). EXAFS provides information about the molecular structure of the oxides by giving the distance between adjacent metal atoms and can be combined with macroscopic (thermodynamic) surface complexation modelling to investigate the sorption of Cr onto the Fe oxides. They concluded that the sorption of Cr(III) initially occurs through inner-sphere surface complex formation but that as the Cr surface coverage increases above 100%, a new surface precipitate phase begins to grow despite the bulk solution being undersaturated with respect to Cr(III) precipitation. This new surface precipitate phase has the same solubility as a homogenous bulk hydrous chromium oxide precipitate. In contrast, a similar investigation into the retention of Pb by goethite using X-ray absorption spectroscopy (Roe et al. 1991) concluded that at low Pb concentration, inner-sphere surface complexes were formed, however at high sorbate (Pb) to sorbent (goethite) ratios, surface polymers of Pb formed and not surface precipitates. In another study based on X-ray absorption spectroscopy, Carroll et al (1998) reported that amorphous or poorly crystalline Fe oxyhydroxides and carbonates are important phases for the uptake of Pb in mine-waste impacted aquatic sediments. Kinetic considerations have also been used to conclude that  $Cu^{2+}$  and  $Pb^{2+}$  are adsorbed onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and goethite as inner-sphere complexes since adsorption is accompanied by the removal of a water molecule from the hydration shell of the metal ion (Grossl et al, 1994).

## 6. Metal retention by kaolinite

Kaolinite surface charge can be divided into three components: permanently negatively charged sites on the silica tetrahedral crystal faces due to isomorphous substitution of Al(III) for Si(IV); variably charged surface hydroxyl groups on the alumina octahedral sheets (e.g.  $\equiv$ AlOH); and variably charged hydroxyl groups at the particle edges due to "broken-bonds" in the silica and alumina crystal lattices, e.g. aluminol,  $\equiv$ AlOH: pH<sub>ZPC</sub>  $\approx$  7.2; silanol,  $\equiv$ SiOH: pH<sub>ZPC</sub>  $\approx$  2 (Sposito, 1984). The combination of these pH-dependent and independent charges produces a net positive surface charge below about pH 4.5 and negative charge at higher pH values, however the aluminol surface hydroxyl groups are thought to remain positively charged up to their pH<sub>ZPC</sub> of about pH 7.2. At the pH<sub>ZPC</sub>, the contribution from positively charged aluminol groups compensates for

the sum of permanently negative face sites and pH-dependent silanol groups. As the pH increases, the excess of positively- over negatively-charged aluminol groups is no longer sufficient to neutralise the permanent negative charge and the net surface charge becomes negative (Bolland et al, 1976).

Previous research has found that the retention of sulphate and heavy metals by kaolinite is influenced by ionic strength (Spark et al, 1995b; He et al, 1997) which suggests ion exchange is more important than surface complexation. Spark et al (1995b) studied the adsorption of various heavy metals including Cu(II) onto kaolinite and found that adsorption of heavy metals may occur at any of the different surface sites depending on the surface charge. Flocculation of particles may occur as a result of the existence of negatively- and positively-charged surface sites and this could decrease the surface area available for adsorption (Yong & Ohtsubo, 1987); this flocculation is enhanced by the presence of AI and Fe oxides (Shuman, 1977). Re-precipitation of dissolved alumina (at lower pH) and silica (at higher pH) may change the nature of the particle surface charge (Bolland et al, 1976) as well as causing co-precipitation of heavy metals. Spark et al (1995b) found that the shape of the Cu(II) retention curve on kaolinite closely followed that of Cu(II) on both silica and alumina in contrast to the adsorption of Zn(II), Co(II) and Cd(II) suggesting that surface complexation by silanol and aluminol groups may be the dominant accumulation mechanism for Cu(II). However Zn(II), Co(II) and Cd(II) adsorption followed a two step process: an initial steep increase in retention with pH followed by a second more shallow increase with pH. Since the importance of this first step decreased with increasing ionic strength, these researchers concluded that initial retention was by electrostatic attraction to silica tetrahedral face sites while the second step mechanism involved adsorption by silica and alumina hydroxyl groups. They ruled out co-precipitation of heavy metals with  $AI(OH)_3$  since AI(III) precipitation was essentially complete before very much metal adsorption had occurred (less than 10% adsorption at pH 5; Spark et al, 1995b). Schroth & Sposito (1998) investigated the adsorption of various heavy metals by a kaolinite clay from single contaminant solutions at low concentration and found that Pb showed a higher affinity for the clay surface than Cu.

# 7. Choice of oxide type - sulphate versus nitrate & mixed oxides

Considerable work has been undertaken on pure Fe and Al oxides precipitated from nitrate salts since nitrate is not expected to interact with the surface or participate in proton consumption reactions (e.g. Dzombak & Morel, 1990 and references therein). However in natural systems such as watercourses draining mine waste areas, amorphous oxides are likely to contain structural or adsorbed sulphate (Bigham et al. 1996; Webster at al. 1994; 1998). To adequately model the retention of metals by natural oxides, it is necessary to conduct research on oxides precipitated from sulphate-rich solutions as well as the better understood nitrate oxides since the oxide composition will affect key properties such as the zero point of charge. The isoelectric point  $(pH_{IFP})$  is equivalent to the zero point of charge when the surface charge is due solely to the adsorption of  $H^*$  and  $OH^*$ ions (Stumm & Morgan, 1996). Parks (1965) reviewed the isoelectric points of various crystalline and amorphous oxides and hydroxides. He reported that the presence of sulphate as a structural impurity in AI and Fe oxides caused the pHIEP to be lowered. The extent of this shift in the isoelectric point depended on the level of sulphate and the oxide: for hydrous  $AI_2O_3$  with 7.4 mole % sulphate, the pH<sub>IFP</sub> fell by 0.7 pH units whereas 1.4 mole % sulphate in hydrous  $Fe_2O_3$ caused a downward shift of 1.6 pH units. The mechanism responsible for this lowering of the isoelectric point is similar to that occurring during the specific adsorption of anions by the oxide surface. Specific adsorption of anions lowers the  $pH_{IEP}$  by increasing the negative charge on the oxide surface (e.g. because  $SO_4^2$  has a minus 2 charge while OH is only minus 1) thus requiring increased proton adsorption (i.e. lower pH) to neutralise the surface charge. The structural incorporation of anions should have the same effect since the =X-anion-H surface group is expected to be a stronger acid than =X-OH (Parks, 1965), where =X represents AI or Fe at the surface of the oxide.

While natural oxides tend to be co-precipitated mixtures of Fe, AI and Si, limited work has been reported on mixed oxides (Anderson & Benjamin, 1990a, b; Fendorf et al, 1992; Meng & Letterman, 1993a, b) and the effect of varying the molar ratio of Fe-AI-Si (Elliott & Huang, 1981). Elliott & Huang (1981) investigated the effect of varying the Si/AI ratio of aluminosilicates on their

surface charge and their ability to adsorb Cu in the presence of complex-forming organic ligands. As the Si/Al ratio decreased (greater Al content), the structural (and hence net surface) charge from isomorphous substitution of Al(III) for Si(IV) increased. At the same time, decreasing the Si/Al ratio created a greater proportion of aluminol groups (=AIOH) on the surface of the solid and so the surface became more positive; this is because silica has an isoelectric point of about pH 2 while alumina is around pH 9 (Parks, 1965). The current Ph.D. research investigates the influence of Fe/Al ratio on surface charge and cation sorption and since both Fe and Al carry the same charge (+3), isomorphous substitution is not expected to contribute to the charge carried by the oxides.

Fendorf et al (1992) used high resolution transmission electron microscopy to provide evidence for the formation of surface precipitates prior to bulk solution precipitation. These researchers suspended  $MnO_2$  (birnessite) and  $TiO_2$  (rutile) particles in a dilute solution of AI (III) and found precipitation of amorphous aluminium hydroxide (Al(OH)<sub>x</sub>) on the surface of the  $MnO_2$  but not the  $TiO_2$  particles suggesting that the presence of a nucleating surface alone is not sufficient to induce surface precipitation. These experiments were conducted at pH 5 where the birnessite is predominantly negatively charged (pH<sub>ZPC</sub> 2.8) while the rutile is positively charged (pH<sub>ZPC</sub> 6.7). Fendorf et al (1992) concluded that electrostatic attraction of Al<sup>3+</sup> to the negatively charged  $MnO_2$  surface sites may cause surface precipitation despite undersaturation in the bulk solution.

#### 8. Use of metal acetate solutions

The majority of previous metal-oxide studies have used non-interacting anions such as  $NO_3^-$  and  $CIO_4^-$  (Kinniburgh et al, 1976; McBride, 1978; Benjamin & Leckie, 1981; Dzombak & Morel, 1990) so as to avoid the potentially complicating effects of metal-ion complexation in solution although whether these indifferent ions are truly non-competitive has been questioned (Schulthess & Sparks, 1989). Low molecular weight aliphatic organic acids including acetic acid have been identified in soils (Hue et al, 1986) and groundwater (Lovley, 1991) while acetate is common in anaerobic sediments where the microbial oxidation of organic compounds is coupled with the reduction of Fe(III) and Mn(IV) oxides to

produce acetate (Lovley & Phillips, 1986). Landfill leachates are a complex mixture of organic and inorganic constituents including acetic acid at concentrations up to 10,000 mg /L (Budhu et al, 1991; Davies et al, 1996; Darkin et al, 1997). Acetate is the dominant organic species in many deep sedimentary basin fluids, particularly hydrothermal brines, at levels up to 10,000 mg /L although concentrations fall to around 300 mg /L as the temperature decreases from 100°C to 25°C (Lundegard & Kharaka, 1990; Fein, 1991). Aquifers contaminated with petroleum hydrocarbons may contain acetate at up to 10 mmol /L (600 mg /L) although 0.2 to 0.3 mmol /L is more typical (Vroblesky et al, 1997). The possibility of this ligand forming complexes with heavy metals such as Pb and Zn has been investigated to assess its role in the transport of metals during the deposition of metal ores (Hennet et al, 1988; Giordano, 1989) and beneath landfill sites (Shackelford et al, 1997), and it has been concluded that acetate could significantly enhance metal mobility by forming soluble complexes.

Researchers have used acetate to better represent the complexity of natural systems such as sewage sludge amended soils (Gao et al, 1997) and diffusion from landfill sites (Shackelford et al, 1997) or to buffer pH (Santillan-Medrano & Jurinak, 1975). Schulthess & McCarthy (1990) studied the adsorption of acetate (as sodium acetate) by an Al oxide and found a strong dependence on both pH and ionic strength; the decrease in adsorption with increasing ionic strength suggests that acetate has a relatively low affinity for oxide surfaces. Davies et al (1996) reported low adsorption of acetate by a montmorillonite clay although other researchers have reported that acetate may be weakly chemisorbed by Fe and Al oxides (McBride & Wesselink, 1988).

Additional research into the retention of heavy metals by oxides from complex solutions containing common organic ligands such as acetate (abbreviated to OAc<sup>-</sup> during this thesis) is necessary to fully assess the fate of these contaminants. The heavy metal cations in the current study demonstrate a high affinity for the oxide surface and it is anticipated that any small degree of acetate adsorption will not affect the availability of surface sites for metals. Furthermore it has been reported that cation adsorption is often minimally affected by anion adsorption (Anderson & Benjamin, 1990c). However, solution complexation is

likely to influence the speciation of the metal ions and therefore their adsorption by the oxides. The use of the acetate salts is intended to introduce competition for metals between surface hydroxyls and soluble ligands without inducing solidligand complexation.

#### 9. Modelling

Modelling of metal adsorption from suspensions containing a single oxide (e.g. Fe or Al oxide) has been extensively investigated (e.g. Kinniburgh et al, 1975, 1976; McBride, 1978, 1982; Benjamin & Leckie, 1981; compilation by Dzombak & Morel, 1990; Kooner, 1992; Tessier et al, 1996) as has adsorption onto natural soils and sediment (Oakley et al, 1981; Zachara et al, 1989; Wang et al, 1997). Adsorption onto binary suspensions of oxides has been less widely reported (Elliott & Huang, 1981; Ainsworth et al, 1989; Anderson & Benjamin, 1990b; Meng & Letterman, 1993b). The surface complexation-surface precipitation modelling approach (Farley et al, 1985) has been used successfully to describe the sorption of various heavy metals and anions by amorphous Fe (Dzombak & Morel, 1990) and Al oxides (Anderson & Benjamin, 1990b) and has recently been extended to sorption by incinerator ash (Meima & Comans, 1998) and bacteria (Daughney & Fein, 1998; Warren & Ferris, 1998). Since natural oxides are often co-precipitated mixtures containing both Fe and AI, it is necessary to evaluate the applicability of the surface complexation model to these more complicated binary oxide systems.

One of the barriers to successful modelling of natural systems has been the difficulty in accounting for the contribution of different soil (or sediment) components to the overall retention of metals. The most common experimental procedure for evaluating metal adsorption has been batch equilibrium tests such as used during this thesis, however this methodology cannot differentiate at the molecular level between adsorption onto for example, the Fe component of mixed Fe-Al oxides as opposed to the Al component. Since natural soils are a complex mixture of clays, amorphous and crystalline oxides (Fe, Al, Si, Mn), humic materials and other minerals (e.g. quartz, feldspar), evaluating the contribution of each soil component to the overall retention is problematic.

A common approach to overcoming this problem has been to assume that the multi-component system can be considered either as having an average collective metal-adsorption capability or can be represented as a collection of discrete pure solid phases (Anderson & Benjamin, 1990c). In the latter case, the metal-binding constants for individual soil components (e.g. Fe oxide, clays, humic materials) are evaluated based on synthetic materials and laboratory experiments, and then metal retention predicted based on the proportion of each component in the natural soil (Oakley et al, 1981; Davies-Colley et al, 1984; Radovanovic & Koelmans, 1998). This "adsorptive additivity" approach has met with some success, at least in qualitative terms, for natural systems but when applied to binary suspensions of oxides such as those used in this thesis, it has been less useful (Anderson & Benjamin, 1990c).

The adsorptive additivity approach assumes that no interaction occurs between the different soil components, but in practice, the reactive nature of amorphous oxides can lead to these materials forming coatings on clays and other particles. Previous research has found that the nature and stability of the association between oxides and other particles is dependent on their zero point of charge ( $pH_{ZPC}$ ) and the system pH (Yong & Ohtsubo, 1987; Ohtsubo et al, 1991).

Yong & Ohtsubo (1987) studied the stability of the bond between suspensions of amorphous Fe oxides (ferrihydrite) and kaolinite as a function of the pH at which the two materials were combined. They found that when the suspensions were mixed at low pH (e.g. pH 3; Fe oxide  $pH_{PC} = 8$ , kaolinite  $pH_{ZPC} = 4$ ) the ferrihydrite was precipitated onto the faces of the clay but not the edges. Kaolinite face surfaces carry a permanent negative charge due to small amounts of isomorphous substitution while at < pH 4, the pH-dependent edge sites are positively charged. The high  $pH_{ZPC}$  of the Fe oxide results in ferrihydrite particles being positively charged at low pH leading to a strong bond to the kaolinite faces. As the pH was raised, the ferrihydrite remained associated with the kaolinite face surfaces since the Fe oxide groups bonded to the kaolinite surface sites were not exposed to the solution and so did not become negatively charged. The net charge on the kaolinite-ferrihydrite particles would therefore be a combination of the kaolinite

permanent negative charge (which was partially masked by ferrihydrite) and the pH-dependent charge carried by the exposed Fe oxide surface hydroxyls. Conversely, if the initial suspensions were mixed above the pH<sub>ZPC</sub> of the Fe oxide (i.e. when both kaolinite and ferrihydrite were negatively charged) and then lowered, bonding between the two components did not begin until below pH 8, and it was not until < pH 4 that significant bonding occurred since the ferrihydrite had formed a separate stable phase. Although the measured specific surface area did not seem to be affected by the pH at which the suspensions were mixed, the net surface charge was. Suspensions mixed at high pH (separate ferrihydrite and kaolinite phases) had a net pH<sub>ZPC</sub> of 5.4 while those mixed at low pH (ferrihydrite coating the kaolinite surface) were observed to have a pH<sub>ZPC</sub> of 6.7. Yong & Ohtsubo (1987) speculated that the lower pH<sub>ZPC</sub> of the suspensions mixed at high pH could be ascribed to the presence of negatively charged kaolinite edge sites that are not coated by ferrihydrite.

Anderson & Benjamin (1990a, b, c) concluded that adsorptive additivity could not explain their results for the adsorption of various cations and anions by binary oxide suspensions containing AI, Fe and/or Si. They found that adsorption of Cd and Ag was inhibited when AI oxides were added to Fe oxide suspensions suggesting a reduction in the number or adsorptive strength of surface sites available to complex these metals (Anderson & Benjamin, 1990b). The best modelling fit to the experimental data was found when 76% of the Fe oxide surface was assumed to be replaced by the precipitation of AI oxide that blocked existing Fe surface sites. Based on changes in the particle size distribution, specific surface area and surface charge in addition to the adsorption results, Anderson & Benjamin (1990a) concluded that if Al oxide is present, all particle surfaces become enriched with AI while existing aggregated particles (e.g. Fe oxide) may be disaggregated to create smaller particles. Meng & Letterman (1993a) concluded that of the various kinds of interaction that can occur between component solids in mixed oxide suspensions (e.g. co-precipitation, formation of a uniform surface coating and heterocoagulation of particles), the dominant mechanism depends on both the identity and relative amounts of each oxide present. They found strong interactions between Al(OH)<sub>3</sub> and SiO<sub>2</sub> but only a weak or negligible one for Fe(OH)<sub>3</sub> and SiO<sub>2</sub>. The prevalence of AI enrichment is most likely due to the higher solubility of AI oxides as compared with Fe or Si oxides since this encourages minor dissolution and re-precipitation of AI(OH)<sub>8</sub>.

Ainsworth et al (1989) studied the adsorption of chromate onto pure crystalline Fe oxides (goethite) and a synthetic Al-substituted goethite (22 mole % Al). The presence of AI in the goethite reduced chromate retention and based on modelling results, these authors concluded that while AI surface sites did not contribute to chromate adsorption, the acid-base behaviour of the AI sites did influence chromate retention. Although Fe sites have chromate adsorption constants three orders of magnitude higher than AI, the protonation of AI sites at higher pH (than Fe) caused ion exchange with indifferent anions that significantly affected the net oxide surface charge. Ainsworth et al (1989) were able to successfully model their experimental results by assuming the oxide surface was partitioned into distinct Fe and AI sites which had different adsorption constants for protons and contaminants. These researchers also found that surface complexation constants derived from low chromate concentration experiments tended to over-predict retention at higher chromate concentrations. They attributed this to a violation of one of the basic assumptions underlying surface complexation modelling, namely that the free energy of adsorption does not increase with increasing adsorption density. As a result, Ainsworth et al (1989) recommended caution in utilising surface complexation constants obtained at low contaminant loading to model systems where significantly higher concentrations are present.

In their investigation of chromate adsorption by natural soils, Zachara et al (1989) found similar retention behaviour to that observed in synthetic Al-substituted crystalline Fe oxides (e.g. Ainsworth et al, 1989) with Fe sites being dominant in retaining chromate. However, the surface site density of soil oxides was considerably lower than synthetic oxides which significantly affected the success of surface complexation modelling. These authors concluded that the use of surface complexation constants obtained in laboratory studies for predictive or even interpretative modelling of natural systems must be undertaken with caution since natural materials may be less reactive than synthetic oxides.

Kanungo (1994) evaluated the adsorption of various metal ions by akaganeite (β-FeOOH) and concluded that the surface is heterogeneous with more than one surface site (e.g. high and low affinity sites). He reviewed the interfacial properties of various hydrous Fe oxides reported in the literature and found amorphous FeOOH pK<sub>a1</sub> values ranging from 1.68 to 5.6 and pK<sub>a2</sub> values from 8.96 to 10.7, illustrating the variability of this parameter. Kooner (1992) found that increasing the concentration of Cu caused the adsorption edge for goethite ( $\alpha$ -FeOOH) to be shifted to higher pH if the surface area was held constant. This was ascribed to the limited number of binding sites being available for Cu adsorption causing competition between Cu ions for individual sites. Increasing the surface area reduced the dependence of adsorption on Cu concentration, presumably due to lower competition for sites. No adsorption by goethite was observed below pH 4 from solutions containing up to 10 mg Cu /L (1.57 x 10<sup>4</sup> mol Cu /L).

While recognising that a continuum appears to exist between surface adsorption and bulk precipitation (Farley et al, 1985), it should be possible to identify the mechanisms controlling metal solubility by comparing experimental results with the metal solubility predicted by modelling of precipitation and surface complexation (adsorption). The current thesis will attempt to clarify the mechanisms involved in particle-particle interactions between the Fe and Al components of mixed amorphous oxides, as well as when these oxides are added to kaolinite clay. The nature of the retention mechanisms for Cu and Pb on various solids will be investigated from a qualitative rather than strictly quantitative perspective to assess the effects of contaminant concentration and variations in the sorbent material.

# CHAPTER 3 MATERIALS & METHODS

Reagent grade chemicals were used for all solutions. Labware was soaked in 6N HCl and then rinsed repeatedly with distilled water before use.

# 1. Synthesis of soils and amorphous oxides

#### 1.1 Amorphous oxides

Natural amorphous oxides containing only iron and aluminium are not obtained easily (Calmano et al, 1988; Yong et al, 1992a) and so laboratory-prepared amorphous materials were used in this study. Five amorphous oxides were synthesised with different proportions of iron and aluminium to reflect the variation encountered in natural systems. In addition to the "pure" aluminium ("Al") and iron ("Fe") end-members, three mixed oxides were prepared: "Fe-3Ai" (Fe/AI molar ratio = 0.3), "Fe-AI" (Fe/AI molar ratio =1), "3Fe-AI" (Fe/AI molar ratio = 3). The molar concentration ((moles Fe + moles AI) / g of oxide) was approximately equal for all five synthetic oxides. Natural amorphous oxides may contain oxides, hydrous oxides and oxyhydroxides and since this study did not attempt to make such a distinction, the term "oxides" should be considered to include all possible amorphous oxide formulae.

#### 1.1.1 Oxide synthesis

Batches of each oxide were synthesised by adding sufficient 1M NaOH to a continuously stirred solution containing 0.2 moles of Fe (as  $Fe_2(SO_4)_3.4H_2O$ ) and/or AI (as  $AI_2(SO_4)_3.18H_2O$ ) per litre to raise the solution to pH 7.1±0.1 (modified from Schwertmann & Cornell, 1991). The suspension was stirred for one hour with a magnetic stir-bar, filtered through two sheets of Whatman No. 42 filter-paper and then rinsed repeatedly with distilled water until the concentration of sodium and sulphate in the filtrate was less than 10 mg /L. The precipitate was air-dried until a constant weight was attained, and lightly ground to pass a 300  $\mu$ m sieve. Various solution volumes were tested in order to maximise the

production from each batch while respecting the limitations of available equipment. The volume utilised for the majority of batches was 1.15 litres of Fe-Al solution plus 550 - 625 mL of NaOH depending on the particular oxide being synthesised. This method produced approximately 25 g of air-dried oxide per batch.

The amorphous nature of the synthetic oxides was confirmed by X-ray diffraction using a Siemens D-500 X-ray diffractometer in accordance with the techniques described by Starkey et al (1984).

#### 1.1.2 Oxide digestion and composition

The concentrations of Fe and AI in the synthetic oxides were determined with a Perkin Elmer Model 3110 atomic absorption spectrophotometer after digestion in 6N HCI. Appropriate blank and standard solutions were regularly prepared by dilution of Fisher Scientific 1000 mg /L reference solutions. Measures were taken to avoid interference by matrix and other effects.

The concentration of sulphate was measured after digestion in 6N HCI using the standard turbidimetric method (Method 426C, American Public Health Association, 1985) in which  $BaCI_2$  is added to the sample and  $BaSO_4(s)$  precipitates. A Hach Model 2100A Turbidimeter/Nephelometer was used to measure the turbidity of the sample by comparison with known standards.

#### 1.2 Kaolinite and kaolinite plus oxides (synthetic clays)

The control material used in this study was a kaolinite clay (hydrite PX from the Georgia Kaolin Company) previously used for soil-amorphous oxide and contaminant-soil interaction studies (e.g. Yong & Ohtsubo, 1987; Yong et al, 1992b; Yong et al, 1993). Hydrite PX kaolinite was chosen because it is a relatively pure mineral containing no carbonates or organic matter (Yong et al, 1993) it has low amounts of amorphous oxides and exhibits pH-dependent surface charge.

To assess the influence of amorphous oxides on the physico-chemical properties of kaolinite, the individual amorphous oxides were added to kaolinite to create five synthetic soils designated as "K-AI" (kaolinite plus AI oxide), "K-Fe3AI" (kaolinite plus Fe3AI oxide), "K-FeAI" (kaolinite plus FeAI oxide), "K-SFeAI" (kaolinite plus FeAI oxide), "K-3FeAI" (kaolinite plus 3FeAI oxide), and "K-Fe" (kaolinite plus Fe oxide). The target concentration of oxide was 0.1 moles (AI+Fe) / 100g of soil so as to ensure a constant concentration of AI+Fe (in moles). For simplicity, these synthetic soils will sometimes be referred to simply as "soils" or "clays" during this thesis, however the reader is reminded that these are laboratory synthesised materials and not natural soils.

## 1.2.1 Kaolinite plus oxide ("artificial soil") synthesis

The kaolinite and oxides were combined in the following manner: 150 grams of air-dried kaolinite was suspended in 1.5 litres of distilled water and stirred. 15 grams of the appropriate air-dried oxide was suspended in 150 mL of distilled water and mixed with a magnetic stirring device. After one hour of separate mixing, the two suspensions were combined and stirred for 24 hours before being poured into a wide tray and allowed to air-dry. The stirring rate was kept constant and as low as possible while preventing deposition of particles. Once a constant weight had been achieved (approximately one week), the soil was lightly ground and repeatedly mixed to ensure uniform distribution of the oxide.

#### 1.2.2 Amorphous oxide content

The amorphous oxide content of the kaolinite and artificial (kaolinite plus oxide) soils was determined by extraction with 0.2M ammonium oxalate-oxalic acid at pH 3 (modified from Kersten & Förstner, 1986; and Sheldrick, 1984). In summary, 0.5g of soil was shaken with 20 mL of extracting solution for 4 hours in a polyethylene tube in darkness. After this shaking period, the suspension was immediately centrifuged at 10,000 rpm for 15 minutes following which the supernatant was decanted. Al and Fe were measured by flame atomic absorption spectrophotometry using a Perkin Elmer Model 3110 machine.

# 2. Physico-chemical characterisation of soils and oxides

The following tests were carried out to assess the physico-chemical properties of the amorphous oxides, synthetic soils and kaolinite.

#### 2.1 Specific Surface Area

The specific surface area was evaluated using ethylene glycol monoethyl ether (EGME) saturation in accordance with the methods of Eltantawy and Arnold (1973) and Sheldrick (1984). These methods are based on the principle that solid materials will absorb a monomolecular layer of a polar liquid such as EGME. "Specific surface" signifies that the area per unit weight of soil (e.g. m<sup>2</sup> / g soil) is being measured (Sheldrick, 1984). Approximately 0.6 g of air-dried soil or oxide was placed in a desiccator over  $P_2O_5$  and repeatedly evacuated with a vacuum pump until a constant weight was achieved. Sufficient EGME was then added to cover the soil and after a 30 minute equilibration period, the sample was returned to the desiccator over anhydrous CaCl<sub>2</sub> and repeatedly evacuated until a constant weight was reached. Measurements were conducted in triplicate on the artificial soils and kaolinite, and in duplicate on several individual batches of each amorphous oxide. Since this method for measuring surface area involves airdrying, the contacts and inter-relationships between particles could be modified (Yong & Ohtsubo, 1987), however in the absence of quantitative information about the effects of these possible modifications, and due to the widespread use of this method, the results are assumed to be valid.

# 2.2 Particle size distribution

The particle size distribution was estimated using two methods. The five oxide samples were dry-sieved in accordance with ASTM method D422-63. Since all the oxides had previously been ground to pass a 300  $\mu$ m sieve (section 1.1.1), the following sieve sizes were used: 150  $\mu$ m, 125  $\mu$ m, 90  $\mu$ m, 75  $\mu$ m and 53  $\mu$ m. Columns of sieves were shaken with a mechanical sieve shaker for 20 minutes and the residue on each sieve was weighed. Particles passing the 53  $\mu$ m sieve were investigated with the pipette method (Black, 1965; McKeague, 1976). Due

to the small amount of oxide produced in each batch, 6 g of oxide was used in the sieve test and the 2-3 g passing the 53 µm sieve was transferred to the pipette test. For the synthetic soils and kaolinite, the pipette method was conducted prior to sieving. 10 g of air-dried soil was suspended in 190 mL distilled water to which 10 mL of 2% sodium hexametaphosphate was added as a dispersing agent. This suspension was shaken for 16 hours on a horizontal shaker to ensure complete dispersion of particles. The samples were then transferred from polyethylene containers to 1000 mL glass cylinders, the suspension volume made up to 1000 mL and the samples allowed to equilibrate for 10 minutes. A wooden hand stirrer was used to vigorously agitate the suspension for one minute, after which the time was noted. At appropriate intervals determined by the specific density of each soil or oxide and Stokes Law. a closed pipette was lowered 10 cm into the suspension and a 25 mL sample withdrawn in about 15 seconds. The pipette was discharged into a pre-weighed glass container, then rinsed with distilled water into the same container which was placed in an oven at 60°C for 48 hours. For the synthetic soils and kaolinite, aliquots were extracted at time intervals corresponding to a particle diameter of 50, 20, 5 and 2  $\mu$ m. For the oxides, aliquots were taken for particle diameters of 20, 5 and 2  $\mu$ m since the soil used in the pipette test had already passed a 53 um sieve. The mass of sodium hexametaphosphate included in each aliquot was calculated and subtracted from the mass of soil removed in each pipette. Following the conclusion of this experiment, the synthetic soil and kaolinite suspensions were washed through three sieves (150 µm, 90 µm, 75 µm) with distilled water. The residue retained on each sieve was oven-dried at 60°C for 48 hours and weighed. This temperature was used to avoid removing structural water from the amorphous oxide.

# 2.3 Specific Gravity

The specific gravity of each oxide and the kaolinite was determined following ASTM Method D854-92. *Method A - Procedure for Oven-Dry Specimens* was used with 5 g of air-dry samples and a 500 mL pycnometer. It was assumed that the specific gravity of the synthetic soils (kaolinite plus oxides) was equivalent to

that of the kaolinite alone since these clays contained only 10% oxide (by weight).

#### 2.4 Cation and Anion Exchange Capacities

The cation exchange capacity (CEC) and anion exchange capacity (AEC) were measured as a function of pH using the procedure described by Hendershot et al (1993) in which the soil is saturated with  $Ca(NO_3)_2$  prior to extraction with KCl over a range of pH values. The BaCl<sub>2</sub> CEC method (Hendershot et al, 1993) was attempted on the Fe and Al oxides but since the suspension pH was below pH 5, very low CEC values were found and this method was not used on the other oxides, kaolinite nor the synthetic soils.

#### 2.5 Potentiometric titrations

The variation of surface charge as a function of pH and ionic strength was investigated using standard potentiometric titration methods (adapted from Hayes et al, 1991; Raij & Peech, 1972; Yates & Healy, 1975; Cornell et al, 1975; Evans et al, 1979; Stumm & Morgan, 1996; Davis & Kent, 1990; Westall & Hohl, 1980). A known mass of soil is suspended in a measured volume of an inert electrolyte at three different ionic strengths. Aliquots of acid or base are added at fixed time intervals following which the pH of the suspension is measured. The apparent surface charge is calculated from the difference between the volumes of acid or base added to the suspensions and blank solutions (no soil) at each pH (Spark et al, 1995a).

One hundred millilitres of either 0.01M, 0.1M or 1M potassium nitrate (KNO<sub>3</sub>) was stirred with a magnetic Teflon covered stir-bar at the lowest rate necessary to ensure complete mixing and avoid particle settling. All containers were sealed with Parafilm<sup>™</sup> while high purity nitrogen gas was continuously bubbled through the solution to expel carbon dioxide which could otherwise buffer added base and acid. The nitrogen flow rate was kept sufficiently low that there could be no loss of soil from bubbling. After a two hour equilibration period, the pH was measured with an Orion combination pH electrode. The pH electrode was re-

calibrated with fresh buffer solutions (pH 4 and pH 7) before each titration. 0.5 g of soil was added and mixed for 15 minutes after which the pH was again measured. 1M hydrochloric acid (HCl) and 1M sodium hydroxide (NaOH) were used as titrants. Separate suspensions were employed for acid and base titrations. The suspensions were titrated with acid or base from pH 3 to pH 9.5 with aliquots of titrant being added at five minute intervals immediately after the pH was measured. Blank solutions to which no soil was added were treated in the same manner. It is generally considered that sorption and desorption of protons on oxides involves an initial fast step (minutes) followed by a much slower second step that has been ascribed to exchange processes within the interior of oxide particles (Dzombak & Morel, 1990). Since the complexation of protons with surface hydroxyl groups was the focus of this study, a five minute equilibration period was chosen.

The potentiometric titration measurements were used to provide information on the particle surface charge, nature and number of surface hydroxyl groups as well as being used to aid in the characterisation of the different soils and oxides during the contaminant modelling with FITEQL (Herbelin & Westall, 1996).

#### 2.6 Suspension pH

The pH of a 1:15 suspension of oxide in distilled water was measured with an Orion combination pH electrode. The pH of a 1:30 suspension in 0.005M  $Ca(NO_3)_2$  was measured with an Orion combination pH electrode during the cation exchange capacity test.

## 3. Contaminant experiments

#### 3.1 Batch tests

The ability of the soils to retain Pb or Cu from single metal solutions as a function of pH was studied by the use of 24 hour suspension tests at a soil:solution ratio of 1:30. Stock heavy metal solutions were prepared from either lead acetate  $(Pb(CH_3COO)_2.3H_2O)$  or copper acetate  $(Cu(CH_3COO)_2.H_2O)$ . These stock

solutions were diluted with distilled water prior to addition to the soil to obtain the following total metal concentrations: 0.5 mmoles /L (103.6 mg Pb /L or 31.8 mg Cu /L); 2.5 mmoles /L (518 mg Pb /L or 158.9 mg Cu /L); 5 mmoles /L (1036 mg Pb /L or 317.7 mg Cu /L); 25 mmoles /L (5180 mg Pb /L or 1588.7 mg Cu /L).

As noted earlier (Section 3, Chapter 2), most previous studies have been conducted at much lower metal concentrations than are presented here. Metal concentrations typically range from  $10^{-8}$  to  $10^{-4}$  M (cf. 5 x  $10^{-4}$  to 2.5 x  $10^{-2}$  M in this study), however these studies have generally used low amorphous oxide concentrations, e.g.  $10^{-4}$  to  $10^{-3}$  mol Fe /L (Dzombak & Morel, 1990) which is equivalent to 90 mg /L. In this thesis, the oxide concentration was 33.3 g /L (ca. 0.3 mol (AI+Fe) /L), and so when calculated on a sorbate / sorbent basis this study is broadly comparable with these previous studies; this current study employed a sorbate / sorbent ratio of 0.0017 to 0.085, while literature ratios typically range from 0.005 to 1, although ratios up to 10 have been used (Dzombak & Morel, 1990). In contrast, experiments with crystalline oxides or soils are often conducted at a 1:10 soil/solution ratio; e.g. 100 g /L (ASTM, 1987).

Batch tests were carried out over a three year period and so several sets of stock solutions had to be prepared to avoid any changes in concentration (e.g. due to adsorption onto container walls) that might occur if solutions were stored for long periods (months). The polyethylene tubes used for batch tests were chosen since metal adsorption onto container walls during the 24 hour period of the experiments was found to be insignificant. Each set of stock solutions was analysed using a Perkin Elmer 3110 atomic absorption spectrophotometer to confirm the actual metal concentrations; the range of concentrations is given in Tables 3.1 & 3.2 for single metal solutions and Tables 3.3 & 3.4 for the mixed metal solutions:

Target (mmoles /L)	0.5	2.5	5	25	
Actual (average)	0.46	2.39	4.84	23.78	
Standard deviation	0.04	0.13	0.47	1.10	
Range (mmoles /L)	0.40 - 0.56	2.20 - 2.76	4.32 - 5.85	21.80 - 26.67	
% range	-15/+20	-8/+15	-11/+21	-8/+12	
No. of solutions	18	17	18	20	
Table 3.1. Cu concentration, single metal solutions.					

	Pb					
Target (mmoles /L)	0.5	2.5	5	25		
Actual (average)	0.52	2.67	5.37	26.51		
Standard deviation	0.04	0.11	0.22	0.96		
Range (mmoles /L)	0.48 - 0.60	2.50 - 2.89	5.03 - 5.78	25.25 - 30.22		
% range	-8/+16	-6/+8	-6/+8	-5/+7		
No. of solutions	19	19	19	19		
Table 3.2. Pb conce	ntration, singl	e metal solutio	DIS.	<u></u>		

	Cu (Cu+Pb)					
Target (mmoles /L)	0.5	2.5	5	25		
Actual (average)	0.49	2.51	4.81	24.05		
Standard deviation	0.03	0.18	0.09	0.72		
Range (mmoles /L)	0.46 - 0.57	2.37 -3.01	4.74 - 5.04	22.30 - 24.77		
Range (%)	-7/+17	-5/+20	-2/+5	-7/+3		
No. of solutions	11	11	11	11		
Table 3.3. Cu conce	ntration, (Cu+	Pb) solutions.	·			

	Pb (Cu+Pb)					
Target (mmoles /L)	0.5	2.5	5	25		
Actual (average)	0.54	2.65	5.34	26.55		
Standard deviation	0.05	0.08	0.18	0.98		
Range (mmoles /L)	0.47 - 0.66	2.55 - 2.81	5.04 - 5.63	25.10 - 28.07		
Range (%)	-13/+23	-4/+6	-6/+5	-5/+6		
No. of solutions	11	11	11	12		
Table 3.4. Pb concentration, (Cu+Pb) solutions.						

Batch suspension tests were conducted in closed polyethylene tubes containing 0.5 g solid and 15 mL contaminant solution. The pH of the contaminant solutions was adjusted below pH 5 by acidification of the stock solutions with acetic acid prior to addition to the solid; above pH 5, 0.1 or 0.01M NaOH was added to the suspension after the heavy metals for a final solid : solution ratio of 1:30. The tubes were shaken for 24 hours on a horizontal shaker followed by centrifugation at 10,000 rpm for 10 minutes to separate the supernatant liquid. The pH was measured using an Orion combination pH electrode following which the supernatant was acidified to below pH 2 with concentrated nitric acid. All samples were analysed using a Perkin Elmer Model 3110 atomic absorption spectrophotometer with appropriate standards, after dilution with distilled water if necessary. The total number of batch tests conducted on each material with each contaminant is given in Table 3.5. Blank tests containing no oxide or synthetic clay were conducted to assess retention by tube walls. Separate precipitation

tests (see Section 3.3, this Chapter) were carried out to investigate precipitation as a function of pH in the absence of soil.

One of the most basic sources of error in speciation studies is in the separation of solute and solid species; adsorption onto filter material can cause losses as high as 40% even for coarse filters (Mattigod, 1995) and so centrifuge techniques were used throughout this study.

Oxide or soil	Cu	Pb	Cu & Pb	Total		
Fe	71	73	45	189		
3FeAl	59	74	59	192		
FeAl	63	79	62	204		
Fe3Al	57	76	57	190		
AI	71	72	57	200		
K-Fe	39	37	46	122		
K-3FeAl	36	37	45	118		
K-FeAl	36	38	45	119		
K-Fe3Al	38	43	45	126		
K-AI	47	53	46	146		
Kaolinite	90	96	90	276		
Total	607	678	597	1882		
Table 3.5. Total number of batch tests conducted, by contaminant and solid.						

## 3.2 Oxalate extraction tests

In an effort to investigate the contribution of the oxide component of the synthetic soils to heavy metal retention, the oxalate extraction test was run after some of the batch tests. After completion of the 24 hour batch test and centrifugation, the supernatant liquid was separated by decantation. The soil was resuspended in 10 mL of distilled water, centrifuged and the supernatant liquid discarded. The oxalate extraction test described in section 1.2.2 (this chapter) was conducted and the concentration of Cu, Pb, Fe and AI extracted was measured with a Perkin Elmer Model 3110 atomic absorption spectrophotometer. Extraction efficiency was very poor for Pb and provided little useful information for Cu so the extraction test was only carried out on about half the synthetic soil and kaolinite batch tests and the results have not been presented. This extraction test is commonly used during sequential chemical extractions yet the poor efficiency observed in this study underlines the need to be cautious if the results of such tests are used to investigate the distribution (speciation) of contaminants.

# 3.3 Precipitation tests

In order to assess the influence of pH on Cu and Pb precipitation, a series of tests were conducted in the absence of oxide or clay. Stock solutions were prepared at concentrations of 0.5, 2.5, 5 and 25 mmoles /L. The pH was adjusted by adding an appropriate amount of 0.1M or 1M NaOH plus distilled water to a glass tube containing 10 mL of contaminant solution to give a final volume of 15 mL. The tubes were shaken for 24 hours on a horizontal shaker followed by centrifugation at 4,000 rpm for 20 minutes to separate the supernatant liquid. This supernatant was filtered through 1.1  $\mu$ m glass fibre filter paper (Ahlstrom Filtration Grade 161, Scientific Specialties Group), the pH was measured with an Orion combination pH electrode following which the sample was acidified to below pH 2 with concentrated HNO<sub>3</sub>. This methodology was used since the high-speed centrifuge utilised in the batch tests was not available.

# CHAPTER 4 PHYSICOCHEMICAL PROPERTIES

# 1. Physicochemical properties of the amorphous oxides

# 1.1 General description of the oxides.

The five oxides were visually distinct both in terms of colour and appearance. The Fe oxide was dark brown and, after air-drying, formed small hard aggregated particles that were difficult to grind sufficiently to pass through the  $300\mu$ m sieve. The 3FeAI oxide (Fe/AI ratio = 3) was similar in appearance and only slightly lighter in colour while the FeAI oxide (Fe/AI ratio = 1) was much paler, easier to grind after air-drying and appeared more voluminous. The Fe3AI oxide (Fe/AI ratio = 0.3) was very pale brown in colour, easy to grind and was visually less dense. The AI oxide was a bright white, soft and fluffy solid. Results from X-ray diffraction tests confirmed the amorphous nature of the oxides.

# 1.2 Oxide Composition

Table 4.1 shows that the total molar concentration of AI and Fe per gram is similar for all of the synthetic oxides while the sulphate concentration increases as the Fe/AI ratio decreases. The standard deviation (s.d.) is shown in parentheses for each oxide.

Oxide	mol Fe / g (s.d.)	mol Al / g (s.d.)	mol (Ai+Fe) / g (s.d.)	Molar Fe/Al ratio	mol SO <sub>4</sub> <sup>2</sup> / g (s.d.)	(Fe/Ai) <sub>T</sub> / S <sub>T</sub> (molar)		
Fe	8.75 (0.59)	0	8.75 (0.6)	-	0.53 (0.14)	50		
3FeAl	6.81 (0.33)	2.21 (.05)	9.02 (0.3)	3	0.83 (0.10)	32		
FeAl	4.59 (0.42)	4.34 (0.22)	8.93 (0.3)	1	1.08 (0.05)	25		
Fe3Al	2.18 (0.06)	6.50 (0.21)	8.68 (0.2)	0.3	1.33 (0.03)	20		
AI	0	8.78 (0.33)	8.78 (0.6)	-	1.65 (0.04)	16		
Table 4	Table 4.1. Oxide composition mol / g (x10 <sup>-3</sup> ) and molar ratio.							

Literature values for natural and synthetic oxide composition are often reported as mg/kg and/or weight %. To allow comparison with the literature, Table 4.2 presents the digestion data in this form. Another common reporting method is to assume a particular chemical formula for the oxide (e.g.  $Fe_2O_3$ , FeOOH,  $Al(OH)_3$ ,  $Al_2O_3$ ); since the materials used in this thesis are amorphous oxides they are likely to have the general formula  $X(OH)_3$  (where X is Al or Fe) but without more detailed chemical analysis than was possible here, it was determined that it would not be appropriate to assume a particular formula. The reader is cautioned to be careful in comparing these values to literature results.

The sulphate concentration gradually decreases as the Fe/AI ratio increases suggesting that the  $SO_4^{2^{-}}$  ion preferentially bonds to AI sites; it is within the range reported for natural oxides in stream sediments draining mine waste areas (e.g. 5.6 - 14.1 wt %, Bigham et al, 1990; Webster et al, 1998).

Oxide	mg Fe / kg (s.d.)	mg Al / kg (s.d.)	mg SO4 <sup>2*</sup> / kg (s.d.)	Fe (wt. %)	Al (wt. %)	SO4 <sup>2.</sup> (wt. %)
Fe	488 (32)	0	51 (13)	49	0	5.1
3FeAl	380 (18)	60 (1)	80 (9)	38	6	8.0
FeAl	256 (11)	117 (5)	103 (5)	26	12	10.3
Fe3Al	122 (4)	175 (2)	128 (3)	12	18	12.8
AI	0	237 (14)	158 (4)	0	24	15.8
Table 4	.2. Oxide com	position, mg/	kg and wt. %	(x 10 <sup>3</sup> ).	<b>4</b>	L

The formulae of the oxides in this study (Table 4.3) was calculated by summing the percentage of Fe, AI and  $SO_4^{2-}$  and assuming that hydroxyl (OH<sup>-</sup>) ions constitute the remainder. Bearing in mind the caution given previously, these should be considered only as approximate chemical formulae. It is likely that some of this remainder is water (H<sub>2</sub>O) or simply O<sup>2-</sup> ions, but the error associated with the hydroxyl assumption should not be too great. Quantification of the water and hydroxyl content was not possible given the equipment available, while some researchers contend that it is not possible to distinguish between structural water

Oxide	Estimated chemical formulae				
Fe	Fe <sub>17</sub> SO <sub>4</sub> (OH) <sub>51</sub>				
3FeAl	Fe <sub>8</sub> Al <sub>3</sub> SO <sub>4</sub> (OH) <sub>34</sub>				
FeAl	Fe <sub>4</sub> Al <sub>4</sub> SO <sub>4</sub> (OH) <sub>29</sub>				
Fe3Al	Fe <sub>2</sub> Al <sub>5</sub> SO <sub>4</sub> (OH) <sub>28</sub>				
AI	Al <sub>5</sub> SO <sub>4</sub> (OH) <sub>22</sub>				
Table 4.3.	Estimated oxide chemical formulae.				

(including OH) and adsorbed water for amorphous oxides (Schwertmann & Cornell, 1991).

Bigham et al (1996) studied the precipitation of an iron-sulphate-hydroxide solid. schwertmannite ( $Fe_{B}O_{B}(OH)_{B}SO_{4}$ ), from acid mine waters and from synthetic solutions containing 0.02 mol of Fe and SO<sub>4</sub><sup>2</sup> /L. The composition of the resultant solids depended on the pH at which precipitation occurred with schwertmannite forming at pH 2.8 to 4.5 and ferrihydrite ( $Fe_5HO_8.4H_2O$ ) or ferrihydrite plus goethite ( $\alpha$ -FeOOH) at pH 6.5 or higher. The Fe<sub>T</sub>/S<sub>T</sub> molar ratio can also used to differentiate between these three possible iron-bearing minerals since typical  $Fe_T/S_T$  values for schwertmannite are 4.6 to 8 (Bigham et al, 1990). Since ferrihydrite and goethite can adsorb SO4<sup>2</sup>, particularly below the pH<sub>ZPC</sub> (Courchesne & Hendershot, 1989), goethite particles (surface area =  $80 \text{ m}^2/\text{g}$ ) containing no structural SO<sub>4</sub><sup>2</sup>, that are fully covered with adsorbed SO<sub>4</sub><sup>2</sup> have a maximum  $Fe_T/S_T$  ratio = 50 while ferrihydrite (surface area = 200 to 600 m<sup>2</sup>/g) should have a lower  $Fe_T/S_T$  (Bigham et al. 1990). The (Fe+AI)<sub>T</sub>/S<sub>T</sub> molar ratios in this study range from 49.7 (Fe) to 16.0 (AI) which suggests the Fe oxide should be considered as a sulphate-bearing ferrihydrite rather than a schwertmannite; this is consistent with the work of Bigham et al (1996) since these oxides were precipitated at pH 7.1±0.1. Süsser & Schwertmann (1991) state that amorphous Al hydroxy-sulphates precipitates would have an OH/AI ratio < 3. The oxides in the present study have OH/(AI+Fe) ratios ranging from 3.1 to 4 further supporting the speculation that these oxides are sulphate-bearing amorphous hydroxides of Fe and AI rather than hydroxy-sulphates.

# 1.3 Specific Gravity

The specific gravity of the each of the oxides is shown in Table 4.4.

Oxide	Specific Gravity			
Fe	3.57			
3FeAl	3.12			
FeAl	2.17			
Fe3Al	2.35			
AI	2.27			
Table 4.4. S	pecific gravity of the oxides.			

The Fe and AI results compare well with literature values (e.g. goethite ( $\alpha$ -FeOOH) = 3.3 to 4.3; gibbsite (AI(OH)<sub>3</sub>) = 2.3; Jackson, 1979) while the 3FeAI and Fe3AI oxides have intermediate values between their Fe and AI components. The FeAI oxide is less dense than expected; a possible explanation is presented in section 2 (this chapter) in conjunction with the specific surface area results.

# 1.4 Specific Surface Area

All five amorphous oxides have high specific surface areas (Figure 4.1); the standard deviation and 95% confidence intervals are shown in Table 4.5. The measured surface area of the oxides tends to increase as the proportion of iron increases although the maximum value is obtained for the FeAI oxide (Fe/AI molar ratio = 1). The increases in measured surface area from AI to Fe3AI, and from 3FeAI to Fe are not statistically significant, however there is a significant difference between the low Fe/AI ratio oxides (AI, Fe3AI) and the high Fe/AI oxides (3FeAI, Fe) as well as between FeAI (Fe/AI = 1) and the other four oxides.

Oxide		Measured	<b>Calculated values</b>				
N sai	No. of samples	95% confidence interval	Standard deviation	Mean			
Fe	8	327 - 355	17	341	341		
3FeAl	5	322 - 372	20	347	330		
FeAl	6	368 - 437	33	402	307		
Fe3Al	9	249 - 297	31	273	277		
AI	9	226 - 292	43	259	259		
Table 4.5. Specific surface area of the oxides. All values in m <sup>2</sup> /g.							

Figure 4.1 shows both the measured surface area and the value calculated from the Fe/AI ratio plus the specific surface area of the "pure" AI and Fe oxides. The calculated values are those expected if the Fe and AI components existed completely independently in the mixed oxides (i.e. no interaction between the AI and Fe components). The surface area of the FeAI is significantly higher than calculated while the values for the other two mixed oxides are within the 95% confidence intervals.

The measured specific surface area results suggest that for  $Fe/AI \neq 1$ , the mixed oxides behave in effectively the same manner as either the AI or Fe component since there is no significant difference between AI and Fe3AI or Fe and 3FeAI. The FeAI oxide exhibits a markedly increased surface area than was calculated by assuming no interaction between the Fe and AI components.



Figure 4.1. Oxide Specific Surface Area (m<sup>2</sup> / g).

Other researchers have also found that amorphous Fe oxides exhibit greater surface area than AI oxides (Anderson & Benjamin, 1990a, b; Meng & Letterman,

1993a). Limited work has been reported on the specific surface area of mixed amorphous Fe-Al oxides but similar results for a co-precipitated Fe-Al oxide (Fe/Al molar ratio = 1) were explained by proposing that soluble  $AI(OH)_3$  species interfere with the formation of large Fe oxide particles and thus increase the total surface area (Anderson and Benjamin, 1990a).



Figure 4.2. Oxide particle size distribution (% finer by weight).

### 1.5 Particle Size Distribution

The particle size distribution results presented in Figure 4.2 show that there is a general trend whereby increasing the Fe/Al ratio is accompanied by a finer particle size. This trend is not clearly maintained for the silt and clay sized particles however, since the FeAl oxide has the smallest proportion of particles less than 50  $\mu$ m (Figure 4.3). The high specific surface area demonstrated by these materials is indicative of a very fine particle size yet the data here do not support this with no samples containing more than 5% clay (Figure 4.3, < 2 $\mu$ m). Furthermore, there is no correlation between particle size and specific surface area demonstrated area. Kaolinite is shown for comparison in Figure 4.2; this mineral has greater

than 90% clay-sized particles (< 2  $\mu$ m) yet as will be presented in Section 3.3 (this Chapter), this material has a significantly lower specific surface area than any of the oxides.



Figure 4.3. Oxide particle size distribution (% of total).

One reasonable explanation for this apparent contradiction between high surface area and low clay fraction is that the oxides are present as aggregated particles. As noted in the General Description (Section 1.1, this Chapter), air-drying of the synthetic oxides resulted in the formation of aggregates that were lightly ground prior to their characterisation and use. The particle size results suggest that the grinding stage simply breaks up the larger aggregates but that smaller assemblages of individual particles remain. Amorphous hydrous oxides of Fe and AI have previously been shown to possess extensive *microporosity*, where *micropores* are defined as having diameters less than 2 nm (Davis & Kent, 1990). It is therefore proposed that the precipitation of the amorphous oxides involves the development of an open (porous) structure of loosely linked small particles whose internal surface area is accessible to the EGME molecules used to evaluate the specific surface area. However the larger aggregates formed during air-drying are sufficiently stable that they remain present through

subsequent grinding, and so the particle size distribution test reports a small proportion of clay particles. Since EGME is a larger molecule (radius = ca. 0.35 nm, Eltantawy & Arnold, 1975) than either  $Pb^{2+}$  or  $Cu^{2+}$  (ionic radii = 0.124 and 0.072 nm respectively, Alloway, 1995), it seems reasonable to assume that if the internal surfaces are accessible to EGME, they will also be available for interaction with heavy metals.

## 1.6 Cation Exchange Capacity

The cation exchange capacity (CEC) is presented in Figure 4.4. The steep increase in CEC as a function of pH is similar for all five oxides; the maximum CEC measured is approximately 0.2 to 0.25 meq /g. Between pH 6.3 and pH 7, the CEC decreases in the order Fe > 3FeAI > AI > Fe3AI > FeAI; this pH range is chosen for discussion since below pH 6 the CEC is zero for the AI and Fe3AI oxides. The sharp increase in cation exchange capacity as the pH increases demonstrates the readiness of the oxides' surface hydroxyl groups to deprotonate as the concentration of protons in solution decreases. The charge carried by the amorphous oxides is supplied only by pH-dependent hydroxyl groups that are distributed across the entire oxide surface.

The cation exchange capacity evaluates the ability of soils to attract cations to negatively charged soil surfaces due solely to electrostatic attraction and so could provide some insight into the attraction of soil surfaces for heavy metal cations. Figure 4.4 suggests that the Fe oxide should start to retain Pb and Cu cations above pH 4.5, while the other oxides should not retain these contaminants until the solution pH is greater than pH 5.5 to 6. If ion exchange is the dominant mechanism of Pb and Cu retention, the CEC results suggest that at pH 6.5, the order of heavy metal retention should be Fe > 3FeAl > Al > Fe3Al > FeAl, however as will be discussed in Chapter 5, neither this order nor the pH of initial metal retention is followed completely.

# 1.7 Anion Exchange Capacity

Figure 4.5 illustrates the anion exchange capacity (AEC) which evaluates the positively charged sites on the soil surface as a function of pH. As expected, the AEC decreases as the pH increases reflecting the de-protonation of surface hydroxyl groups and the consequent reduction in positively charged surface hydroxyl groups. In the range pH 4 to 6, the AEC decreases in order FeAl > Al > Fe3Al > 3FeAl > Fe which is almost the opposite to that found for the CEC. Since this study was mainly concerned with the retention of cations, this aspect of the work has not been further explored.

# 1.8 Net Surface Charge and Point of Zero Charge

Subtracting the anion exchange capacity from the cation exchange capacity at any given pH value allows calculation of the net charge carried by the surface (Sposito, 1984) as illustrated in Figure 4.6. Table 4.6, column A lists the points of zero net charge (pH<sub>ZPC</sub>) for the oxides estimated from the ion exchange experiments. The presence of sulphate as a structural impurity in AI and Fe oxides is reported to lower the pH<sub>ZPC</sub> (Parks, 1965; Greenland & Hayes, 1978); this would explain the lower values for the oxides than expected from literature reports (e.g. pH 7 to 8 for amorphous Fe oxides (nitrate salt); pH 9 to 9.5 for amorphous AI oxides (nitrate salt); Kinniburgh et al, 1976; Anderson & Benjamin, 1990a, b). The mechanism responsible for lowering the pH<sub>ZPC</sub> is similar to that occurring during the specific adsorption of anions on the oxide surface. Specific adsorption of anions lowers the pH<sub>ZPC</sub> by increasing the negative charge on the oxide surface thus requiring increased proton adsorption (i.e. lower pH) to neutralise the surface charge (Cornell et al, 1975; Bohn et al, 1979; Sparks, 1986; Courchesne & Hendershot, 1989; Dzombak & Morel, 1990). The structural incorporation of  $SO_4^{2-}$  should have a similar effect since the =X-( $SO_4^{2-}$ )-H surface group is expected to be a stronger acid than =X-OH (Parks, 1965), where =X represents AI or Fe at the surface of the oxide. This has implications for the modelling of metal adsorption in natural systems since natural oxides may have significantly lower surface hydrolysis constants than predicted from laboratory
studies on nitrate-based oxides; similar concerns were recently put forward by Webster et al (1998).

At pH values above the point of zero charge the net charge on the particle surface is negative and so cations should be attracted, while below the  $pH_{ZPC}$  the net charge is positive and thus cations should be repelled. If electrostatic attraction is the dominant force driving contaminant retention then there should be no retention of heavy metals below the  $pH_{ZPC}$ ; however, as will be discussed in Chapter 5, Cu and Pb were retained below the  $pH_{ZPC}$ .

The pH<sub>ZPC</sub> of the oxides appears to be controlled by the Fe/Al ratio. For Fe/Al less than or equal to 1 (Al, Fe3Al and FeAl), the pH<sub>ZPC</sub> is essentially constant while for Fe/Al > 1 (3FeAl and Fe) it decreases by up to one pH unit. This supports the proposal in the discussion on specific surface area that for Fe/Al < 1, the oxide surface is controlled by the Al component while the Fe component dominates at Fe/Al >1. However, as discussed in the following section (Section 1.9, Potentiometric Titrations), the relationship between the Fe/Al ratio and pH<sub>ZPC</sub> appears to vary considerably depending on the method of estimation. Due to the relatively low sensitivity of the AEC measurement method, it is recommended that the pH<sub>ZPC</sub> estimated from the ion exchange capacity tests should be viewed as indicative of a trend rather than an absolute value. The pH<sub>ZPC</sub> estimated from 1.9, Potentiometric Titrations.



Figure 4.4. Cation Exchange Capacity (meq /g) for the oxides: Fe (◊), 3FeAI (+), FeAI (□), Fe3AI (Δ), AI (x) and kaolinite (ο).



Figure 4.5. Anion Exchange Capacity (meq /g) for the oxides: Fe (◊), 3FeAI (+), FeAI (□), Fe3AI (Δ), AI (x) and kaolinite (ο).



Figure 4.6. Net charge (CEC - AEC, meq /g) for the oxides: Fe ( $\diamond$ ), 3FeAI (+), FeAI ( $\Box$ ), Fe3AI ( $\Delta$ ), AI (x) and kaolinite (o).

	A	B	С	D				
Oxide	pH <sub>ZPC</sub> (CEC - AEC)	pH <sub>ZPC</sub> (zero salt effect)	pH <sub>2PC</sub> (surface charge density)	pH <sub>ZPC</sub> ½(pK <sub>a1</sub> + pK <sub>a2</sub> )				
Fe	5.3	5.1	4.32	n.a.				
3FeAl	5.8	5.9	4.76	n.a.				
FeAl	6.4	5.9	5.64	5.67				
Fe3AI	6.2	5.9	5.06	5.17				
AI	6.2	5.6	4.92	5.04				
Table 4	Table 4.6. Oxide pH <sub>ZPC</sub> estimated by different methods (n.a. = not available).							

A possible explanation for the disparity observed between the different points of zero charge in Table 4.6 is that the different methods used are measuring different surface charge densities. Sposito (1984) divides the surface charge density into five parts:

- *structural* surface charge density due to isomorphous substitution which will affect the synthetic clays and kaolinite but should be zero for the oxides;
- proton surface charge density produced by proton association and dissociation reactions;
- inner-sphere complex charge which is equal to the net total surface charge of all ions except H<sup>\*</sup> and OH<sup>\*</sup> that have formed specifically adsorbed innersphere complexes with surface functional groups;
- outer-sphere complex charge which is the net total surface charge of nonspecifically adsorbed ions
- dissociated charge which quantifies the contribution to the surface charge density from ions in solution that have not been complexed by surface functional groups.

The ion exchange experiments (cation and anion exchange capacities) measure the surface charge density due to outer-sphere complex charge and dissociated charge (Column A, Table 4.6). The potentiometric titrations on the other hand, are designed to evaluate the proton surface charge density (Column C, Table 4.6), but may also be used to assess the point of zero salt effect (Column B, Table 4.6) which is when the change in proton surface charge density as a function of ionic strength is equal to zero. The difference between the points of zero surface charge noted in Table 4.6 may therefore be due to operational differences in the definition of the surface charge density rather than an actual difference.

Potentiometric titrations assume that when acid or base is added to the suspension, the protons and/or hydroxide ions will either remain as free ions or react only with surface functional groups whose charge is pH-dependent. If other reactions result in the consumption of protons or hydroxide ions, then the experiment is not measuring the charge due solely to protonation and deprotonation. Typical interfering reactions include the displacement of ions such as Na<sup>\*</sup> that have previously been adsorbed by the surface (outer-sphere complexes), complexation by the electrolyte ions and partial dissolution of the solid material (e.g. Al(OH)<sub>3</sub> + 3H<sup>\*</sup> = Al<sup>3\*</sup> + 3H<sub>2</sub>O). These interfering reactions are particularly likely when clay minerals such as kaolinite which contain surface impurities are present but should be less of a problem, except at low and high pH, for the amorphous oxides.

The ion exchange experiments measure a slightly different surface charge density since the ions used ( $Ca^{2^+}$ ,  $NO_3^-$ ) have different reactivities and bonding strengths for surface hydroxyl groups than the ions utilised in the potentiometric titrations ( $H^+$ , OH). The pH<sub>ZPC</sub> calculated from the ion exchange experiments reflects surface charge density due to non-specifically adsorbed ions which may be displaced by leaching with an appropriate solution.

In addition to the possible experimentally-induced interference outlined above, the interaction between adjacent =AIOH and =FeOH groups on the surface of the mixed oxides may affect the reactivity of these surface functional groups relative to that found in the "pure" AI and Fe oxides. Unfortunately the ability to measure the reactivities of individual surface functional groups was beyond the capability of the experimental methods available in this study which was limited to measuring the *average* surface charge density for the entire oxide surface.

The different results for the points of zero charge will be further discussed in Section 3.8.2 (this Chapter).

# 1.9 Potentiometric titrations

The variation in surface charge carried by the oxides as a function of pH was investigated using potentiometric titration tests. This method should provide a more accurate reflection of the surface charge characteristics than the ion exchange tests because the titrations evaluate the charge due solely to protons and hydroxyl ions under more strictly controlled conditions (e.g. constant ionic strength, exclusion of CO<sub>2</sub>) than during the ion exchange experiments (Sposito, 1984). Since the hydroxyl groups found on the surface of oxides exhibit amphoteric behaviour in water, they can bind and release protons and hence acquire a surface charge (Dzombak & Morel, 1990). Surface hydroxyl groups may therefore exist as neutral species,  $\equiv$ XOH<sub>2</sub><sup>+</sup>, or negatively charged species,  $\equiv$ XOH<sub>2</sub><sup>+</sup>, or negatively charged species,  $\equiv$ XOH<sub>2</sub><sup>+</sup>, or negatively charged as:

#### Equation 4.1

 $\equiv XOH + H^* = \equiv XOH_1^*$ 

# **Equation 4.2**

 $\equiv XOH = \equiv XO^- + H^+$ 

where  $\equiv$ XOH represents a surface hydroxyl group and X may be Al<sup>3+</sup> or Fe<sup>3+</sup>.



Figure 4.7a. Fe, potentiometric titrations for I = 0.01M, 0.1M and 1M.

It follows from these reactions that adding acid to an oxide suspension produces an excess of protons at the surface (Equation 4.1) and hence a positive charge, while addition of a base causes surface hydroxyl groups to de-protonate (Equation 4.2) and thus exhibit a negative charge.



Figure 4.7b. 3FeAI, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.7c. FeAI, potentiometric titrations for I = 0.01M, 0.1M and 1M.

Titration curves were obtained by plotting the surface excess of protons (calculated as moles of acid  $(H^*)$  added minus moles of base (OH<sup>-</sup>) added) against pH. The surface excess was calculated by subtracting the amount of

titrant taken up by the blank at a given pH value from that taken up by the suspension (Cornell et al, 1975); the curves were subtracted at intervals of 0.1 pH units (Evans et al, 1979). The surface excess of acid, Q, is defined as (Davis & Kent, 1990):

#### **Equation 4.3**

 $Q = (\equiv XOH_2^+) - (\equiv XOH^-) = C_A - C_B - [H^+] + [OH^-]$ 

where  $(=XOH_2^{+})$  and  $(=XO^{-})$  are the concentration of positively and negatively charged surface groups respectively;  $C_A$  is the molar concentration of added acid and  $C_B$  of added base; [H<sup>+</sup>] and [OH<sup>-</sup>] are calculated from the pH measurements.

#### 1.9.1 Point of Zero Charge (Potentiometric Titrations)

The pH<sub>ZPC</sub> is the pH value at which the titration curves obtained at the three different ionic strengths intersect. As the results presented in Figure 4.7 show, increasing the ionic strength had a fairly small but measurable effect on the location and shape of the titration curves. This caused difficulties in clearly identifying the pH at which the curves intersected and so the pH<sub>ZPC</sub> values reported as "zero salt effect" (Table 4.6, Column B), are best considered as indicating differences between the oxides rather than absolute values. Conversely, the points of zero charge estimated from the surface proton excess, Q (Figure 4.8), or surface charge density,  $\sigma$  (Figure 4.9), suggest a systematic variation with Fe/Al ratio, increasing from Fe to 3FeAl to FeAl, followed by a gradual decrease from Fe3AI to AI (Figure 4.10). It has been suggested that if the intersection point of titrations conducted at different ionic strengths does not lie on the pH axis, the apparent surface charge density can be converted to an absolute surface charge density by assigning zero surface charge to the intersection point (Spark et al, 1995a). This conversion was not performed on these results due to the uncertainty in identifying the intersection point, as well as the good agreement between the pH<sub>ZPC</sub> estimated from the surface excess of protons, Q, and that calculated from the acidity constants (pKa1 and pKa2) extracted with FITEQL (section 1.9.2 below).

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Figure 4.7d. Fe3AI, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.7e. Al, potentiometric titrations for I = 0.01M, 0.1M and 1M.

The lower point of zero charge observed here for Fe oxides is consistent with the literature as noted in Section 1.8 above with Fe oxides typically having lower  $pH_{ZPC}$  than Al oxides by one to two pH units (Parks, 1965). The ability of the FITEQL/MINTEQA2 models to accurately reproduce the experimental titration data (see Figure 4.11 and Section 1.9.2 below) suggest that the  $pH_{ZPC}$  estimated using the surface charge density may be the most reliable method, at least in the present study where ionic strength has a relatively minor effect on the surface charge characteristics.



Figure 4.8. Excess acid, Q, (mol / L x 10<sup>3</sup>).



Figure 4.9. Surface charge density,  $\sigma$  (C / m<sup>2</sup>).

To more easily compare the variation in surface charge between the different oxides, the surface excess of protons (Q) at 0.1M KNO<sub>3</sub> is shown in Figure 4.8. At high pH (pH 9.5), the surface proton excess increases (becomes more negative) with decreasing Fe/AI ratio, hence AI > Fe3AI >> FeAI > 3FeAI > Fe. At low pH (< pH 4), the magnitude of the proton excess follows the same order but

with the surface becoming more positive with decreasing Fe/AI ratio. From the overall shape of the titration curves, the oxides can be divided into three groups on the basis of Fe/AI ratio: Fe and 3FeAI; FeAI; Fe3AI and AI. The Fe and 3FeAI oxide curves are very similar to each other, as are the AI and Fe3AI curves. Up to about pH 5.5, the FeAI oxide exhibits an intermediate surface excess of protons that has a similar shape to the high Fe/AI oxides (Fe, 3FeAI), but the curve then becomes more parallel to the low Fe/AI oxides (AI, Fe3AI) at higher pH, crossing the Fe curve at about pH 8. The AI and Fe3AI curves cross the 3FeAI and Fe curves at around pH 6.

The graphs of Q versus pH were converted into surface charge density,  $\sigma$  (C /m<sup>2</sup>), using the following relationship (Davis & Kent, 1990):

# **Equation 4.4**

$$\sigma = Q \frac{F}{AS}$$

where F is the Faraday constant (96,485 C /mol), Q the surface excess of protons (mol /L), A the specific surface area ( $m^2$  /g) and S the solid concentration (g /L).



Figure 4.10. Zero Point of Charge estimated by surface charge.

The calculation of the surface charge density (Equation 4.4) normalises the titration data to surface area causing some researchers to question its reliability since this parameter depends on the method of measurement, and can be quite variable for amorphous oxides (Dzombak & Morel, 1990). It is however instructive to consider the surface charge density presented in Figure 4.9 since the surface area values in this study are the result of multiple measurements.

The surface charge density curves for the different oxides are more spaced out than in Figure 4.8 and while the effect of Fe/AI ratio is unchanged at low to medium pH, at high pH the FeAI oxide exhibits a less negative charge density than either the Fe or 3FeAI oxide. This is because FeAI has the largest surface area of any of the oxides (Table 4.5) and so the surface charge (either negative or positive) is distributed across a wider area.

Figures 4.8 and 4.9 support the suggestion made as a result of the specific surface area data that AI controls the surface properties of the low Fe/AI oxide, Fe3AI, while Fe controls the mixed oxide, 3FeAI; at an Fe/AI ratio of one, the surface properties of the mixed oxide (FeAI) are influenced by both components. This suggestion will be explored further in Section 2 (this Chapter).

#### 1.9.2 FITEQL modelling

The least squares optimisation program, FITEQL (Herbelin & Westall, 1996), was used to estimate the optimum values for the *intrinsic* equilibrium acidity constants,  $K_{a1}$ ,  $K_{a2}$ , for the reactions describing the protonation and deprotonation of surface hydroxyl groups, as well as the total concentration of these surface functional groups. This program optimises the values of adjustable parameters by changing their values until the sum of the squares of the residuals between the measured titration data and FITEQL calculated values is minimised (Hayes et al, 1991). FITEQL can be used with several surface complexation models which differ in their representation of the interfacial structure, and hence consider different surface reactions and electrostatic correction factors (Davis & Kent, 1990). Further detail on both FITEQL and surface complexation modelling

in general will be provided in Chapter 7. The diffuse double layer model (DDLM) was applied to the titration data in this thesis because it was desirable to have the acidity constants referenced to an ionic strength of zero since this would allow their later application to variable ionic strength contaminant solutions. Due to the assumptions made in this model, it is restricted to use at ionic strengths up to 0.1M (Hayes et al, 1991) and so only the 0.01M and 0.1M titration data were used in the FITEQL calculations.

The values extracted by FITEQL from the titration data were used in the geochemical speciation program, MINTEQA2 (Allison et al, 1991), to generate theoretical titration curves by invoking the diffuse layer model option (Figure 4.11). The effectiveness of this combination of models in reproducing experimental titration and contaminant sorption data has been demonstrated for natural soils (e.g. Wang et al, 1997).

FITEQL was used to extract the *intrinsic* equilibrium constants,  $K_{a1}$  and  $K_{a2}$ , for the reactions below that describe the protonation and de-protonation of surface hydroxyl groups, as well as the total concentration of these surface functional groups:

#### **Equation 4.5**

$-YOH + H^{+}YOH^{+}$	$K = \{\equiv XOH_2^+\}$
$= \lambda O \Pi + \Pi = = \lambda O \Pi_2$	$\pi_{a1} = \overline{\{\equiv XOH\}\{H^+\}(e^{-F\Psi/RT})\}}$

#### **Equation 4.6**

 $= XOH - H^{+} = = XO^{-} \qquad K_{a2} = \frac{\{=XO^{-}\}}{\{=XOH\}\{H^{+}\}^{-1} (e^{-F\Psi/RT})^{-1}}$ 

## **Equation 4.7**

 $T_{=XOH} = \{\equiv XOH_2^+\} + \{\equiv XO^-\} + \{\equiv XOH\}$ 

=XOH represents a surface hydroxyl group where X may be  $Al^{3+}$  or  $Fe^{3+}$ ,  $T_{XOH}$  is the concentration of amphoteric surface hydroxyl groups [XOH], and {} represent

activities. The exponential term relates the surface potential to the surface charge, this is further discussed in Chapter 7; F is the Faraday constant,  $\Psi$  is the electrostatic potential at the surface, R the universal gas constant and T the temperature (K). It is not possible to measure the activity of surface species (Stumm & Morgan, 1996) so the activity coefficients for all surface species are assumed to be equal at a particular ionic strength; hence they divide out of the mass law expressions (Dzombak & Morel, 1990.

The equilibrium constants,  $K_{a1}$  and  $K_{a2}$ , are termed *intrinsic* constants since they have been corrected to zero surface charge and zero ionic strength. It should therefore be possible to apply them to solutions at other ionic strengths by choosing appropriate activity coefficients. Table 4.7 summarises the values of  $K_{a1}$ ,  $K_{a2}$  and  $T_{XOH}$  that were estimated with FITEQL.

Oxide	log K <sub>a1</sub>	log K <sub>a2</sub>	Tot [XOH] (mmol /L)	N <sub>s</sub> (sites / nm <sup>2</sup> )	variance
Fe	2.15	-6.44	0.664	0.234	69-118
3FeAl	2.68	-6.87	0.992	0.344	47-74
FeAl	3.71	-7.63	1.221	0.366	6 - 14
Fe3Al	3.52	-6.82	1.785	0.788	5 - 9
AI	3.05	-7.02	1.767	0.822	3 - 14
Table 4.7	. FITEQL	paramet	ers - oxides.		i

The model did not converge for Fe and 3FeAl when  $K_{a1}$  was included as a parameter to be optimised and so the values given in Table 4.7 for these two oxides were calculated according to the relationship (Stumm & Morgan, 1996):

#### **Equation 4.8**

$$pH_{ZPC} = \frac{1}{2} \left( pK_{a1} + pK_{a2} \right)$$

Based on some initial test runs with FITEQL and MINTEQA2, the value of  $pH_{ZPC}$  for Fe and 3FeAl was estimated from the average pH at which Q = 0 in the 0.01M and 0.1M titrations;  $pK_{a2}$  was taken from initial FITEQL runs in which  $K_{a1}$  was set equal to -20 and not optimised in accordance with recommendations from the FITEQL manual (Herbelin & Westall, 1996). FITEQL was subsequently repeated

for Fe and 3FeAI with  $K_{a1}$  fixed at the value calculated by Equation 4.8 to estimate new values of  $K_{a2}$  and  $T_{XOH}$  which were then used in MINTEQA2.

As reported previously (Section 1.8, this Chapter), the value of  $pH_{ZPC}$  varied depending on the method of evaluation. Two approaches were used to extract the point of zero charge from the titration data; firstly the  $pH_{ZPC}$  was estimated from the intersection point of titrations conducted at different ionic strengths (Table 4.6, column B); the second method used the average pH at which the surface charge density was equal to zero from the 0.01M and 0.1M titrations (Table 4.6, column C). As a check, Equation 4.8 was used to calculate the  $pH_{ZPC}$  for AI, Fe3AI and FeAI based on the FiTEQL acidity constants; the respective values of 5.04, 5.17 and 5.04 (Table 4.6, Column D) are in good agreement with both the trend and absolute values calculated from the surface charge density. These modelling results therefore support the earlier recommendation that the  $pH_{ZPC}$  is best estimated using the surface charge density rather than the ion exchange tests or the pH of zero salt effect, at least for materials in which the ionic strength has a small effect on the surface charge.

The FITEQL model provided slightly different results depending on whether the 0.01M or 0.1M experimental titration data were being investigated. The issue of selecting the "best estimate" of the equilibrium constants has been extensively reviewed by Dzombak & Morel (1990) and their recommended approach was utilised here; this approach is explained in Chapter 7.

In addition to the equilibrium constants,  $K_{a1}$  and  $K_{a2}$ , the third parameter for which FITEQL optimises is the concentration of surface sites,  $T_{XOH}$  (mol /L). This is a function of the concentration of solids and the specific surface area, and is often converted to the surface site density,  $N_s$  (sites / nm<sup>2</sup>), to aid in comparing different materials. This conversion is achieved through the relationship defined below (Hayes et al, 1991):

#### **Equation 4.9**

$$N_{s} = \frac{T_{XOH} N_{A}}{(SSA)C_{s}(1x10^{18})}$$

where N<sub>A</sub> is Avogadro's Number (6.02 x  $10^{23}$ ), C<sub>S</sub> is the concentration of solids (5 g /L for all titrations), SSA is the specific surface area (m<sup>2</sup> /g) and 1 x  $10^{18}$  converts from m<sup>2</sup> to nm<sup>2</sup>.

Inspection of the surface site densities listed in Table 4.7 shows that this parameter increases as the Fe/AI ratio decreases and there is a distinct division between the high to medium Fe/AI oxides (Fe, 3FeAI and FeAI) and the low Fe/AI oxides (Fe3AI, AI). Since the concentration of solids is equal for all the oxides, the site concentration,  $T_{XOH}$ , allows comparison of the availability of surface sites for complexation with protons or, as will be discussed in Chapter 7, contaminant ions. Figure 4.12 compares the site density and site concentration of the different oxides calculated by FITEQL in graphical form.

The goodness of fit of the proposed model to the experimental data is provided by the variance with values between 0.1 and 20 indicating a reasonably good fit. For Fe and 3FeAI the variance was higher than this ideal range, however as can be seen in Figure 4.11, the model generated titration curves are relatively accurate. Since the intent of the modelling study was to provide information about trends in the surface charge properties between the different oxides rather than absolute values, a systematic optimisation of the constants extracted by the FITEQL model was not conducted. While such optimisation may have improved the fit of the MINTEQA2 curves to the experimental data, it would have involved altering the experimentally measured specific surface area and arbitrarily fixing the equilibrium constants at different values; it was not believed that data manipulation of this kind would substantially aid an understanding of the differences in behaviour caused by varying the Fe/AI ratio. For example, in their extensive review of the use of surface complexation modelling with ferrihydrite, Dzombak & Morel (1990) recommended using a specific surface area of 600 m<sup>2</sup> /g to optimise FITEQL modelling despite measured values for this material ranging from 200 to 800 m<sup>2</sup> /g. Similarly, Davis & Kent (1990) proposed that a single value (2.31 sites /nm<sup>2</sup>) should be used for the site density regardless of the material (oxides, soils etc.) being investigated. However, when the site density was fixed at this value and the titration data re-modelled with FITEQL, the program failed to converge and so this parameter was allowed to vary until the optimum value was found. The site densities extracted by FITEQL were somewhat lower than literature values (Davis & Kent, 1990; Smith & Jenne, 1991; Schroth & Sposito, 1998).



Figure 4.11. Experimental data and model predictions (MINTEQA2/FITEQL).

Figure 4.11 shows that FITEQL/MINTEQA2 was relatively successful in reproducing the experimental titration data and although the fit is less good for AI and Fe3AI at low pH (< pH 4) where the model underestimates the surface charge density, this figure provides confidence that the surface complexation modelling approach is valid for these materials. One reason for the less than perfect reproduction of the titration data by the FITEQL/MINTEQA2 models is that more than one type of surface site (e.g. =AIOH and =FeOH) is probably involved in the protonation and de-protonation reactions. The use of an average surface site to represent oxide and soil surfaces is common due to the difficulty (impossibility ?) of differentiating between surface functional groups with different acid-base characteristics (Davis & Kent, 1990). Without proof of multiple site types from spectroscopic or other techniques, there is general agreement that the minimum number of surface site types should be utilised to explain experimental data (Dzombak & Morel, 1990; Herbelin & Westall, 1996); this approach was taken in the current thesis.



Figure 4.12. Surface site density and concentration calculated with FITEQL.

The output generated by MINTEQA2 includes the calculated concentrations of the different surface species, =XOH,  $=XOH_2^+$  and  $=XO^-$ , and these are presented

in Figure 4.13. This output should provide information about the surface species likely to be participating in contaminant-surface complexation reactions. The earlier caution to consider this output as indicating trends rather than absolute values is worth remembering at this point, and for this reason the vertical scale in Figure 4.13 has been allowed to vary.



Figure 4.13a. Fe - surface speciation calculated using MINTEQA2.



Figure 4.13b. 3FeAI - surface speciation calculated using MINTEQA2.

The importance of the uncharged species,  $\equiv$ XOH is clear for all the oxides up to ca. pH 7. Above this pH, the negatively charged surface species  $\equiv$ XO<sup>\*</sup> is most

abundant for Fe and 3FeAI, while for the lower Fe/AI ratio oxides, the uncharged species remains dominant until about pH 8.



Figure 4.13c. FeAI - surface speciation calculated using MINTEQA2.



Figure 4.13d. Fe3AI - surface speciation calculated using MINTEQA2.

Positively charged surface hydroxyl groups do not appear to have a wide pH range, being restricted to less than pH 5 for the low Fe/Al oxides (Al, Fe3Al, FeAl) and less than pH 4 for Fe and 3FeAl. Notwithstanding the model's underestimation of the positive surface charge for Al and Fe3Al at < pH 4.5, the

 $\equiv$ XOH<sub>2</sub><sup>+</sup> species is dominant only for FeAl at < pH 3; at this pH, Al<sup>3+</sup> and Fe<sup>3+</sup> are likely to dissolve from the oxide surface thus changing its surface charge behaviour (Stumm & Morgan, 1996). The implications of these surface speciation calculations will be further explored in Chapter 5.



Figure 4.13e. Al - surface speciation calculated using MINTEQA2.

# 2. Discussion - physicochemical properties of the oxides

The increased concentration of sulphate as the Fe/AI ratio decreases may be a factor in the specific surface area results. Bigham et al (1990) reported a maximum surface area for synthetic iron oxyhydroxysulphate precipitates when the SO<sub>4</sub><sup>2-</sup> concentration was 10 to 12%; higher or lower SO<sub>4</sub><sup>2-</sup> contents had reduced surface areas. Their study used electron microscopy to show changes in the dominant particle size and shape at this SO<sub>4</sub><sup>2-</sup> concentration. It is worth noting that in the present study, the FeAI oxide (Fe/AI = 1) contains 10% SO<sub>4</sub><sup>2-</sup> (Table 4.2). Sulphate has been reported to inhibit the growth of AI(III) particles, and may enhance precipitation by causing the aggregation of polynuclear AI species in solution (Bertsch & Parker, 1996) or by preventing the crystallisation of AI(OH)<sub>3</sub> (Jardine & Zelazny, 1996). Sulphate is strongly adsorbed to hydrous AI oxides (HohI et al, 1980) and can stabilise the high surface area mineral, schwertmannite, a poorly crystalline iron oxyhydroxysulphate (Bigham et al,

1996). Adsorbed  $SO_4^{2^-}$  has been reported to act as a binuclear bridging surface complex between metal atoms in both Al and Fe oxides; e.g. Fe-O-S(O<sub>2</sub>)-O-Fe and Figures 4.14 to 4.16 (Parfitt & Smart, 1978; Rajan, 1978; Bigham et al, 1990; Sjöström, 1994).

During the precipitation of oxides in the current study, Fe-rich particles should initially form since Fe(III) precipitates at a lower pH than Al(III) (Stumm & Morgan, 1996). As the pH increases, Al(III) will begin to precipitate but may also be adsorbed onto existing Fe particles as a ternary complex via adsorbed SO<sub>4</sub><sup>2-</sup> as has been reported for other metal ions (Webster et al, 1998). Increasing the pH to > pH 6 should cause the release of most adsorbed SO<sub>4</sub><sup>2-</sup> as a result of displacement by hydroxyl ions (Courchesne & Hendershot, 1989) however appreciable SO<sub>4</sub><sup>2-</sup> remains incorporated within the oxides (Table 4.2) despite the solution pH being held above pH 7 during precipitation. In a review of the effect of sulphate on aluminium solubility, Nordstrom (1982) proposed that both adsorption and precipitation of sulphate occurs in the aluminium-sulphate system and that distinguishing between the two processes is not always possible.

Schwertmann & Cornell (1991) reported that the isomorphous substitution of Al<sup>3+</sup> for Fe<sup>3+</sup> during oxide precipitation leads to slightly smaller unit cell edge lengths (identifiable using X-ray diffraction) and hence particle size due to the smaller ionic radius of Al<sup>3+</sup> (0.053 nm) compared to Fe<sup>3+</sup> (0.064 nm). Unfortunately, the amorphous nature of the oxides in the current study precluded the use of X-ray diffraction to investigate crystal size. Deng & Stumm (1994) found that Fe(III) oxyhydroxide precipitated in the presence of Al oxide ( $\delta$ -Al<sub>2</sub>O<sub>3</sub>) had a higher reactivity (as measured by dissolution rate) than when it formed in the absence of other particles. This was interpreted as being due to Fe(III) polymerisation predominantly happening in two dimensions across the surface of the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> particles and hence producing a high quantity of reactive surface sites instead of the three dimensional polymerisation that occurred when no particles were present.

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Figure 4.14. Schematic representation of molecular structure of Fe3AI amorphous oxide. Fe/AI ratio of 0.3; i.e. three AI ions for each Fe ion.

The influence of the Fe/Si molar ratio of amorphous oxides on various physicochemical properties was studied by Yong et al (1992a). These researchers systematically varied the ratio (calculated as  $Fe_2O_3 / [Fe_2O_3 + SiO_2]$ ) from 0 (solely SiO<sub>2</sub>) to 1 (only Fe<sub>2</sub>O<sub>3</sub> present) and found a critical ratio of 0.40. At this molar ratio, the amorphous Fe-Si oxide exhibited the lowest specific surface area, the largest cation exchange capacity and hence maximum negative surface charge density. Using infra-red spectrophotometry, Yong et al (1992a) observed that the strongest hydrogen bonding occurred at a Fe/Si ratio of 0.4, and this was accompanied by a reduction in Si-O bond strength. One reason proposed was that silico-iron polymerisation, in which an Fe-O-Si chain is formed, weakens the Si-O bond since Fe attracts the oxygen ions more strongly than Si. This greater attraction is because Fe has a less stable atomic structure since the outer electrons have a higher energy than the outer electrons of Si (Segal, 1989), and are therefore more easily displaced to allow bonding with, for example, oxygen ions. A similar mechanism may be active in the mixed Fe-Al amorphous oxides being considered in the current thesis since AI has an electronic configuration

comparable to Si. The specific surface area of the FeAl oxide (Fe/Al ratio = 1) was significantly greater than any other oxide; this may be due to this oxide having the maximum opportunity for alumino-iron polymerisation in which Fe and Al ions alternate with oxygen ions as illustrated schematically in Figure 4.15. The formation of Fe-O-Al chains may consequently lower the bond strength of Al-O groups and therefore encourage the oxide structure to remain weakly bonded in a similar manner to the action of SO<sub>4</sub><sup>2</sup> ions discussed above in which the growth of larger particles is inhibited. Unfortunately infrared spectrophotometry was not utilised in the current experimental program so it is not possible to provide conclusive evidence. It is interesting to note that if the Fe/Al ratio is recalculated in a similar manner to the method of Yong et al (1992a), the FeAl oxide has a ratio of 0.5 (moles Fe / [moles Al + moles Fe]) which is close to that of their maximum specific surface area Fe-Si oxide (ratio = 0.4).

It is therefore proposed that  $SO_4^{2^\circ}$  acts as a bridge between Fe(III) and Al(III) ions during oxide formation and is thus incorporated into the oxide structure. The large  $SO_4^{2^\circ}$  ions (radius = 0.5 nm; Bigham et al, 1990) may inhibit the growth of large particles by blocking the extension of the hydrous oxide structure and disrupting regular crystal formation. The development of an open (porous) structure of loosely linked small particles is therefore encouraged with the most open structure being found at Fe/Al ratio = 1. At this Fe/Al ratio, the presence of equal concentrations of Fe(III) and Al(III) prevents either from controlling the structure of the oxide and results in particles whose surfaces are a mixture of Fe and Al oxides. Furthermore the formation of Fe-O-Al chains reduces the bond strength of Al-O groups and limits the development of regular oxide crystals. At higher or lower Fe/Al ratio, the oxide structure is effectively determined by the "pure" Fe or Al components.



Figure 4.15. Schematic representation of molecular structure of FeAI amorphous oxide. Fe/AI ratio of 1; i.e. equal numbers of AI and Fe ions.

The suggested molecular structure of the mixed amorphous oxides shown in Figures 4.14 to 4.16 is adapted from Yong et al (1992a). It can be considered a two dimensional slice through an uneven, possibly porous amorphous oxide particle where the electric charge is provided by the protonation and deprotonation of hydroxyl functional groups at the surface, with Al<sup>3+</sup>, Fe<sup>3+</sup>, OH<sup>-</sup>, O<sup>2-</sup>, H<sup>\*</sup> and S (as SO<sub>4</sub><sup>2</sup>) ions being present. As has been previously discussed (Chapter 2), the hydroxyl functional groups may carry a positive, negative or neutral charge depending on the solution pH with the net surface charge being determined by the sum of all charges present. The surface charge will be balanced by sorption of cations (e.g. Na<sup>+</sup>, H<sup>+</sup>) on negative sites and anions (e.g.  $SO_4^2$ , OH) on positive sites. Oxide precipitation is expected to be a result of the formation of soluble hydroxides (e.g.  $Fe(OH)_3$  (aq)) which combine with other hydroxyls and sulphate ions until they are sufficiently large that precipitation commences. Additional work (e.g. infrared spectrophotometry) is necessary to support this proposal and to clarify the particle size distribution, particularly for the  $< 2 \mu m$  fraction.



Figure 4.16. Schematic representation of molecular structure of 3FeAI amorphous oxide. Fe/AI ratio of 3; i.e. three Fe ions for each AI ion.

# 3. Physicochemical properties of the synthetic clays and kaolinite

# 3.1 General description of the synthetic clays

The kaolinite and K-AI samples were both bright white and could not be visually separated while the remaining synthetic clays were visually distinct from each other and from the kaolinite in terms of colour which followed the gradation observed for the component oxides (Section 1.1, this Chapter): K-Fe was dark brown; K-3FeAI was slightly paler; K-FeAI was a pale orange-brown; K-Fe3AI was a very pale tan colour. In contrast to the oxides, all these materials were very easily ground after air-drying.

# 3.2 Amorphous oxide content

The amorphous oxide contents determined by oxalate extraction are shown in Tables 4.8 & 4.9.

Soil	Actual values			Actual - kaolinite			Target values			
	%Fe	%AI	Sum % Fe+Al	%Fe	%AI	Sum % Fe+Al	%Fe	%AI	Sum % Fe+Al	рH
Kaolinite	0.01	0.06	0.07							1 -
K-Fe	4.22	0.04	4.26	4.21	0.00	4.21	4.8	0	4.80	4.83
K-3FeAI	3.27	0.58	3.85	3.26	0.52	3.78	3.6	0.6	4.20	5.40
K-FeAl	2.61	1.12	3.73	2.60	1.06	3.66	2.5	1.2	3.70	5.33
K-Fe3AI	1.19	1.69	2.88	1.18	1.64	2.81	1.2	1.8	3.00	5.39
K-AI	0.01	2.20	2.21	0.00	2.14	2.14	0	2.3	2.30	4.68
Table 4.8	Table 4.8. Amorphous oxide content (%) - synthetic clays.									

The pH listed is the pH of the suspension after 24 hours of mixing. The kaolinite contained small amounts of amorphous Fe and Al oxides which were subtracted from the amounts extracted from the synthetic clays to give the "Actual - kaolinite" column. The measured oxide contents were 88 to 104% of the target values for Fe and 87 to 93% for Al (Table 4.9). This is within the range of extraction efficiencies reported for amorphous oxides by the oxalate method (Kersten & Förstner, 1986).

Literature values for the AI and Fe oxide content of natural soils and sediments vary from 0 to 5 wt. % (EI-Swaify & Emerson, 1975; McLaughlin et al, 1981; Oakley at al, 1981; Lion et al 1982; McBride, 1982; Davies-Colley et al, 1984; Tessier et al, 1984; Elliott et al, 1986; Lovley & Phillips, 1986; Davison & DeVitre, 1992; Fu & Allen, 1992) but the molar ratio is rarely reported (Yong & Sethi, 1977; Yong et al, 1992a) and so equimolar concentrations of AI and Fe are typically used in the few mixed oxide studies available (Anderson & Benjamin, 1990a, b; Meng & Letterman, 1993a, b). The caution given in Section 1.2 that literature results are often reported after assuming a particular chemical form (e.g.  $Fe_2O_3$ ) is repeated here with the reminder that the values presented in Table 4.8 are for wt. % Fe or AI and not %  $Fe_2O_3$  etc. The synthetic soils used in this study can therefore be seen to cover the range in amorphous oxide contents of naturally occurring soils and sediments.

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Soil	Actual			Actual - Target kaolinite mol		Fe/Al ratio Actual	% extracted			
	mol Fe / g	mol Al / g	Sum mol Al+Fe / g	mol Al+Fe / g	(Al+Fe) / g	(target)	Fe	AI		
Kaolinite	0.002	0.022	0.024			0.08				
K-Fe	0.75	0.02	0.77	0.75	0.86	45.3	88			
K-3FeAI	0.58	0.22	0.80	0.78	0.87	2.7 (2.9)	91	87		
K-FeAl	0.47	0.41	0.88	0.86	0.89	1.1 (1.0)	104	88		
K-Fe3AI	0.21	0.63	0.84	0.82	0.88	0.3 (0.3)	98	91		
K-AI	0.002	0.82	0.82	0.79	0.85	0.002		93		
Table 4.9	Table 4.9. Amorphous oxide content - mol Al, Fe / g (x10 <sup>-3</sup> ).									

Table 4.9 shows the amorphous oxide content in terms of mol (Al+Fe) / g along with the actual and target values for the Fe/Al ratio. Although the absolute amounts of oxide extracted are slightly lower than intended, the Fe/Al ratio is essentially as planned. The intent of this study was to cover the natural range of soils and sediments rather than investigate absolute oxide concentrations.

# 3.3 Specific Surface Area

The specific surface area is shown in Figure 4.17 and summarised in Table 4.10. Relative to the kaolinite alone, all of the synthetic clays have a greatly enhanced surface area, with a general increase in measured surface area with increased Fe/AI ratio. The "calculated" value was estimated from the amount of each oxide and kaolinite present plus the specific surface area of the individual oxides and kaolinite. The synthetic clays were assumed to contain 0.1 g of oxide and 0.9 g of kaolinite, however very little difference was found if the calculations were made based on the concentration of AI+Fe present (mol / g) and the surface area (m<sup>2</sup> / mol (AI+Fe)) measured for the appropriate oxide (Section 1.4, this Chapter). The calculated values are therefore those expected if the oxides and kaolinite exist as separate non-interacting phases.

Clay	1	Calculated						
-	No. of samples	Mean	Standard deviation	95% confidence interval	values			
K-Fe	3	70	2	65 - 75	53			
K-3FeAl	3	63	1	59 - 66	54			
K-FeAI	4	64	4	57 - 70	62			
K-Fe3Al	3	57	1	53 - 60	49			
K-AI	3	55	5	42 - 68	47			
Kaolinite	4	24	4	18 - 29	-			
Table 4.10	Table 4.10. Specific surface area - synthetic clays. All values in m <sup>2</sup> /g.							

The calculated value corresponds well to the measured value of K-FeAI but underestimates the surface area for the other oxides by 12 % (K-AI) to 35% (K-Fe); statistical analysis (95% confidence interval) suggests that this difference was significant for K-Fe, K-3FeAI and K-Fe3AI but not K-AI.





This underestimation of the surface area is surprising since oxides are known to act as binding agents for other soil particles (Yong et al, 1985); such binding should lead to an increase in particle size and hence a decrease in specific surface area. Similarly the surface area should decrease if the oxides precipitate

onto the kaolinite surface since this will block some of the available surface of both the oxide and the kaolinite. The measured increase relative to that calculated could be due to the method by which the two suspensions were mixed. It has been proposed that the oxides are composed of aggregated particles (Section 1.5, this Chapter), however the 24 hour mixing period used to create these synthetic clays may have been sufficient for the aggregates to break down, thus exposing more surface area than present in the measurement of the oxide surface area. The resultant increased contribution from the oxide could then cancel out any reduction caused by the precipitation of oxides onto the clay surface and/or the binding of adjacent kaolinite particles.

Previous research has also found that adding amorphous Fe oxides to kaolinite causes a greater increase in measured surface area than adding AI oxides (El-Swaify & Emerson, 1975). These researchers concluded that Fe oxides have a more open structure than AI oxides and are therefore less effective at binding clay particles together.



Figure 4.18. Synthetic clay particle size distribution (% finer by weight).

## 3.4 Particle Size Distribution

Figure 4.18 presents the particle size distribution of the synthetic clays and kaolinite. Kaolinite clearly has the greatest proportion of fines and contains over 90% clay sized particles. It is not possible to discern any definite correlation between Fe/AI ratio and particle size distribution but the presence of added oxides increases the percentage of sand and silt-sized particles. When the data are re-plotted as a column chart (Figure 4.19) it can be seen that K-Fe3AI and K-AI have a larger proportion of silt ( $2 - 20 \mu m$ ) than the other synthetic clays.



Figure 4.19. Synthetic clay particle size distribution (% of total).

The introduction of amorphous oxides to the kaolinite might be expected to increase the proportion of larger particles by acting as a binding agent between individual clay particles. However the method of mixing used in this study in which pre-formed oxides were suspended in distilled water prior to a 24 hour mixing period with a kaolinite suspension might have prevented this cementing action. The calculated specific surface area (Section 3.3, this Chapter) of the synthetic clays based on the proportion of kaolinite and oxide present, was

similar to the measured values, possibly reflecting a lack of interaction between the two components. Furthermore, after the pipette test was completed, the remaining suspension and sediment were rinsed through a series of sieves; for the high Fe/AI ratio synthetic clays, the material retained by the sieves was brown and visually very similar to the pure oxides, while the white kaolinite appeared to pass through even the finest mesh sieve. The increased proportion of larger particles for the synthetic clays could simply be due to the presence of oxide aggregates (Section 1.5, this Chapter). These results suggest that while some kaolinite particles may have been bound together by the oxides, the majority of the oxides in the synthetic clays were present as distinct particles. This theory will be tested by comparing the surface properties of the synthetic clays with their component oxides using the potentiometric titration results (Sections 1.9 and 3.8, this Chapter); for example, if the surface charge density of K-Fe is similar to that of Fe but different to kaolinite, it may be inferred that the Fe oxide is coating the surface of the kaolinite.

## 3.5 Cation Exchange Capacity

The influence of pH on the cation exchange capacity (CEC) of the synthetic clays and kaolinite is clearly demonstrated in Figure 4.20. Kaolinite is seen to have the largest CEC below pH 7.8, while the K-3FeAI, K-Fe and K-AI samples appear to be virtually collinear from pH 3.5 to 9. However below pH 6.5 the K-Fe shows a slightly greater CEC than K-3FeAI and K-AI while above pH 8, the order is K-3FeAI > K-AI > K-Fe. The curves for these three synthetic clays cross the kaolinite curve at about pH 8.5. The K-FeAI and K-Fe3AI lines are also very similar to each other, showing zero CEC below pH 5.5 but then increasing more steeply than the other samples, exceeding the kaolinite CEC at ca. pH 8 and reaching approximately the same magnitude as the other three synthetic clays at pH 9. The variation in data points for each sample do not allow very firm conclusions to be drawn except that the synthetic clays can be divided into two groups which do not correspond to Fe/AI ratio: K-Fe, K-3FeAI and K-AI in one group; K-FeAI and K-Fe3AI in the other. The different shape observed for the kaolinite and oxide-amended clays and the reduction in CEC at low pH suggest that the permanent charge carried by the kaolinite particles is being masked in the presence of the oxides. Isomorphous substitution within the kaolinite crystal lattice provides some permanent (pH-independent) negative charge on the particle faces in addition to that contributed by pH-dependent hydroxyl groups which are located at the particle edges where the clay crystal lattice is broken (Spark et al, 1995b). The higher CEC measured for the kaolinite than the oxide-amended clays at < pH 7.5 could be due to the permanent face charge of the synthetic soils being partially satisfied by positively-charged Fe (with K-Fe), 3FeAI (K-3FeAI) and AI (K-AI) oxide particles and completely masked by the FeAI (K-FeAI) and Fe3AI (K-Fe3AI) oxides.

At the mixing pH of the K-Fe and K-3FeAI clays (Table 4.8), the oxide components are predominantly negatively charged (Table 4.6) so the oxides should be repelled by the kaolinite face sites. Conversely, the FeAI oxide is positively charged at it's mixing pH and would therefore be attracted to the permanently charged face sites. However, the AI and Fe3AI oxides should behave similarly to FeAI when added to kaolinite but as discussed above, this is not observed: since there is a degree of uncertainty over the exact value of the  $pH_{ZPC}$  for all of the oxides (Section 1.8, this Chapter), it is difficult to draw firm conclusions based on the experimental results available. In reality, individual particles of the same oxide are likely to have slightly varying points of zero charge. Yong & Ohtsubo (1987) mixed suspensions of ferrihydrite and kaolinite at both high and low pH, and subsequently varied the solution pH and found that the degree of particle-particle association was determined by the initial mixing pH. Ferrihydrite remained associated with the faces of kaolinite particles for mixtures prepared at pH 3 despite pH increases. However in suspensions mixed at pH 9.5, ferrihydrite began to be retained by kaolinite below the pH<sub>ZPC</sub> of the oxide (ca. pH 7), but was not fully associated with the clay until the pH was less than the  $pH_{ZPC}$  of kaolinite (pH 4.2).

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# 3.6 Anion Exchange Capacity

The kaolinite has a very low AEC at all pH values investigated as would be expected from literature values of the point of zero charge (Spark et al, 1995b) and while the other synthetic clays appeared to have a higher anion exchange capacity, the variability in the experimental data was too great to allow much interpretation of these results (Figure 4.21). Since this study was mainly concerned with the retention of cations, this aspect of the work has not been further explored.

# 3.7 Net Surface Charge and Point of Zero Charge

Figure 4.22 illustrates the variation in surface charge with pH as calculated by subtracting the AEC from the CEC at each pH value. The variability observed for the AEC (Figure 4.21) in conjunction with the relatively low sensitivity of the AEC measurement method, suggests that the  $pH_{ZPC}$  estimated from the ion exchange capacity tests may not be very reliable. The points of zero charge are listed in Table 4.11. Since the net charge line for kaolinite does not reach zero (Figure 4.22), the  $pH_{ZPC}$  was calculated by extrapolating this line to zero; the figure of pH 3.7 is somewhat lower than that found previously for Hydrite PX kaolinite (e.g. Yong et al, 1992b) but within the range reported in the literature (Spark et al, 1995b). Notwithstanding the earlier caution over the AEC measurements, the zero point of charge seems to increase as the Fe/AI ratio decreases, although K-AI lies below K-FeAI and K-Fe3AI.

Clay	pH <sub>ZPC</sub> (CEC - AEC)	pH <sub>ZPC</sub> (zero salt effect)	pH <sub>ZPC</sub> (surface charge density)
K-Fe	5	4.0	4.18
K-3FeAl	6	4.8	4.48
K-FeAl	6.8	5.25	4.72
K-Fe3Al	7	5.25	4.80
K-AI	6.5	5.5	4.81
Kaolinite	3.7	5.2	4.32
Table 4.1	1. pH <sub>ZPC</sub> estimat	ed by different meth	ods - synthetic clays.

The  $pH_{ZPC}$  values estimated from zero salt effect and surface charge density are discussed in the next section, Potentiometric Titrations.



Figure 4.20. Cation Exchange Capacity - synthetic soils. Lines by eye-fit.


Figure 4.21. Anion Exchange Capacity - synthetic soils.



Figure 4.22. Net surface charge calculated from ion exchange - synthetic soils.

#### 3.8 Potentiometric titrations

#### 3.8.1 Point of Zero Charge (Potentiometric Titrations)

Titrations were conducted in the same manner as for the oxides and the reader is referred to Section 1.9 (this Chapter) for a fuller explanation of the terms and calculations presented here. Figure 4.23 displays the titration results at each ionic strength in terms of Q (surface proton excess) versus pH. Although increasing the ionic strength had a greater effect than was observed for the oxides, it was still difficult to identify a single intersection point. As a result, the reader is reminded that the  $pH_{ZPC}$  values listed in Table 4.11 should be used to interpret trends between the different synthetic clays and kaolinite rather than taken as absolute values. Decreasing the Fe/Al ratio causes the  $pH_{ZPC}$  of the oxide-amended clays to rise while kaolinite falls in the middle of the range.

Figure 4.24 compares the surface proton excess, Q, for each of the synthetic clays and kaolinite at an ionic strength of 0.1M. At low pH (< pH 4), Q (positive charge) decreases in order K-Fe3Al > K-Al > K-FeAl > K-3FeAl > K-Fe > kaolinite, although K-Fe and K-3FeAI are very similar. At higher pH (> pH 8) however, the order of proton excess shows a clearer relationship with Fe/AI ratio; lower Fe/AI ratio corresponding to a greater excess of hydroxyl ions and hence a more negative surface. Normalising the surface proton excess to the specific surface area does not have a large effect except for kaolinite since the oxideamended clays all have fairly similar surface areas (Figure 4.17). The low surface area of kaolinite causes the surface charge density,  $\sigma$ , of this material to virtually overlap that of K-Fe throughout the pH range investigated. The  $pH_{ZPC}$  was calculated from the surface charge density at 0.01M and 0.1M, with the average from the two ionic strengths shown in Table 4.11. The importance of Fe/AI ratio is again clear with an increase in pH<sub>ZPC</sub> as the Fe/AI ratio decreases; the value calculated for kaolinite, pH 4.32, is closer to that expected from previous research using this clay (pH 4.2, Yong et al, 1992b), providing additional support for this method of estimating the pH<sub>ZPC</sub>.

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# 3.8.2 Points of Zero Charge - oxides versus synthetic clays

In the discussion of the particle size distribution it was postulated that the  $pH_{ZPC}$  for the oxide-amended clays might elucidate the nature of the oxide-kaolinite interaction; for example, if the oxide completely covered the clay surface then the zero point of charge should be similar to that of the oxide. Table 4.12 summarises the  $pH_{ZPC}$  obtained from the surface charge density (potentiometric titrations) for the materials in this study. The results allow the observation that while the oxides exert a strong influence, they do not completely dominate the surface charge.

Clay	pH <sub>ZPC</sub> clay	Oxide	pH <sub>ZPC</sub> oxide
K-Fe	4.18	Fe	4.32
K-3FeAl	4.48	3FeAl	4.76
K-FeAI	4.72	FeAl	5.64
K-Fe3Al	4.80	Fe3Al	5.06
K-AI	4.81	Al	4.92
Kaolinite	4.32		
Table 4.12. pF	IZPC of synthetic cla	ys & oxides by poten	tiometric titration.

The kaolinite  $pH_{ZPC}$  is equal to that measured for the Fe oxide yet when these two materials are combined, the resultant mixture has a lower  $pH_{ZPC}$  of 4.18. For the other synthetic clays, the  $pH_{ZPC}$  is between the value measured for the separate components. The  $pH_{ZPC}$  estimated by potentiometric titration is higher for the individual amorphous oxides than for the comparable synthetic clays. However, if the  $pH_{ZPC}$  calculated using the ion exchange experiments (CEC -AEC) is considered, a different trend is observed (Table 4.13).

Clay	pH <sub>zPC</sub> clay	Oxide	pH <sub>ZPC</sub> oxide
K-Fe	5	Fe	5.3
K-3FeAl	6	3FeAl	5.8
K-FeAl	6.8	FeAI	6.4
K-Fe3Al	7	Fe3Al	6.2
K-AI	6.5	AI	6.2
Kaolinite	3.7		
Table 4.13. pH	ZPC of synthetic clay	ys & oxides by ion ex	change.

In contrast to the titration results (with the exception of K-Fe), the  $pH_{2PC}$ estimated by the ion exchange experiments is higher for the synthetic clays than for the corresponding oxide. This apparent contradiction may be due to the fact that these two different methods of estimating pH<sub>ZPC</sub> are not measuring the same mechanism. In Section 1.8 of this Chapter, the different components that constitute the surface charge density were discussed and it was noted that while potentiometric titrations evaluate the surface charge density due to the protonation and de-protonation of pH-dependent surface hydroxyl groups, ion exchange experiments measure the charge due to outer-sphere adsorption of cations and anions which may occur at site that are not amphoteric. A higher pH<sub>ZPC</sub> means the particle surface is positively charged until a higher pH value since a greater concentration of OH<sup>-</sup> ions in solution is needed to neutralise the positive surface charge. The cation exchange capacity experiments used Ca<sup>2+</sup> as the saturating ion; it may be assumed that all the pH-dependent surface sites can adsorb Ca<sup>2+</sup> ions as well as protons, and that adsorption can also take place on some pH-independent sites. If this is the case then it follows that a greater number of cations may be adsorbed in the ion exchange experiments than in the potentiometric titrations (which only evaluate pH-dependent adsorption) thus explaining the higher pH<sub>ZPC</sub> observed in the ion exchange tests. This hypothesis requires the presence of pH-independent surface sites; for the kaolinite such sites have been documented on the face surfaces of particles due to isomorphous substitution of Al(III) for Si(IV) ions in the silica tetrahedra (Sposito, 1984; Schroth & Sposito, 1998). Unfortunately the different points of zero charge measured for the kaolinite cannot be explained by this theory since the ion exchange pH<sub>ZPC</sub> value is lower than that obtained for the potentiometric titration. The difficulty in accurately measuring the surface charge at high and low pH is well known for clays since more soluble materials (e.g. Al(OH)<sub>3</sub>) present as impurities on particle surfaces may partially dissolve. Furthermore the  $pH_{ZPC}$ obtained from the ion exchange experiments had to be extrapolated to a net charge of zero and it is possible that this extrapolation resulted in a lower  $pH_{ZPC}$ ; previous work with this kaolinite clay found a  $pH_{ZPC}$  of 4.2 (Yong et al, 1992b).

While the presence of these pH-independent sites may explain the higher  $pH_{ZPC}$  calculated by ion exchange for the synthetic clays relative to their component

oxides alone, it does not explain the disparity between the  $pH_{ZPC}$  results measured by the two methods for the oxides since these particles are not expected to have any pH-independent sites. However, if at a given pH the pHdependent surface sites can adsorb the same number of Ca<sup>2+</sup> ions as protons, then the higher  $pH_{ZPC}$  observed may be due to the difference in the charge carried by Ca<sup>2+</sup> ions as compared with H<sup>+</sup>. For this hypothesis to be valid, some of the Ca<sup>2+</sup> ions must be adsorbed as inner-sphere complexes since if only outersphere complexation is occurring, each Ca<sup>2+</sup> ion would satisfy the negative charge carried by two surface hydroxyl groups. Although the CEC method used is designed to evaluate non-specific adsorption, there is evidence that Ca<sup>2+</sup> ions can be specifically adsorbed by some materials including oxides (Sposito, 1984).



Figure 4.23a. K-Fe, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.23b. K-3FeAI, potentiometric titrations for ! = 0.01M, 0.1M and 1M.



Figure 4.23c. K-FeAI, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.23d. K-Fe3AI, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.23e. K-Al, potentiometric titrations for I = 0.01M, 0.1M and 1M.



Figure 4.23f. Kaolinite, potentiometric titrations for I = 0.01M, 0.1M and 1M.

#### 3.8.3 FITEQL modelling

Additional attempts to clarify the nature of the oxide-kaolinite interactions were conducted using FITEQL to estimate the surface acidity constants and the surface hydroxyl site density. Since the model did not converge for any of the clays when  $K_{a1}$  was included as a parameter to be optimised, the same approach was taken as explained in Section 1.9.2 (this Chapter) with the value of  $K_{a1}$  being estimated from the pH<sub>ZPC</sub> that had been calculated from the surface charge density.

Based on some initial test runs with FITEQL and MINTEQA2, the value of  $pH_{ZPC}$  was estimated from the average pH at which Q = 0 in the 0.01M and 0.1M titrations;  $pK_{a2}$  was taken from initial FITEQL runs in which  $K_{a1}$  was set equal to - 20 and not optimised in accordance with recommendations from the FITEQL manual (Herbelin & Westall, 1996). FITEQL was subsequently repeated with  $K_{a1}$  fixed at the value calculated by Equation 4.8 to estimate new values of  $K_{a2}$  and  $T_{XOH}$  which were then used in MINTEQA2.



Figure 4.24. Excess acid, Q (mol /L x  $10^3$ ) - synthetic clays at I = 0.1M (blank adjusted).

Oxide	log K <sub>e1</sub>	log K <sub>a2</sub>	Tot [XOH] (mmol /L)	N, (sites / nm²)	variance
K-Fe	2.34	-6.02	0.068	0.117	70-86
K-3FeAI	2.50	-6.46	0.076	0.147	65-89
K-FeAl	3.08	-6.36	0.117	0.222	51-85
K-Fe3Al	3.22	-6.38	0.124	0.264	46-88
K-AI	2.95	-6.67	0.222	0.486	43-70
Kaolinite	3.91	-4.70	0.019	0.098	68-72
Table 4.1	4. FITEO	L parame	eters - synthetic	c clays.	·

The effectiveness of surface complexation modelling using the diffuse double layer model and a single site type is illustrated in Figure 4.26 where MINTEQA2 was used to generate titration curves based on the FITEQL extracted constants. The sensitivity of the model to the value of  $K_{a1}$  is shown for the synthetic clays where the dotted line was calculated using the pH<sub>ZPC</sub> (zero salt effect) rather than the pH at which the surface charge density equalled zero.



Figure 4.25. Surface charge - synthetic clays at I = 0.1M (blank adjusted).



Figure 4.26a. K-Fe, experimental data and model predictions.

The fit of the model to the data is reasonable but not as good as found for the oxides. The variance listed in Table 4.13 for the FITEQL constants does not make this moderate fit unexpected since the variance should be between 0.1 and 20 for a good fit. The fit was relatively good in the pH 4 to 7 range except for kaolinite, which was encouraging since this is the range at which most of the contaminant studies were conducted. However, the fit was poor at lower pH for K-Fe, K-3FeAI and K-Fe3AI and at higher pH for all the synthetic clays. It seems that the use of a single site type to represent an average surface hydroxyl group

is inadequate for these materials. This was not totally unexpected since the reactivity of the kaolinite and oxides are quite different while the kaolinite possesses three different types of surface site (Section 6, Chapter 2).



Figure 4.26b. K-3FeAI, experimental data and model predictions.



Figure 4.26c. K-FeAI, experimental data and model predictions.

The concentration of surface hydroxyl groups,  $T_{XOH}$ , is about one order of magnitude lower for the synthetic clays (Table 4.13) than for the oxides (Table 4.7). This is to be expected since the synthetic clays contain 90% (by weight) of the less reactive kaolinite. When normalised to the surface area however, the site densities (sites / nm<sup>2</sup>) of the oxide-amended clays are approximately half that calculated for the appropriate oxide. The trend of increasing site density with

decreasing Fe/AI ratio that was observed for the oxides is repeated here, and along with the high site density compared with the kaolinite, this supports the idea of the oxides covering much of the clay surface.



Figure 4.26d. K-Fe3AI, experimental data and model predictions.



Figure 4.26e. K-AI, experimental data and model predictions.



Figure 4.26f. Kaolinite, experimental data and model predictions.

Although the FITEQL/MINTEQA2 graphs (Figure 4.26) only provide an approximate fit, it is still worthwhile considering the surface speciation calculated by the model (Figure 4.27). These were generated for the "best-fit" values of the acidity constants which are the same as listed in Table 4.13 (estimated from the surface charge density,  $pH_{ZPC}$ ) except for K-Fe3Al where  $K_{a1} = 4.12$  was estimated from the zero salt effect, pHzPC. The results are similar to those observed for the oxides with a large region (up to pH 6) dominated by the uncharged surface species, =XOH, while at higher pH, the negatively charged species, =XO<sup>-</sup> is most abundant. The low pH region is poorly modelled (Figure 4.26) for K-Fe3AI, K-3FeAI and K-Fe but the relatively low measured pHzPc suggests that the positively charged  $= XOH_2^+$  species is not important above ca. pH 4 to 4.5. In contrast to the oxide-amended clays, kaolinite shows only a narrow pH region where =XOH is the most important surface species with either the negatively- or positively-charged species dominating above pH 5 or below pH 4 respectively. The large pH region that has =XOH as the dominant surface species for the oxide-amended clays provides further support for the proposal that the kaolinite surface sites are mostly blocked by the oxides which results in the surfaces of the synthetic clays being closer in character to the oxides than to kaolinite. The implications of the surface speciation will be further explored in Chapter 6.



Figure 4.27a. K-Fe, surface speciation.



Figure 4.27b. K-3FeAl, surface speciation.



Figure 4.27c. K-FeAI, surface speciation.



Figure 4.27d. K-Fe3AI, surface speciation.



Figure 4.27e. K-Al, surface speciation.



Figure 4.27f. Kaolinite, surface speciation.

#### 4. Summary - physicochemical properties

#### 4.1 Oxide structure

The amorphous oxides were found to have very large specific surface areas (259 to 402 m<sup>2</sup>/g) with the Fe/AI ratio clearly influencing this property. The high Fe/AI ratio oxides (Fe, 3FeAI) had significantly greater surface areas than low Fe/AI oxides (Fe3AI, AI), however, the maximum surface area was found at Fe/AI = 1 (FeAI). The surface area of the 3FeAI and Fe3AI oxides was successfully calculated using the values from the pure end-members (Fe, AI) and the oxide

composition, but the calculated surface area of the FeAI oxide was significantly lower than that measured. At Fe/AI ratio = 0.3 (Fe3AI), the specific surface area was not significantly different from the AI oxide suggesting that the mixed oxide structure is controlled by the AI component. Similarly the specific surface area of 3FeAI (Fe/AI = 3) was close to the Fe oxide meaning the Fe component controls the structure.

A molecular structure is proposed wherein  $SO_4^{2-}$  anions act as bridges between  $Al^{3+}$  and  $Fe^{3+}$  ions (e.g. -Fe-O-S(O<sub>2</sub>)-O-Al-) during the precipitation of solids while adsorbed  $SO_4^{2-}$  ions inhibit the formation of larger crystals. The oxide structure is considered to develop as an open (porous) structure of loosely linked small particles with the most open structure being found at Fe/Al ratio = 1. At this Fe/Al ratio, the presence of equal concentrations of Fe and Al prevents either from controlling the structure of the oxide resulting in particles whose surfaces are a combination of Fe and Al oxides. The formation of Fe-O-Al chains reduces the bond strength of Al-O groups due to cation-cation repulsion and further limits the development of regular oxide crystals.

# 4.2 Oxide surface charge

The conceptual model of the solid : solution interface is that the oxide surface is covered with a mixture of amphoteric surface hydroxyl groups, e.g. =XOH, =XOH<sub>2</sub><sup>+</sup> and =XO<sup>-</sup> (where X represents Al<sup>3+</sup> and/or Fe<sup>3+</sup> at the surface). If this model is valid, raising the solution pH should result in the surface becoming increasingly negatively charged as more surface hydroxyls are de-protonated (i.e. form =XO<sup>-</sup>). Furthermore this model implies retention of heavy metals by surface complexation mechanisms as will be discussed in Chapters 5 and 6.

Oxide surface charge, as estimated by ion exchange experiments, was very dependent upon pH. Cation exchange capacity increased from near zero below pH 4.5 to pH 6 to approximately 0.25 meq /g at above pH 7 with a general order of Fe > 3FeAl > A! > Fe3Al > FeAl (pH 6.3 to 7). The oxide points of zero charge (pH<sub>ZPC</sub>; estimated from ion exchange experiments) could be divided into two groups: Fe/Al less than or equal to 1 (Al, Fe3Al, FeAl; pH<sub>ZPC</sub> = 6.2 to 6.4) and Fe/Al > 1 (3FeAl, Fe; pH<sub>ZPC</sub> = 5.3 to 5.8).

Potentiometric titrations were also used to investigate the oxide surface charge. Differences in the surface charge density of the oxides allow their division into three groups based on the Fe/Al ratio: high (Fe, 3FeAl), medium (FeAl) and low (Fe3Al, Al). At high pH, decreasing the Fe/Al ratio causes the surface charge density to become more negative; at low pH, the surface becomes more positive with decreasing Fe/Al ratio. Therefore surface hydroxyl groups on the low Fe/Al ratio oxides appear to be more sensitive to pH changes (more easily protonated and de-protonated) than the oxides containing a higher proportion of Fe.

Modelling with FITEQL and MINTEQA2 allowed some confidence in the conceptual model of the solid : solution interface as a series of amphoteric surface hydroxyl groups. Remembering that the model provides only a general trend rather than absolute values, the uncharged surface species, =XOH, is dominant below pH 7 for all the oxides; the positively charged species, =XOH<sub>2</sub><sup>+</sup>, is only important below pH 4 to 5; and at higher pH, the de-protonated surface species, =XO<sup>-</sup>, is prevalent.

# 4.3 Synthetic clays

Synthetic clays were formed by the addition of pre-precipitated Fe-Al oxides to kaolinite so as to investigate the influence of small proportions of oxide on the surface properties of kaolinite. The presence of approximately 10% (by weight) of amorphous oxide significantly enhanced the specific surface area of the synthetic clays (55 to 70 m<sup>2</sup>/g) relative to kaolinite (24 m<sup>2</sup>/g). The measured surface areas of the individual oxides and kaolinite were used to calculate the total surface area by assuming no interaction between the two components, however these calculations underestimated the measured surface area for K-Fe, K-3FeAl and K-Fe3Al. The most likely cause of this disparity is the breakdown of aggregated oxide particles during the synthetic clay preparation process when the oxides and kaolinite were mixed in suspension for 24 hours. This mixing is expected to expose greater amounts of oxide surface than was present in the oxides alone and this may have cancelled out any reduction in surface area that might have

been caused by the oxides covering the kaolinite surface or binding together adjacent clay particles.

### 4.4 Synthetic clay surface charge

The kaolinite showed the largest cation exchange capacity below pH 7.8 while at higher pH, the CEC for the synthetic clays rapidly increased and exceeded the kaolinite. The kaolinite carries a small permanent negative charge from isomorphous substitution, but the oxides appear to largely mask this at low pH when they are positively charged (and so have zero CEC), suggesting that the oxides cover much of the kaolinite surface. The cation exchange capacity varied considerably with pH, although to a lesser degree than was observed for the oxides alone.

Although the measurement of zero point of charge appeared to be influenced by the method of estimation (results differed between the ion exchange experiments and the potentiometric titrations), there is a general increase in the  $pH_{ZPC}$  as the Fe/Al ratio of the synthetic clays increases with K-Fe > K-3FeAl > K-FeAl > K-Fe3Al > K-Al.

Modelling of the surface charge with FITEQL and MINTEQA2 was less successful than for the oxides. This is most likely due to the use of a single site type to describe the surface reactive groups; while it may be possible to use a single *average* surface hydroxyl group to represent the oxide surface, kaolinite contains at least three different types of surface sites including both permanently charged and pH-dependent groups and so the modelling approach was too simplistic.

# CHAPTER 5 CONTAMINANT RETENTION - AMORPHOUS OXIDES

# 1. Contaminant precipitation - no oxide present

1.1 Single metal solutions: Experimental data and MINTEQA2 predictions

Figure 5.1 presents the removal of Cu from single metal solutions in the absence of oxides or clay from experimental data and as predicted by the geochemical speciation program, MINTEQA2 (Allison et al, 1990); the principles underlying this model are discussed in Chapter 7. Figure 5.1 shows that complete precipitation occurs over a narrow (less than one pH unit) for all Cu concentrations. The Cu concentration does not appear to make a significant difference to the location of the precipitation curve and although a slightly greater proportion of Cu is removed for 2.5 mmol /L than for the other three concentrations, the difference is probably within the experimental error.



Figure 5.1. Cu precipitation (single metal series).

Initial results from MINTEQA2 had a similar steep shape but were displaced to lower pH by about 0.7 pH units with tenorite (CuO) being predicted to precipitate. When this mineral was excluded from the database, an improved fit to the experimental data was found with the formation of copper hydroxide (Cu(OH)<sub>2</sub>). This result underlies the importance of a good understanding of the chemistry of systems prior to commencing modelling since MINTEQA2 is an equilibrium model which does not take account of reaction rates (kinetics). Although tenorite has a lower solubility than Cu(OH)<sub>2</sub>, the hydroxide will initially precipitate from these solutions but will tend to be transformed to CuO in time due to dehydration. The model provides an excellent fit of the 0.5 and 2.5 mmol Cu /L data but slightly underestimates precipitation at 5 and 25 mmol Cu /L.



Figure 5.2. Pb precipitation (single metal series).

The results for Pb are quite different with experimental data showing significant precipitation occurring only at 0.5 mmol /L (Figure 5.2), although even at this concentration less than 70% of the added Pb is removed from solution by pH 7. At the higher concentrations, maximum precipitation is less than 10% by pH 7.5 with the 2.5 and 5 mmol /L curves overlapping and demonstrating greater precipitation than at 25 mmol /L (maximum = 5%). All of the experimental data show shallow gradient precipitation curves in contrast to that predicted by

MINTEQA2 (Figure 5.2). The model predicts removal from solution to increase from 0 to 100% between pH 5.5 and 7 with the precipitation of Pb hydroxide (Pb(OH)<sub>2</sub>). The MINTEQA2 results suggest that the Pb concentration should influence the degree of removal with precipitation occurring earlier in the higher concentration solutions and the 0.5 mmol /L solution starting to precipitate at the highest pH (pH 5.8). The experimental results show the opposite trend however, with decreased precipitation as the Pb concentration increases.

The inability of the MINTEQA2 program to accurately predict precipitation of the Pb solutions is surprising since this model has been widely used to calculate the speciation of aqueous solutions in environmental situations (e.g. Loeppert et al, 1995). The most likely reason for the difference between the experimental and modelled results is kinetic limitations on the formation of insoluble precipitates. MINTEQA2 is an equilibrium speciation model (see Chapter 7 for additional discussion of this model) and does not account for rates of reaction. Although the 24 hour period of the precipitation tests was expected to be sufficient for equilibrium to be reached, soluble Pb-acetate complexes may inhibit the formation of insoluble Pb hydroxides within the experimental time frame. Giordano (1989) reported that at concentrations of acetate above 0.01M, the solubility of anglesite (PbSO<sub>4</sub>) increased markedly due to acetate complexing Pb<sup>2+</sup> ions; in the current study, acetate concentrations varied from 0.001 to 0.05M for the single metal solutions and 0.002 to 0.1M for the Cu+Pb solutions. Soluble Pb-acetate complexes (e.g.  $PbOAc^{+}$ ,  $Pb(OAc)_2^{0}$  where OAc represents the CH<sub>3</sub>COO<sup>-</sup> acetate ion) successfully compete with hydroxyls and may inhibit the creation of soluble complexes that are the precursors to insoluble hydroxides; precipitation of  $Pb(OH)_2$  (s) is typically preceded by the formation of soluble PbOH<sup>+</sup> and Pb(OH)<sub>2</sub><sup>0</sup> (aq) complexes (Pankow, 1991; Stumm & Morgan, 1996). Unfortunately the effects of reaction rates were not studied during the present experimental program, in part due to equipment constraints, but it is recommended that the possibility of this disparity between the experimental results and the MINTEQA2 predictions being due to kinetic effects is explored in future studies. Although possible kinetic effects were not systematically investigated, some supernatant solutions were not acidified until a day after being separated from the precipitate; additional precipitation was seen in these

solutions which strongly supports the hypothesis that the low Pb precipitation observed is due to kinetic constraints.

Another possible explanation for the MINTEQA2 results is that the reaction constants provided in the program database are inaccurate. Considerable uncertainty surrounds many reaction constants despite the systematic tabulation of values extracted from the literature (e.g. Martell & Smith, 1974) and errors in the MINTEQA2 database have been noted previously (Lindsay & Ajwa, 1995). Published research into the formation of metal-acetate complexes has noted the lack of reliable thermodynamic data (Giordano, 1989) with reported equilibrium constants for Pb-acetate complexes in particular showing considerable variation (Burns & Hume, 1956; Sillen & Martell, 1964; Bunting & Thong, 1970; Gobom, 1970; Nakagawa et al, 1980). The main reason proposed for this variability has been an apparent sensitivity to differences in experimental conditions, with ionic strength and temperature being the primary influences (Bunting & Thong, 1970); the Pb salt used has also been identified as a source of variability with different complexation constants being obtained depending on whether the study involves PbS, PbCl<sub>2</sub> or PbSO<sub>4</sub> (Giordano, 1989).

A further possible cause of these unexpected results is the experimental methodology utilised. If precipitation within the time-scale of the batch test resulted in the formation of very small particles of Pb(OH) (or other Pb solids), these may have remained in the supernatant solution after centrifugation and filtering. All supernatant samples were acidified to below pH 2 prior to analysis by atomic absorption spectrophotometry and any colloidal Pb present in the supernatant would therefore have been re-dissolved. Although the majority of the bulk precipitation batch tests were filtered through a 1.1  $\mu$ m glass fibre filter paper, a limited number were filtered using a 0.45  $\mu$ m filter which is a common operationally defined division between dissolved and particulate species. There was no noticeable difference between samples filtered through the different sizes of filter paper and so experimental artefacts are not thought to be the cause of these unexpected results.

Finally the MINTEQA2 database does not include any Pb- or Cu-bearing solids that also contain acetate whereas such mixed solids may be present. Dissolved acetate concentrations were not measured during the current experimental program; such measurements would assist in interpreting the results and should be carried out in future studies utilising acetate salts of heavy metals.

The results of these precipitation tests, and particularly the inability of MINTEQA2 to accurately model the Pb data, is worrying given the increasing propensity for modelling natural systems with geochemical equilibrium speciation models.

#### 1.2 Mixed metal solutions (Cu+Pb): Experimental data and MINTEQA2

Figure 5.3 illustrates the precipitation of Cu from solutions containing equimolar concentrations of both Cu and Pb (Cu+Pb solutions). The results are very similar to those from the single metal precipitation tests although some Cu appears to remain in solution for the 5 and 25 mmol /L concentrations even at pH 7.5. The MINTEQA2 predictions are similar to the single metal tests providing CuO is excluded as a possible solid, and although the model slightly underestimates precipitation at 0.5 and 2.5 mmol Cu /L it provides an excellent fit for 5 and 25 mmol Cu /L.



Figure 5.3. Cu precipitation (multi-contaminant "Cu+Pb" series).

The precipitation of Pb from the Cu+Pb solutions is shown in Figure 5.4. For 0.5 mmol Pb /L the experimental results present a much steeper curve than in the single metal tests, with precipitation commencing about 0.5 pH units higher. Complete removal of Pb occurs at around pH 6.5 in comparison with a maximum of 70% at pH 7.5 for the single metal solutions. For Pb concentrations of 2.5 and 5 mmol /L, the results show a slightly greater proportion of added Pb being removed and precipitation beginning at a lower pH than in the single metal tests while at 25 mmol Pb /L there is very little difference between the single and Cu+Pb solutions.



Figure 5.4. Pb precipitation (multi-contaminant "Cu+Pb" series).

MINTEQA2 predicts Pb removal to happen over an even narrower pH range than in the single metal tests with very little variation due to changes in concentration. The shape of the MINTEQA2 curve is relatively accurate for 0.5 mmol /L although the model predicted line is located about 0.3 pH units below the observed results.

The increased precipitation of Pb from the Cu+Pb solutions could be due to the coprecipitation of Pb with Cu solids. As Cu begins to precipitate (as hydroxide), some Pb ions could be incorporated within the Cu solid crystal and hence be removed from solution. This seems especially likely for the lowest concentration (0.5 mmol /L) since the Pb and Cu precipitation curves are very similar. The solubility of ions in solid solutions is known to be lower than in pure crystals since the activity of an ion is a function of its mole fraction in the solid (Stumm & Morgan, 1996). Therefore less Pb will remain in solution at a given pH if co-precipitation with Cu solids occurs; this is observed for 0.5, 2.5 and 5 mmol Pb /L.

Cu is known to form strong complexes with organic ligands (Boyd et al, 1981) such as acetate but the precipitation data suggest that hydroxyl ions compete more effectively with acetate for Cu than for Pb which was not expected. The aqueous complexation constants in the MINTEQA2 database do not appear to be adequate to predict precipitation for Pb-acetate solutions, at least within a 24 hour experimental time period.

The main reason for conducting the precipitation tests was to help explain the results from the batch adsorption tests with the oxides and clays, and they will be discussed further in Section 2, this Chapter.



Figure 5.5a. Cu aqueous speciation (0.5 mmol /L).

## 1.3 Aqueous speciation - MINTEQA2

Despite the uncertainty over the MINTEQA2 results, particularly for Pb, it is useful to consider the speciation predicted for dissolved metal species since this can provide insight into the species likely to be interacting with the functional groups on particle surfaces. The dissolved speciation of Cu and Pb in the single metal and Cu+Pb solutions is presented in Figures 5.5 to 5.8.

The solution speciation of Cu in single metal solutions is illustrated in Figure 5.5. For 0.5 mmol /L, over 85% of dissolved Cu occurs as the "free" ion,  $Cu^{2+}$ , throughout the pH range of interest (Figure 5.5a) with CuOAc<sup>\*</sup> (for brevity the acetate ion, CH<sub>3</sub>COO<sup>-</sup>, will be abbreviated to OAc<sup>-</sup>) providing the balance. As the total Cu concentration increases to 2.5 mmol /L (Figure 5.5b), Cu<sup>2+</sup> remains the dominant soluble species, however at pH 5.7 (when precipitation is predicted to begin), CuOAc<sup>\*</sup> provides about 30% of the total dissolved Cu.



Figure 5.5b. Cu aqueous speciation (2.5 mmol /L).

Since this species carries a charge of plus one, it is less likely to be electrostatically attracted to a negatively charged surface than Cu<sup>2+</sup>; conversely, if the surface is positively charged then CuOAc<sup>+</sup> will undergo less repulsion. An additional factor to be considered is that the ionic radius of the Cu<sup>2+</sup> ion is smaller

than the CuOAc<sup>+</sup> species. The larger ionic radius of CuOAc<sup>+</sup>, combined with the lower charge (+1) causes the charge density of this species to be less than Cu<sup>2+</sup> further reducing any electrostatic repulsion from positive surfaces (Shackelford et al, 1997). Another consideration is that larger molecules require more energy to be moved to the particle surface (Stumm & Morgan, 1996) while adsorption may be limited by steric effects (Spark et al, 1995a).



Figure 5.5c. Cu aqueous speciation (5 mmol /L).

As the concentration increases (Figures 5.5c & d), the importance of acetate complexes rises with CuOAc<sup>+</sup> providing 40% of the total Cu at pH 5.5 for 5 mmol Cu /L. In 25 mmol Cu /L solutions, CuOAc<sup>+</sup> dominates over Cu<sup>2+</sup> above pH 4.4, reaching a maximum of 50%, while at pH 5.5 ca. 20% of the soluble Cu is present as the uncharged species, Cu(OAc)<sub>2</sub><sup>0</sup>, and about 25% as Cu<sup>2+</sup>. At higher pH, Cu(OH)<sub>2</sub> is predicted to begin precipitating with a consequent reduction in soluble Cu.



Figure 5.5d. Cu aqueous speciation (25 mmol /L).



Figure 5.6a. Pb aqueous speciation (0.5 mmol /L).

The presence of uncharged Cu species will reduce retention by electrostatic mechanisms such as cation exchange which are expected to be important for kaolinite, and for the oxides at pH above their  $pH_{ZPC}$  (see Chapter 4). However if Cu is being specifically adsorbed through chemical (covalent) bonding to surface functional groups as is expected for the oxides, the absence of a positive charge

on dissolved species may enhance retention at pH below the oxide pH<sub>ZPC</sub> since the positively charged surface should repel positively charged ions.



Figure 5.6b. Pb aqueous speciation (2.5 mmol /L).



Figure 5.6c. Pb aqueous speciation (5 mmol /L).

The MINTEQA2 predicted speciation of Pb in single metal solutions is shown in Figures 5.6a to d. For 0.5 mmol Pb /L (Figure 5.6a), just over 30% of dissolved Pb is present as PbOAc<sup>+</sup> at pH 5.7 with the remainder being Pb<sup>2+</sup>. In contrast to Cu speciation, acetate complexes are important at lower concentrations with Pb. Figure 5.6b (2.5 mmol Pb /L) predicts that above pH 4.7, PbOAc<sup>+</sup> becomes the dominant Pb species over Pb<sup>2+</sup>, reaching a maximum proportion of 60% at pH 5.7, after which precipitation of Pb(OH)<sub>2</sub> commences. As the total concentration of Pb increases, the pH at which acetate complexes become dominant is lowered, occurring at pH 4.3 (5 mmol Pb /L) and pH 3.7 (25 mmol Pb /L). The maximum contribution of PbOAc<sup>+</sup> is 70% for both 5 (Figure 5.6c) and 25 mmol Pb /L (Figure 5.6d). In a similar manner to the Cu speciation predictions, the uncharged species, Pb(OAc)<sub>2</sub><sup>0</sup>, comprises approximately 20% of the total Pb at pH 5.5 (25 mmol Pb /L, Figure 5.6d) having exceeded the contribution from Pb<sup>2+</sup> at pH 4.9.



Figure 5.6d. Pb aqueous speciation (25 mmol /L).

The experimental data demonstrate that precipitation from Pb solutions greater than 2.5 mmol /L begins above pH 6 and removes a maximum of less than 10% by pH 7.5 (Figure 5.1b), suggesting that dissolved acetate complexes (e.g. PbOAc<sup>+</sup>, Pb(OAc)<sub>2</sub><sup>0</sup>) may be even more important above pH 6 than predicted by

MINTEQA2. The comments made in the Cu speciation section concerning retention mechanisms for charged and uncharged species apply equally here.



Figure 5.7a. Cu aqueous speciation (Cu+Pb, 0.5 mmol /L).

Figures 5.7 and 5.8 present MINTEQA2 speciation predictions for Cu and Pb in solutions containing equimolar concentrations of Cu and Pb (designated Cu+Pb solutions). It should be remembered that these Cu+Pb concentrations refer to the metal (either Cu or Pb) while the concentration of acetate is four times higher since 2 moles of acetate accompany each mole of Cu or Pb. Thus the maximum acetate concentration is 100 mmol /L at 25 mmol Cu or Pb /L.



Figure 5.7b. Cu aqueous speciation (Cu+Pb, 2.5 mmol /L).



Figure 5.7c. Cu aqueous speciation (Cu+Pb, 5 mmol /L).

For Cu, the percentage of each species is similar to those found in the single metal solutions although the maximum proportion of acetate complexes is about 10% higher in the Cu+Pb solutions. As a result, CuOAc<sup>+</sup> is equal in concentration to Cu<sup>2+</sup> at pH 5.2 for 5 mmol /L. (Figure 5.7c) and is dominant for 25 mmol /L

above pH 4.2 (Figure 5.7d). At this highest concentration, the uncharged species  $Cu(OAc)_2^0$  is predicted to dominate over  $Cu^{2*}$  above pH 4.8.



Figure 5.7d. Cu aqueous speciation (Cu+Pb, 25 mmol /L).



Figure 5.8a. Pb aqueous speciation (Cu+Pb, 0.5 mmol /L).

The Pb model results for Cu+Pb solutions show a similar behaviour relative to the single metal systems with acetate complexes becoming important at lower pH values. The pH values at which PbOAc<sup>+</sup> surpasses Pb<sup>2+</sup> are pH 5.8 (0.5 mmol Pb /L), pH 4.2 (2.5 mmol Pb /L), pH 4 (5 mmol Pb /L) and pH 3.4 (25 mmol Pb /L).



Figure 5.8b. Pb aqueous speciation (Cu+Pb, 2.5 mmol /L).

The proportion of total Pb present as the uncharged  $Pb(OAc)_2^0$  species is equal to  $Pb^{2*}$  for 5 mmol Pb /L at pH 5.6 (Figure 5.8c) and exceeds  $Pb^{2*}$  above pH 4.3 at 25 mmol Pb /L (Figure 5.8d). Based on the experimental results which show less than 10% precipitation at pH 7.5, and extrapolation of the MINTEQA2 speciation predictions,  $Pb(OAc)_2^0$  is probably the dominant dissolved Pb species above pH 6.5 for a concentration of 25 mmol Pb /L.

The presence of acetate as a complexing ligand suppresses the formation of hydroxyl complexes for both Cu and Pb (e.g. CuOH<sup>\*</sup>, Cu(OH)<sub>2</sub><sup>0</sup>, PbOH<sup>\*</sup>, Pb(OH)<sub>2</sub><sup>0</sup>) and MINTEQA2 predicts less than 1% of any of these species will form. The formation of acetate complexes will complicate the interaction of Cu and Pb with particle surfaces although whether retention will be enhanced or reduced will depend on whether physical (electrostatic) or chemical (specific/covalent) adsorption is dominant. Species carrying a plus one charge

will be less attracted to negatively charged surfaces than species with a plus two charge, however if the surface is positively charged (below  $pH_{ZPC}$ ) uncharged species may be most strongly attracted.



Figure 5.8c. Pb aqueous speciation (Cu+Pb, 5 mmol /L).



Figure 5.8d. Pb aqueous speciation (Cu+Pb, 25 mmol /L).
As noted in the literature review, acetate concentrations of up to 10,000 mg /L (equivalent to 170 mmol /L) have been reported for landfill leachates (Davies et al, 1996; Darkin et al, 1997) suggesting that the possibility of acetate complexes enhancing the solubility and mobility of metals such as Cu and Pb should be included in any studies into the fate and transport of contaminants from landfill sites. Future research should also be conducted using non-complexing metal salts (e.g. nitrate) to clarify the impact of acetate complexes on metal retention.

### 2. Single metal contaminant tests (Pb or Cu) - oxides

### 2.1 Contaminant retention - Pb (single metal series)

Figure 5.9 shows the proportion of total Pb added that is retained by the oxides as a function of pH for four different concentrations of Pb. As expected, the proportion of added Pb that is retained by the oxides increases with pH. This corresponds to the results of previous researchers (e.g. Yong et al, 1993; Coston et al, 1995) and is due to three main factors: increasing the pH causes a greater proportion of surface hydroxyl sites to be negatively charged (e.g. =Al-O<sup>-</sup>) encouraging electrostatic attraction of Pb cations to these sites; in addition, rising pH decreases the concentration of hydrogen ions and so competition between Pb ions and protons for adsorption sites on the particle surface is reduced; finally, higher pH encourages Pb ions to precipitate out of solution in the form of hydroxides and oxides (e.g. Pb(OH)<sub>2</sub>).

Bulk precipitation was evaluated by the tests run in the absence of oxides (Pbppt.) and is markedly affected by Pb concentration with about 70% precipitation from 0.5 mmol /L solutions at pH 7.5 (Figure 5.9a) but less than 10% removal from 25 mmol /L solutions at the same pH (Figure 5.9d). The results in Figure 5.9 suggest that for all concentrations of Pb, the predominant retention mechanism by the oxides is adsorption rather than bulk precipitation.



Figure 5.9a. Pb retention by oxides (0.5 mmol /L). Lines are by eye-fit.



Figure 5.9b. Pb retention by oxides (2.5 mmol /L). Lines are by eye-fit.

In Figure 5.9a, the total concentration of Pb added is 0.5 mmol /L and with the exception of the Al oxide, more than 90% of the added Pb is retained even at pH 4.5; complete retention is not achieved by the Al oxide until pH 6.4. Since bulk precipitation removes less than 30% of added Pb at pH 6, the main retention

mechanism is almost certainly adsorption rather than precipitation. It is recognised however, that particle surfaces may act as nucleation sites and initiate precipitation at lower pH values than in the absence of solids by lowering the activation energy barrier (Stumm & Morgan, 1996). Furthermore it has been suggested that at the molecular level, there is a continuum between adsorption (surface complexation), surface precipitation and bulk precipitation (Farley et al, 1985) and distinguishing between these mechanisms is not possible with the methods available in this study (a fuller explanation of these retention mechanisms is presented in Chapter 7).

Figure 5.9b (2.5 mmol Pb /L) shows that increasing the total concentration of lead added raises the pH at which 100% is retained. For all the oxides, 100% retention is achieved at approximately pH 6; at lower pH values there is a clear order of increased retention with Fe > 3Fe-Al > Fe-Al > Fe-3Al > Al.



Figure 5.9c. Pb retention by oxides (5 mmol /L). Lines are by eye-fit.

Similar results are found for a concentration of 5 mmol Pb /L (Figure 5.9c) with 100% retention being achieved at approximately pH 6.3; at lower pH values there is a clear order of increased retention with Fe > 3FeAI > FeAI > Fe3AI > AI. At these intermediate contaminant concentrations, higher Fe/AI ratio oxides exhibit

a shallower increase in sorption with rising pH, not least since retention is high even at < pH 4. The 3FeAI and FeAI oxides show very similar retention patterns for 2.5 and 5 mmol /L and are considerably more effective at lowering soluble Pb levels than the Fe3AI and AI oxides; at pH 4.5, FeAI retains 15 to 25% more Pb than Fe3AI from 2.5 and 5 mmol /L solutions. The low Fe/AI ratio oxides (Fe3AI, AI) show a steeper increase in retention with pH which is probably due to the different acid-base properties of AI and Fe surface sites (e.g.  $\equiv$ AI-OH and  $\equiv$ Fe-OH) as discussed in Section 1.9, Chapter 4, where it was found that the negative charge density of AI and Fe3AI increases more rapidly than for the other oxides.



Figure 5.9d. Pb retention by oxides (25 mmol /L). Lines are by eye-fit.

At the highest concentration of 25 mmol /L (Figure 5.9d), the same retention order is found for the oxides but complete Pb retention is not obtained until pH 6.7. In contrast to the lower Pb concentrations, the sorption curves for the different oxides are fairly evenly spaced and have broadly similar shapes and gradients. The results at lower concentrations suggest that Fe surface sites possess a higher affinity for Pb ions than Al sites since retention occurs at lower pH while the bulk precipitation tests suggest that precipitation is not an important retention mechanism. If surface complexation is the dominant sorption

mechanism for all Pb concentrations then the sorption edges would be expected to continue to show differences depending on the Fe/Al ratio.

Since the 25 mmol /L sorption curves are all broadly parallel, it is reasonable to suggest that one mechanism is responsible for Pb retention by all the oxides at this concentration. This is unlikely to be surface complexation since each oxide possesses different proportions of =AI-OH and =Fe-OH surface sites and these sites have differing acid-base, and metal complexation properties. It is therefore proposed that since the shallow sorption curves are broadly parallel to the bulk precipitation line, surface precipitation of  $Pb(OH)_2$  is occurring on all the oxides. The Fe/AI ratio continues to influence the location of the retention curves since surface complexation takes place until the surface sites are fully occupied, hence oxides with more high affinity Fe sites will retain more Pb at lower pH. Furthermore, surface precipitation is influenced by the identity (=AI-OH or =Fe-OH) of the surface sites (Karthikeyan et al, 1997). Once complete saturation of surface sites occurs, surface (or possibly bulk) precipitation becomes dominant and the increase in Pb retention with rising pH is similar for all the oxides.



Figure 5.10a. Fe oxide - Pb retention. Lines are by eye-fit.

The effect of total Pb concentration on sorption by each individual oxide is presented in Figure 5.10a to e. These figures clearly show that increasing the Pb concentration decreases the proportion of added Pb that is retained at a given pH while the Fe/AI ratio distinctly influences the magnitude of the decrease in sorption. Table 5.1 tabulates the percentage of total Pb retained at pH 4.5 (pH 4.7 for AI) by each oxide and for bulk precipitation.

	% Pb retention at pH 4.5 (AI = pH 4.7)					
Total Pb (mmol /L)	0.5	2.5	5	25		
Fe	100	97	95	80		
3FeAl	100	90	88	65		
FeAI	98	88	80	50		
Fe3Al	95	72	55	42		
AI	82	48	55	38		
No oxide (Pb-ppt)	0	0	0	0		
Table 5.1. % Pb reten	tion at pH 4.	5 - oxi <b>des</b> .				

The Fe oxide shows the smallest concentration effect (Figure 5.10a) with retention from the 25 mmol /L solution being a little lower (20%) than from the 0.5 mmol /L solution.



Figure 5.10b. 3FeAl oxide - Pb retention. Lines are by eye-fit.

The mixed oxide, 3FeAI, also demonstrates only a small difference between sorption from the 0.5, 2.5 and 5 mmol /L solution (< 10%) but the concentration effect is larger for 25 mmol /L with an almost 25% reduction in sorption (Figure 5.10b).



Figure 5.10c. FeAl oxide - Pb retention. Lines are by eye-fit.

For the FeAI oxide, which contains equal proportions of Fe and AI, increasing the concentration has a more substantial effect but the difference between retention from 0.5 and 5 mmol /L remains less than 20% (Figure 5.10c), however 30% less Pb is retained as the concentration rises from 5 to 25 mmol /L.



Figure 5.10d. Fe3Al oxide - Pb retention. Lines are by eye-fit.

The Fe3Al oxide (Fe/Al ratio = 0.3) has a more pronounced change in sorption with increasing concentration (Figure 5.10d). With each increase in total Pb, the proportion retained drops by about 15% with a large fall (40%) between 0.5 and 5 mmol /L.

The AI oxide (no Fe surface sites) exhibits a different trend and experiences the greatest reduction in Pb retention as the concentration increases from 0.5 to 2.5 mmol /L (Figure 5.10e). In contrast to the other oxides in which the shape of the 25 mmol /L sorption curve is shallower than the lower concentrations, retention is not markedly different (< 20%) between the 2.5, 5 and 25 mmol /L solutions and the curves are approximately parallel.



Figure 5.10e. Al oxide - Pb retention. Lines are by eye-fit.

Figure 5.10 supports the contention that the Fe and AI surface sites have different affinities for Pb and confirms that the capacity for Pb complexation by AI at lower pH is considerably less than for Fe sites. The low Fe/AI ratio oxide, Fe3AI, appears to behave in a similar fashion to the pure AI oxide suggesting that the surface of this mixed oxide contains a greater proportion of AI sites than would be expected on the basis of the bulk composition; this is in agreement with the conclusions made from the specific surface area results (Section 1.4, Chapter 4).

Another potential factor influencing Pb retention as the concentration increases is the identity of the species being sorbed (e.g.  $Pb^{2+}$ ,  $PbOH^+$ ,  $PbOAc^+$ ,  $Pb(OAc)_2^0$ ). MINTEQA2 was used to predict the aqueous speciation (Section 1, this Chapter) and the results are combined with the Pb retention data for 5 and 25 mmol /L in Figure 5.11. It should be remembered that MINTEQA2 was unable to accurately reproduce the bulk precipitation experiments and so these speciation predictions should be considered as qualitative at best. For 5 mmol /L, PbOAc<sup>+</sup> is the dominant soluble Pb species above pH 4.3, but it is difficult to discern whether this exerts any appreciable influence on Pb retention.

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Figure 5.11a. Pb speciation & retention (5 mmol /L).



Figure 5.11b. Pb speciation & retention (25 mmol /L).

Similarly at 25 mmol /L, PbOAc<sup>+</sup> is dominant throughout the pH range for which experimental data are available but it is not possible to determine whether the slightly shallower shape of the retention curves at this concentration is due to sorption of this species, or complete occupancy of higher affinity surface sites. Elucidation of the influence of soluble Pb-acetate complexes on Pb retention

would require data from batch tests using a non-complexing ion (e.g. nitrate); unfortunately such tests were not conducted as part of the current experimental program.

## 2.2 Contaminant retention - Cu (single metal series)

Figure 5.12 presents the proportion of total added Cu that is retained by the oxides as a function of pH for four different concentrations of Cu. These are the same molar concentrations as those for Pb in Figure 5.9. As with the Pb results, the proportion of added Cu that is retained increases with pH, although increasing the Fe/AI ratio of the oxides has a smaller influence on Cu retention than with Pb.



Figure 5.12a. Cu retention by oxides (0.5 mmol /L). Lines are by eye-fit.

At low Cu concentrations, the retention order remains Fe > 3FeAl > FeAl > Fe3Al > Al (Figure 5.12a - 0.5 mmol /L), but as the metal concentration increases, the difference in retention behaviour by the individual oxides becomes smaller although the sorption curves remain broadly parallel. Sorption by the Al and Fe3Al oxides from 2.5 and 5 mmol /L solutions (Figures 5.12b & c) is very similar to each other but less than demonstrated by the other, higher Fe/Al ratio, oxides.

However at high Cu concentration (25 mmol /L, Figure 5.12d) the retention curves cease being parallel while the selectivity order changes at about pH 4.6. The Fe sorption curve is located about 0.4 pH units lower than the similarly shaped 3FeAl curve which is in turn ca. 0.2 pH units lower than the FeAl curve. The sorption curves for these three oxides (intermediate to high Fe/Al ratio) are broadly parallel with each other and with the bulk precipitation line. In contrast, for the Fe3Al and Al curves which are essentially collinear, the proportion retained with pH increases much more quickly; as a result, these oxides retain more Cu than FeAl, 3FeAl and Fe above ca. pH 4.6, 4.7 and 4.8 respectively.



Figure 5.12b. Cu retention by oxides (2.5 mmol /L). Lines are by eye-fit.

The different shape of the retention curves between the low and high Fe/AI ratio oxides suggests that the dominant sorption mechanism at high metal concentrations is determined by the nature of the sorbing substrate. The similarity between the Fe3AI and AI oxides implies that AI surface groups dominate the surface chemistry of the Fe3AI oxide, while the steep increase in retention relative to the higher Fe/AI ratio oxides allows the conclusion that these AI surface sites have a higher affinity for Cu than do Fe surface sites. The strength of this affinity appears to pH-dependent however, as the high Fe/AI ratio oxides are more effective at retaining Cu below pH 4.6 to 4.8.

These results concur with the Pb results at high metal concentration and confirm that Al oxides are less effective than Fe sites at forming surface complexes with Cu and Pb at low pH (< pH 4.5 to 4.8). Alternatively, the steep increase in retention from 25 mmol /L solutions by Al and Fe3Al could be due to the onset of surface precipitation since the sorption curves are broadly parallel to the bulk precipitation line.



Figure 5.12c. Cu retention by oxides (5 mmol /L). Lines are by eye-fit.

Bulk precipitation of Cu occurs over a much narrower pH range (pH 5.7 to 6.5) than for Pb, and complete removal of Cu from solution occurs at all concentrations in contrast to Pb. Since all the added Cu is retained below the pH at which precipitation begins at any concentration, adsorption is expected to be the dominant retention mechanism although sorption may include surface precipitation at higher metal loading.



Figure 5.12d. Cu retention by oxides (25 mmol /L). Lines are by eye-fit.

Figure 5.13 and Table 5.2 illustrate that increasing the total Cu concentration causes the sorption curves to shift to a higher pH for all the oxides.

Total Cu (mmol /L)	% Cu retention at pH 4.5				
	0.5	2.5	5	25	
Fe	92	88	85	71	
3FeAI	92	85	78	48	
FeAl	92	82	70	34	
Fe3Al	94	65	48	23	
AI	88	63	50	20	
No oxide (Cu-ppt)	0	0	0	0	
Table 5.2. % Cu reten	tion at pH 4.	5 - oxides.	• • • • • • • • • • • • • • • • • • •	•	

This concentration effect is even more pronounced for Cu than was observed for Pb and also varies with Fe/Al ratio. The Fe oxide shows the smallest decrease in percent retained at pH 4.5 with increased metal loading (21% reduction from 0.5 to 25 mmol /L).



Figure 5.13a. Fe oxide - Cu retention. Lines are by eye-fit.

The 3FeAI mixed oxide behaves similarly with Cu as with Pb (Table 5.1 & Figure 5.13b), showing a relatively small decrease in sorption (14%) from 0.5 to 5 mmol /L but then a 30% reduction as the concentration rises to 25 mmol /L.



Figure 5.13b. 3FeAl oxide - Cu retention. Lines are by eye-fit.

A slightly larger concentration effect is observed for the FeAl oxide with a 22% reduction from 0.5 to 5 mmol /L and an additional 36% decrease at 25 mmol /L.



Figure 5.13c. FeAl oxide - Cu retention. Lines are by eye-fit.

However the Fe3AI and AI oxides show the sharpest decrease in contaminant accumulation at pH 4.5 of 30 to 35% from 0.5 to 2.5 mmol /L, followed by 13 to 17% at 5 mmol /L, and then an additional 25 to 30% reduction in retention as the concentration rises to 25 mmol /L.



Figure 5.13d. Fe3Al oxide - Cu retention. Lines are by eye-fit.



Figure 5.13e. Al oxide - Cu retention. Lines are by eye-fit.

These results further support the proposal based on the Pb data that the affinity shown by Fe surface sites for metals is different from Al sites. Although the 25 mmol /L results indicate that the Al surface sites have a greater affinity for Cu than the Fe sites, at low pH (< pH 4.8) the Fe sites are more effective at retaining Cu than Al sites. The capacity of all these oxides to retain Pb and Cu is very high

since complete retention occurred prior to the bulk precipitation pH even from 25 mmol /L solutions resulting in solid Cu and Pb concentrations of approximately 48,000 and 155,500 mg/kg respectively.



Figure 5.14a. Cu speciation & retention (5 mmol /L).



Figure 5.14b. Cu speciation & retention (25 mmol /L).

Figure 5.14 presents aqueous speciation predictions from MINTEQA2 in an effort to further clarify the mechanism of Cu retention by identifying the identity of the species being sorbed (e.g.  $Cu^{2*}$ ,  $CuOH^*$ ,  $CuOAc^*$ ,  $Cu(OAc)_2^0$ ). The somewhat steeper sorption edges observed as the Fe/AI ratio decreases could be linked to the gradual reduction in the proportion of soluble Cu that is present as  $Cu^{2*}$  as the pH rises although no clear trend is discernible for 5 mmol /L (Figure 5.14a). The theoretical background for surface complexation is discussed more fully in Chapter 7, however the basic principle is that adsorption by particle surfaces involves the displacement of protons by the sorbing cations, thus:

#### Equation 5.1

 $= XOH + Cu^{2*} = = XOCu^* + H^*$ 

where  $\equiv$ XOH represents a surface site and X may be AI or Fe.

Reactions in accordance with Equation 5.1 cause the surface to obtain an increased positive charge which results in greater electrostatic repulsion of positively charged ions. Increased positive surface charge has been measured for oxides as a result of surface complexation of cations using electrophoretic measurements (James & Healy, 1972). However if this reaction is occurring, a decreased steepness of the sorption edge would be expected as the metal concentration increases which is not observed, at least for the AI and Fe3AI oxides (Figure 5.14a & b). These low Fe/AI oxides do not retain appreciable guantities of Cu from 25 mmol /L solutions until the pH is above 4.5; at this pH. the dominant dissolved Cu species is CuOAc<sup>\*</sup>. Since this species carries a charge of plus 1 (compared to plus 2 for Cu<sup>2+</sup>), surface complexation in accordance with Equation 5.1 will not result in a change to the oxide surface charge. As a result, adsorption does not cause increased electrostatic repulsion of cations and so the CuOAc<sup>+</sup> species should be less repelled by the positive surface charge caused by protonation of the surface hydroxyl groups below the pH<sub>ZPC</sub>. This could explain why the AI and Fe3AI sorption edges are steeper than for the higher Fe/Al ratio oxides which begin to sorb Cu when Cu<sup>2+</sup> is the dominant dissolved species and consequently obtain an increased positive surface charge with each Cu<sup>2+</sup> ion that is complexed by the surface.

### 2.3 Discussion - metal sorption mechanisms

Comparing the pH at which metal cations are retained, and the surface charge and hydroxyl speciation of the oxide at that pH (as determined by titrations and ion exchange tests) should clarify the mechanisms by which Pb and Cu ions are held to the oxide surfaces. Since the majority of the heavy metals are retained when the ion exchange experiments indicate that the oxide surfaces carry a net positive charge, simple electrostatic attraction cannot explain contaminant retention. This suggests that specific adsorption is occurring in which the high affinity between the metal cations and surface hydroxyl groups promotes the formation of chemically bonded surface complexes despite unfavourable electrostatic conditions (James & Healy, 1972; Stumm et al, 1976). This proposal is supported by the cation exchange capacity results since the Fe oxide does not demonstrate a significant number of negatively charged ion exchange sites until greater than pH 4.5 while the other oxides should not physically adsorb metals until > pH 5.5 to 6. Another possibility is that the formation of metal-hydroxide surface complexes promotes surface precipitation by acting as a nucleation site (Fendorf et al, 1992). The surface speciation calculated by MINTEQA2 from the potentiometric titrations (Section 1.9, Chapter 4) implies that the uncharged species, =XOH, dominates for the pH range in which most metals are retained. In spite of the different description of the surface charge estimated by the ion exchange and titration tests, both methods suggest that the metals are complexed by either positively- or uncharged surface hydroxyl groups indicating chemical bonding rather than simple physical (electrostatic) attraction.

As the total concentration of Pb or Cu increases, the pH at which a given percentage of metal is retained shifts to higher pH. Higher metal concentrations lead to increased competition between surface hydroxyls and dissolved ligands (e.g. acetate) for dissolved metals and protons so adsorption is less favourable until the concentration of protons is reduced (i.e. higher pH). Surface hydroxyl sites have a very high affinity for metal ions via surface complexation (Dzombak & Morel, 1990) but once these sites are "full", other retention mechanisms such as surface precipitation (Farley et al, 1985) and bulk precipitation become important. As the concentration of Cu and Pb increases, the proportion of total metal ions that can be accommodated by surface complexation decreases and

so the retention curve is shifted to a higher pH value. Another possible reason for this upward shift with increasing concentration is that the reactivity of individual surface hydroxyl groups may vary considerably due to such factors as the relative proximity of adjacent surface sites and the morphology of the oxide surface at the molecular level (Benjamin & Leckie, 1981).

It has been proposed that a small proportion (ca. 2.5%) of the total surface sites on amorphous Fe hydroxides have a very high affinity for metals (Dzombak & Morel, 1990). Initially these sites will form complexes with Pb and Cu ions, but once they are fully occupied other sites with lower affinities become responsible for metal retention. The density of high affinity surface sites is typically evaluated from constant pH sorption isotherms (log sorbed metal concentration versus log equilibrium soluble metal concentration) as the sorption density at which the isotherm slope becomes less than one (Dzombak & Morel, 1990). Sorption isotherms with a slope of unity imply that sorption affinity is constant and is consistent with a single type of binding site, whereas if multiple sites with differing sorption affinities are participating in retention, the isotherm slope becomes less than one. Constant pH sorption isotherms were generated for the current data but it was not possible to estimate the density of high affinity sites since the isotherm slopes were always less than unity and so these graphs have not been presented. At the relatively high metal concentrations utilised in the current experimental program, it is therefore expected that the majority of sorption will be occurring on lower affinity sites since the small number of high affinity sites should be fully occupied even with 0.5 mmol /L solutions.

### 2.4 Selectivity - Cu versus Pb - single metal solutions

Figure 5.15 compares the Pb and Cu retention data at 2.5 mmol /L for each oxide. These experiments were conducted with either Pb or Cu as the only heavy metal present. The influence of Fe/Al ratio on the relative amount of each metal retained is clear with the proportion of Pb being retained increasing relative to Cu as this ratio rises. The high Fe/Al ratio oxides clearly retain a greater proportion of added Pb than Cu (Figure 5.15a, Fe; Figure 5.15b, 3FeAl). When the Fe/Al ratio is equal (FeAl), slightly more Pb than Cu is adsorbed (Figure 5.15c). For the

Fe3AI oxide (Figure 5.15d), the Pb and Cu retention behaviour becomes very similar while the AI oxide (Figure 5.15e) distinctly retains more Cu than Pb at a given pH.

Kinniburgh et al (1976) found the order of cation selectivity from multicontaminant solutions to be Pb > Cu for amorphous Fe oxides and Cu > Pb for amorphous Al oxides; the same selectivity was found in the current thesis for the pure Fe and Al oxides as can be seen in Figures 5.17 and 5.21. They proposed that the Fe oxide surface structure was more open thus allowing the large Pb cation greater access to internal surface adsorption sites than with the Al oxide; as will be presented below, an alternative proposition is that selectivity can be explained by the principle of hard and soft Lewis acids and bases. Karthikeyan et al (1997) recently compared coprecipitation and adsorption of Cu at low concentrations (0.07 mmol /L) with amorphous oxides containing either Fe or Al. They concluded that Al oxides have a lower adsorption (surface complexation) capacity than Fe oxides but that Al oxide induces surface precipitation at lower soluble Cu levels than does Fe oxide to give an apparent higher retention capacity.



Figure 5.15a. Fe oxide - retention of Pb and Cu (single metal solutions of 2.5 mmol /L).



Figure 5.15b. 3FeAl oxide - retention of Pb and Cu (single metal solutions of 2.5 mmol /L).



Figure 5.15c. FeAl oxide - retention of Pb and Cu (single metal solutions of 2.5 mmol /L).



Figure 5.15d. Fe3Al oxide - retention of Pb and Cu (single metal solutions of 2.5 mmol /L).

The preference shown by soil surfaces for different cations has been related to the unhydrated ionic radius (Yong et al, 1992a) and the first hydrolysis product of the metal cation (Kinniburgh et al, 1976) but the results presented here are in agreement with Karthikeyan et al (1997) in suggesting that the nature and reactivity of the soil surface functional group (e.g. =AI-OH versus =Fe-OH) may be as important as the nature of the cation, at least for amorphous oxides. The selectivity of particle surfaces for cations of equal valence can be related to the relative hydrated sizes of the cations and relative energies of hydration. lons of smaller unhydrated radius have a larger hydrated radius because their greater density of charge per unit volume (increased polarising power) attracts water molecules more strongly (Evans, 1989). Smaller hydrated cations can approach the soil surface more closely since their positive charge is less shielded by the hydration layer and they can interact more closely with the seat of negative charge on the soil (Bohn et al, 1979, p. 149). It follows that cations which are only partially hydrated (i.e. three water molecules instead of the usual six for heavy metals) will be able to approach the soil surface even more closely and will therefore have an even stronger coulombic attraction to the surface. The Pb<sup>2+</sup> ion has a larger unhydrated radius than Cu<sup>2+</sup> (0.124 nm cf. 0.072 nm; Alloway, 1995), and hence should have a smaller hydrated radius; this may help explain

why Pb is retained in preference to Cu at Fe/Al > 1. In general, Pb is preferentially specifically adsorbed over Cu because although they have very similar first hydrolysis constants, Pb has a greater unhydrated ionic size (Yong et al, 1992b).



Figure 5.15e. Al oxide - retention of Pb and Cu (single metal solutions of 2.5 mmol /L).

The principle of hard and soft Lewis acids and bases (HSAB) has been applied to cation selectivity in soils (Sullivan, 1977) and it may assist in explaining these results. Fe oxides act as hard bases (Alloway, 1995) and since Al<sup>3+</sup> is "harder" than Fe<sup>3+</sup> (Sullivan, 1977), it is reasonable to assume that Al oxides behave as harder bases. Due to its smaller unhydrated ionic radius, Cu<sup>2+</sup> is a harder acid than Pb<sup>2+</sup> (Alloway, 1995) and so the HSAB principle suggests that it should preferentially associate with Al oxide since this is the harder base. The preference shown by Cu for Al oxide, and by Pb for Fe oxides in this study is therefore in agreement with the HSAB principle. The formation of soluble complexes (e.g. metal-acetate) may interfere with this principle since chemical speciation affects HSAB characteristics (Sullivan, 1977).

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Figure 5.16a. Fe oxide - retention of Pb and Cu (single metal solutions of 25 mmol /L).



Figure 5.16b. 3FeAl oxide - retention of Pb and Cu (single metal solutions of 25 mmol /L).



Figure 5.16c. FeAl oxide - retention of Pb and Cu (single metal solutions of 25 mmol /L).



Figure 5.16d. Fe3AI oxide - retention of Pb and Cu (single metal solutions of 25 mmol /L).

At higher contaminant concentration (25 mmol /L, Figures 5.16a to e), the mixed oxides retain greater Cu than Pb until the Fe/Al ratio is greater than one (3FeAl, Figure 5.16b). At this concentration the Cu retention order between the different oxides is not clear (see Figure 5.12d) which suggests that the mechanism involved in Cu retention (e.g. surface complexation versus surface and/or bulk precipitation) is sensitive to the total contaminant concentration as would be expected from other research (e.g. Dzombak & Morel, 1990). It is not possible to confirm whether the proposal that Al oxides induce surface precipitation of Cu more effectively than Fe oxides (Karthikeyan et al, 1997) can explain these results without conducting more sophisticated tests, such as X-ray absorption spectroscopy (Roe et al, 1991), than was possible within the constraints of this thesis.



Figure 5.16e. Al oxide - retention of Pb and Cu (single metal solutions of 25 mmol /L).

Figures 5.15 and 5.16 confirm the earlier proposition based on the specific surface area results (Figure 4.1) that the AI component controls the oxide structure and surface at Fe/AI ratio < 1 while mixed oxides behave similarly to Fe oxides at Fe/AI > 1.

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# 3. Mixed metal solution contaminant tests (Cu+Pb)

# 3.1 Contaminant retention - Pb versus Cu (Cu+Pb solutions)

In addition to the single metal batch tests, a series of experiments was conducted in which equimolar concentrations of Cu and Pb were added to the oxides to evaluate the effect of competition on the retention of the individual heavy metals. The concentration of either Cu or Pb was the same as that used in the single metal tests (0.5, 2.5, 5 or 25 mmol /L) to give a total metal concentration of 1, 5, 10 or 50 mmol Cu+Pb /L.



Figure 5.17a. Fe oxide - Cu+Pb retention (0.5 mmol /L).

Figure 5.17 shows that the Fe oxide preferentially retains Pb over Cu at all metal concentrations and demonstrates that the identity of the sorbing ion is the main influence on retention selectivity with pH also being important. The difference in the percentage of Pb and Cu retained varies with concentration and at pH 3.8 is 20% for 0.5 mmol /L (Figure 5.17a), 40% for 2.5 mmol /L (Figure 5.17b), 40% for 5 mmol /L (Figure 5.17c), and 45% for 25 mmol /L (Figure 5.17d). Over 90% of added Pb is retained throughout the pH range studied except for 25 mmol /L

(60%), whereas the minimum percentage of Cu sorbed varies from 15 to 80% with greater metal concentration causing decreasing retention at low pH.



Figure 5.17b. Fe oxide - Cu+Pb retention (2.5 mmol /L).



Figure 5.17c. Fe oxide - Cu+Pb retention (5 mmol /L).

The pH at which 100% removal of Pb and Cu is observed is tabulated in Table 5.3 (pH<sub>100</sub>); for Pb it is below pH 5 for all concentrations except 25 mmol /L (pH 6.9) while for Cu the pH<sub>100</sub> values are about 0.5 pH units higher than for Pb except for 25 mmol /L which remains at pH 6.9. The pH<sub>100</sub> value for Cu at 0.5 mmol /L may be an overestimate due to a paucity of data points between pH 4 and 6.



Figure 5.1	7d. Fe	oxide	- Cu+Pb	retention	(25 mmol	/L).
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pH <sub>100</sub>	Pb (Cu+Pb) conc. (mmol /L)				Cu (Cu+Pb) conc. (mmol /L)			
<u> </u>	0.5	2.5	5	25	0.5	2.5	5	25
Fe	<4.0	5.1	5.4	6.9	6.1	5.4	5.5	6.9
3FeAI	5.6	5.2	5.6	6.8	6.7	5.6	6.4	6.5
FeAl	6.3	5.5	6.2	6.7	6.5	5.7	6.2	6.5
Fe3AI	6.1	5.7	6.8	6.8	5.6	5.7	5.6	5.7
AI	6.3	6.6	6.8	6.8	6.2	6.0	5.9	5.5
Table 5.	3. pH <sub>100</sub> (	Cu+Pb s	olutions -	oxides.	•	•	•	·



Figure 5.18a. 3FeAl oxide - Cu+Pb retention (0.5 mmol /L).



Figure 5.18b. 3FeAl oxide - Cu+Pb retention (2.5 mmol /L).

The 3FeAI oxide also preferentially accumulates Pb over Cu at a given pH although the difference is less marked than for Fe. Figure 5.18 shows that at pH 4.4, 20% more Pb is retained than Cu for 0.5 mmol /L, and this percentage

difference is fairly constant with increasing concentration, being 25% (2.5 mmol /L), 20% (5 mmol /L) and 25% for 25 mmol /L.



Figure 5.18c. 3FeAl oxide - Cu+Pb retention (5 mmol /L).



Figure 5.18d. 3FeAl oxide - Cu+Pb retention (25 mmol /L).



Figure 5.19a. FeAl oxide - Cu+Pb retention (0.5 mmol /L).



Figure 5.19b. FeAl oxide - Cu+Pb retention (2.5 mmol /L).

The  $pH_{100}$  values for Pb are only slightly higher than for the Fe oxide (Table 5.3) but less Pb is retained by the 3FeAl oxide below pH 5 than by the Fe oxide. The effect of lowering the oxide Fe/Al ratio on the Cu results is similar with the entire sorption edge being shifted to a slightly higher pH for 3FeAl than for Fe oxide. The Pb and Cu sorption edges have broadly parallel shapes and since the bulk

precipitation curves (Figures 5.3 and 5.4) show Cu being removed over a much narrower pH range than Pb (for which there is very little precipitation below pH 7.5), it is reasonable to speculate that adsorption (surface complexation) is a more likely retention mechanism than precipitation.



Figure 5.19c. FeAl oxide - Cu+Pb retention (5 mmol /L).



Figure 5.19d. FeAl oxide - Cu+Pb retention (25 mmol /L).

As the Fe/Al ratio decreases, the difference in Pb and Cu sorption behaviour becomes less marked so that for the FeAl oxide at pH 4.5, only about 10% more Pb is retained from solutions containing 0.5 mmol Cu or Pb /L (Figure 5.19a). For 2.5 mmol /L, the preference for Pb remains about 10% at pH 4.5 although as the pH increases, the Pb and Cu curves become very close before joining at pH 5.4 (100% retention).



Figure 5.20a. Fe3Al oxide - Cu+Pb retention (0.5 mmol /L).

Similar results are shown in Figure 5.19c (5 mmol /L) while at 25 mmol /L, although about 20% more Pb is retained than Cu at pH 4.5, the Cu sorption edge surpasses the Pb edge at pH 5 and rises more steeply until complete removal occurs (Figure 5.19d). The FeAl oxide has a greater availability of Al surface sites (Fe/Al ratio = 1) and the preference shown for Cu over Pb at high contaminant loading suggests that Cu has a higher affinity for Al than for Fe sites. This was proposed in the discussion of the single metal results (Section 2, this Chapter) and appears to be confirmed here although whether the retention mechanism is surface complexation or surface precipitation remains uncertain.

For the Fe3Al oxide (Fe/Al ratio = 0.3), the trend towards preferring Cu over Pb at higher concentrations is continued, presumably due to the increased proportion
of Al surface sites, and Pb is only preferred over Cu at 0.5 mmol /L (Figure 5.20a). At a concentration of 2.5 mmol /L, equal percentages of added Cu and Pb are retained at all pH values, while for 5 mmol /L, Cu shows a higher affinity than Pb for the surface above pH 4.6 (Figure 5.20c). The general shape of the Cu and Pb sorption edges is similar with Cu being only marginally steeper which causes 100% removal to occur at a slightly lower pH.



Figure 5.20b. Fe3Al oxide - Cu+Pb retention (2.5 mmol /L).

However retention curves from solutions containing 25 mmol Cu or Pb /L clearly show a much shallower Pb sorption edge with more Cu being retained than Pb above pH 4.9 (Figure 5.20d). While this shallower retention curve means complete Pb accumulation occurs at a higher pH than for Cu, at lower pH (< pH 4.5), considerably more Pb (35-40%) is retained than Cu (15%). This could be explained if Pb is being retained primarily on Fe sites and Cu on Al sites due to the different acid-base properties of each surface site (Section 1.9, Chapter 4). The pH<sub>ZPC</sub> of the Fe oxide is lower than that of the Al oxide (pH 4.3 versus 4.9) with a resultant lower pH at which =Fe-OH groups become protonated (=Fe-OH<sub>2</sub>\*) and hence positively charged. Although it has been argued previously that adsorption is occurring despite apparent repulsion of cations from positively charged surface sites, the absence of such unfavourable electrostatic conditions

should aid adsorption and it may be that electrostatic attraction is a more important component of Cu surface complexation by AI sites than for Pb complexation by Fe sites. This proposition will be tested using the AI oxide results and would be supported if more Pb than Cu is retained from high metal concentration solutions at low pH.



Figure 5.20c. Fe3Al oxide - Cu+Pb retention (5 mmol /L).

The Al oxide shows a clear preference for Cu over Pb throughout the pH range for which data are available at 0.5 and 2.5 mmol /L (Figures 5.21a and b). For 5 mmol /L however, Cu is only preferentially retained above pH 4.3 (Figure 5.21c) while at the highest concentration (25 mmol /L) more Cu than Pb is retained above pH 4.8 (Figure 5.21d). These results do not support the earlier proposal that the difference between the acid-base properties of Fe and Al sites could be used to explain the preference for Cu or Pb ions. The steeper shape of the Cu sorption edge at higher metal loading suggests that the characteristics and aqueous speciation of the individual cations determines the order of Cu and Pb retention, at least for very high metal concentrations.



Figure 5.20d. Fe3Al oxide - Cu+Pb retention (25 mmol /L).



Figure 5.21a. Al oxide - Cu+Pb retention (0.5 mmol /L).

In summary, for high Fe/AI ratio oxides (Fe, 3FeAI), Pb is preferentially retained over Cu at all concentrations. For low to intermediate Fe/AI ratios (FeAI, Fe3AI) Cu is selectively sorbed over Pb at high concentration (25 mmol /L) and higher pH (> pH 5) while at low concentration (0.5 mmol /L) or low pH (< pH 5 for 5 or 25 mmol /L), Pb shows a stronger affinity for the surface. The AI oxide (no Fe

present) retains more Cu than Pb for all concentrations although Pb is preferred to Cu below pH 4.8 when contaminant loading is very high (25 mmol /L).



Figure 5.21b. Al oxide - Cu+Pb retention (2.5 mmol /L).



Figure 5.21c. Al oxide - Cu+Pb retention (5 mmol /L).



Figure 5.21d. Al oxide - Cu+Pb retention (25 mmol /L).

3.2 Contaminant retention - Pb (single metal) versus Pb (Cu+Pb solutions)



Figure 5.22a. Fe oxide - Pb retention (single & multi-contaminant solutions), 0.5 mmol /L.



Figure 5.22b. Fe oxide - Pb retention (single & multi-contaminant solutions), 2.5 mmol /L.

The presence of competing ions could be expected to inhibit sorption if the retention mechanism is on discrete adsorption sites and there is a finite number of these sites. The effect of competing ions on the retention of Pb and Cu can be clarified by comparing the retention of each metal from single metal solutions with the results from the Cu+Pb multi-contaminant solutions. It should be remembered that while the concentration of Pb (or Cu) is the same in both single metal and Cu+Pb solutions, the multi-contaminant solutions (Cu+Pb) have total metal concentrations twice those in the single metal solutions. Thus the ionic strength is higher and overall competition is greater.



Figure 5.22c. Fe oxide - Pb retention (single & multi-contaminant solutions), 5 mmol /L.



Figure 5.22d. Fe oxide - Pb retention (single & multi-contaminant solutions), 25 mmol /L.

The Fe oxide results presented in Figure 5.22 do not show the expected trend due to competing ions. At 0.5 mmol /L, complete Pb removal is observed at all pH values reflecting an excess of metal binding sites, while at medium concentrations (2.5, 5 mmol /L) 5 to 10% more Pb is retained from solutions also

containing Cu than from single metal solutions. At high metal concentrations (25 mmol /L, Figure 5.22d), about 10 to 15% more Pb is retained from single metal solutions above pH 4.5, however the presence of Cu continues to enhance Pb retention (from Cu+Pb solutions) at lower pH.



Figure 5.23a. 3FeAl oxide - Pb retention (single & multi-contaminant solutions), 0.5 mmol /L.

While bulk precipitation of Pb is increased in the Cu+Pb solutions, this is unlikely to affect the observed selectivity since precipitation does not appear to occur until at least one pH unit higher than that at which all added Pb was retained. The aqueous speciation model results (Figures 5.6 and 5.8) predict that 10% more Pb will be present as PbOAc<sup>+</sup> in the Cu+Pb than the single metal solutions and the lower charge on this complex may reduce electrostatic repulsion from the Fe oxide which is positively charged up to pH 4.3 (Section 1.8, Chapter 4). At 25 mmol /L (Figure 5.22d), there is a distinct change in the slope of the single metal retention curve at pH 4.5 which might be due to a change in slope is close to the pH at which Pb(OAc)<sub>2</sub><sup>0</sup> becomes more prevalent than Pb<sup>2+</sup> (pH 4.7), no such effect is found for the Cu+Pb solutions despite MINTEQA2 predicting a larger proportion of added Pb being present as the Pb(OAc)<sub>2</sub><sup>0</sup> species above pH 4.3 (Figure 5.8d). It is possible that the sharp slope change is due to experimental

variation and that additional data would show it to be an artefact. The inability of MINTEQA2 to accurately predict the precipitation of Pb in the absence of soil should also be remembered and the aqueous speciation figures should be considered qualitative at best.



Figure 5.23b. 3FeAI oxide - Pb retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.23c. 3FeAl oxide - Pb retention (single & multi-contaminant solutions), 5 mmol /L.



Figure 5.23d. 3FeAI oxide - Pb retention (single & multi-contaminant solutions), 25 mmol /L.

The 3FeAl oxide accumulates a slightly greater proportion of added Pb from single metal solutions than from solutions also containing Cu, although the effect of competing ions is small. Figures 5.23a to c (0.5 to 5 mmol /L) show an approximately 5% reduction in Pb retention while for 25 mmol /L (Figure 5.23d) the difference is about 10% at < pH 5 but zero at higher pH. While this could be ascribed to a surface charge effect ( $pH_{ZPC} = 4.8$ ) it is more likely that the combination of competition from Cu ions and protons for surface complexation sites at low pH causes a slight suppression in the adsorption of Pb compared to solutions in which protons are the only competitor.

There appears to be a somewhat larger effect of competition from Cu ions for the FeAI oxide (Figure 5.24), with greater retention of Pb from single metal solutions at all metal concentrations, and again, the effect seems to be enhanced at lower pH. Figures 5.24b & c show that at pH 4.5, competition from Cu reduces Pb sorption by about 20% while above pH 5 there is very little difference in retention. Although Figure 5.24d shows similar results for high metal concentrations (25

mmol /L), the experimental variation is quite large and so it is difficult to draw clear conclusions.



Figure 5.24a. FeAl oxide - Pb retention (single & multi-contaminant solutions), 0.5 mmol /L.



Figure 5.24b. FeAl oxide - Pb retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.24c. FeAI oxide - Pb retention (single & multi-contaminant solutions), 5 mmol /L.



Figure 5.24d. FeAl oxide - Pb retention (single & multi-contaminant solutions), 25 mmol /L.

The low Fe/Al ratio oxide, Fe3Al, seems to undergo very little change in Pb retention in the presence or absence of Cu (Figure 5.25). It is only for 25 mmol /L that competition with Cu ions affects Pb accumulation with a reduction of 5 to 10% (Figure 5.25d).

The results for the AI oxide are similar to Fe3AI with little competition effect, although this oxide retains less Pb than Cu from either single metal or Cu+Pb solutions throughout the pH range and concentrations studied. At 2.5 mmol /L (Figure 5.26b), less Pb appears to be retained from single metal solutions, however there are not many data points for this system so it may be an experimental artefact. At the highest concentration of 25 mmol /L (Figure 5.26d), competition with Cu seems to reduce Pb retention but unfortunately the variation in data points limits quantification of this effect.



Figure 5.25a. Fe3Al oxide - Pb retention (single & multi-contaminant solutions), 0.5 mmol /L.



Figure 5.25b. Fe3Al oxide - Pb retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.25c. Fe3Al oxide - Pb retention (single & multi-contaminant solutions), 5 mmol /L.

The bulk precipitation data suggest that accumulation is primarily by surface complexation for all of the amorphous oxides since precipitation in their absence did not remove much Pb, except for 0.5 mmol /L. At this lowest metal

concentration, only the AI oxide does not remove 100% of added Pb below pH 5.5, but even this oxide retains over 80% before bulk precipitation commenced from single metal solutions (pH 5.2) or Cu+Pb solutions (pH 5.8).



Figure 5.25d. Fe3Al oxide - Pb retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.26a. Al oxide - Pb retention (single & multi-contaminant solutions), 0.5 mmol /L.



Figure 5.26b. Al oxide - Pb retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.26c. Al oxide - Pb retention (single & multi-contaminant solutions), 5 mmol /L.

The results for Pb retention in the presence and absence of Cu suggest that the sites responsible for Pb complexation are less affected by competition than those for Cu. Figure 5.27 shows that the general shape of the Pb sorption curves from single and multi-contaminant solutions is unchanged for 5 (Figure 5.27a & b) and

25 mmol /L (Figure 5.27c & d) although at the higher concentration, the curves are shifted upward by about 0.4 to 0.5 pH units when Cu is present (see also Table 5.4, 25 mmol /L). This upwards shift is consistent with Cu ions occupying some surface sites and thus inhibiting Pb complexation.



Figure 5.26d. Al oxide - Pb retention (single & multi-contaminant solutions), 25 mmol /L.

рН <sub>50</sub>	25 mmol /L		
	Pb (single metal)	Pb (Cu+Pb)	
Fe	-	•	
3FeAl	4.1	4.4	
FeAl	4.6	5.1	
Fe3AI	4.8	5.4	
AI	5.1	5.6	
Table 5.4	. pH <sub>50</sub> (25 mmol Pb /L) ·	oxides.	

Since Cu does not appear to significantly interfere with Pb retention at concentrations of 5 mmol /L or less, the capacity of higher affinity surface sites may only be exceeded at the highest metal loading. As the concentration increases, lower affinity sites become more important but since they have lower complexation constants, they are less effective at removing Pb from solution. The single metal results (Section 2, this Chapter) demonstrated that increasing the Pb concentration does shift the Pb sorption curves to higher pH which supports the

proposal that the oxide surface possesses a variety of surface sites with differing complexation capacities (Benjamin & Leckie, 1981).



Figure 5.27a. Oxides - retention of Pb (Cu+Pb solutions, 5 mmol /L).



Figure 5.27b. Oxides - retention of Pb (single metal solutions, 5 mmol /L).



Figure 5.27c. Oxides - retention of Pb (Cu+Pb solutions, 25 mmol /L).



Figure 5.27d. Oxides - retention of Pb (single metal solutions, 25 mmol /L).

## 3.3 Contaminant retention - Cu (single metal) versus Cu (Cu+Pb solutions)

Figure 5.28 compares the accumulation of Cu by the Fe oxide from single metal solutions and from solutions containing equimolar concentrations of Cu and Pb (Cu+Pb). Retention is complete for all concentrations studied from either type of solution before the pH at which precipitation in the absence of particles begins, except for 25 mmol /L Cu+Pb solutions (Figure 5.28d) where 90% of added Cu is sorbed.



Figure 5.28a. Fe oxide - Cu retention (single & multi-contaminant solutions), 0.5 mmol /L.

For the three lower concentrations (0.5, 2.5, 5 mmol /L; Figures 5.28a to c) the presence of Pb as a competing ion appears to have no effect on the sorption of Cu. There is however, a substantial reduction in Cu retention from 25 mmol /L Cu+Pb solutions above pH 4, reaching a maximum of 30% at pH 5 (Figure 5.28d). The 25 mmol /L Cu+Pb sorption curve is much more shallow than for the single metal despite the bulk precipitation data showing a very steep increase from 0 to 80% retention in about 0.5 pH units.



Figure 5.28b. Fe oxide - Cu retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.28c. Fe oxide - Cu retention (single & multi-contaminant solutions), 5 mmol /L.

These results could be explained by postulating surface complexation by amphoteric surface hydroxyl groups as the primary retention mechanism with Pb and Cu having different affinities for the surface sites. As the pH increases, competition for surface sites from protons decreases and increasing amounts of Cu are accumulated. However when the metal concentration is very high (25 mmol /L) and both Cu and Pb are present, available sites initially form complexes



with Pb before sorbing Cu. If no Pb is present, Cu can form surface complexes more easily and sorption occurs over a narrower pH range.

Figure 5.28d. Fe oxide - Cu retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.29a. 3FeAI oxide - Cu retention (single & multi-contaminant solutions), 0.5 mmol /L.

The 3FeAl oxide (Fe/Al ratio = 3) has a lower capacity for Cu than the Fe oxide as is evidenced by reduced (15% at pH 4.5) Cu retention from Cu+Pb solutions even at the lowest concentration, 0.5 mmol /L (Figure 5.29a). At higher metal concentrations, the difference between Cu sorption from single metal and Cu+Pb

solutions remains but there does not appear to be a significant concentration effect (2.5 and 5 mmol /L; Figures 5.29b & c).



Figure 5.29b. 3FeAl oxide - Cu retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.29c. 3FeAl oxide - Cu retention (single & multi-contaminant solutions), 5 mmol /L.

For the 25 mmol /L solutions, Cu accumulation in the presence of Pb (Cu+Pb) is shifted to higher pH by about 0.4 pH units (Figure 5.29d) however competing ions do not seem to affect the shape of the retention curve. The 3FeAI oxide removes all of the added Cu before bulk precipitation occurs at all concentrations studied.



Figure 5.29d. 3FeAl oxide - Cu retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.30a. FeAI oxide - Cu retention (single & multi-contaminant solutions), 0.5 mmol /L.

Cu retention by the FeAI oxide follows a similar pattern to the 3FeAI oxide with the presence of Pb causing a shift in the sorption curves to a slightly higher pH. Due to the steep slope of the curves for 2.5 and 5 mmol /L, the effect of competing ions is to reduce sorption by 25-30% at pH 4.5 (Figures 5.30b & c) while accumulation from 25 mmol /L solutions is reduced when Pb is present by about 40% at pH 5 (Figure 5.30d). Complete retention of Cu is observed from all concentrations of both single metal and Cu+Pb solutions prior to bulk precipitation.



Figure 5.30b. FeAI oxide - Cu retention (single & multi-contaminant solutions), 2.5 mmol /L.

The Fe3AI oxide (Fe/AI ratio = 0.3) shows similar Cu retention behaviour to the other mixed oxides at low metal concentrations (0.5 mmol /L) in that more Cu is sorbed from single metal solutions than from Cu+Pb solutions (Figure 5.31a). As the concentration increases to 2.5 and 5 mmol /L, the impact of competing ions is less marked and below pH 4.5, the trend is reversed with more Cu being retained from Cu+Pb solutions than when Cu is the only sorbing ion (Figures 5.31b & c).



Figure 5.30c. FeAl oxide - Cu retention (single & multi-contaminant solutions), 5 mmol /L.



Figure 5.30d. FeAI oxide - Cu retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.31a. Fe3Al oxide - Cu retention (single & multi-contaminant solutions), 0.5 mmol /L.



Figure 5.31b. Fe3Al oxide - Cu retention (single & multi-contaminant solutions), 2.5 mmol /L.

The shapes of the sorption edges are somewhat different with the single metal curves showing a much steeper increase in percent retained as the pH rises; for 25 mmol /L, retention increases from 10 to 100% in 0.5 pH units while sorption from the Cu+Pb solutions is less steep (from 10 to 100% over about 1.5 pH

units). The gap between single metal and Cu+Pb solutions is quite large for 25 mmol /L since the single metal retention curve is very steep and at pH 5, the presence of Pb causes a reduction in Cu retention of about 60% (Figure 5.31d).



Figure 5.31c. Fe3Al oxide - Cu retention (single & multi-contaminant solutions), 5 mmol /L.

Sorption by the AI oxide displays similar characteristics to the Fe3AI oxide with Pb suppressing Cu retention from 0.5 mmol /L solutions (Figure 5.32a), having very little effect at 2.5 mmol /L (Figure 5.32b), and a more significant reduction at 5 mmol /L (Figure 5.32c).



Figure 5.31d. Fe3Al oxide - Cu retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.32a. Al oxide - Cu retention (single & multi-contaminant solutions), 0.5 mmol /L.

For 25 mmol /L (Figure 5.32d), Cu retention by the Al oxide from single metal solutions is about 55% higher than from Cu+Pb solutions at pH 5, however the shapes of the two retention curves are similar. The single metal sorption edge increases from 10 to 100% over 0.5 pH units while the Cu+Pb curve rises from 10 to 100% retention over about 1 pH unit.



Figure 5.32b. Al oxide - Cu retention (single & multi-contaminant solutions), 2.5 mmol /L.



Figure 5.32c. Al oxide - Cu retention (single & multi-contaminant solutions), 5 mmol /L.

The influence of heavy metal concentration on the slope of the sorption curves varies with both solution composition (single metal or Cu+Pb solutions) and Fe/Al ratio. At 5 mmol /L, the introduction of a competing ion (Pb) causes the mixed oxide sorption curves to be shifted to a slightly higher pH and it becomes difficult to distinguish between the different oxides (Figures 5.33a & b). The Al and Fe

oxides seem less affected by the presence of Pb with neither sorption curve showing much change from the single metal results (Figure 5.33b).



Figure 5.32d. Al oxide - Cu retention (single & multi-contaminant solutions), 25 mmol /L.



Figure 5.33a. Oxides - retention of Cu (Cu+Pb solutions, 5 mmol /L).

At the higher concentration of 25 mmol /L, the response to Pb is quite different (Figures 5.33c & d), particularly for the Fe oxide which shows a much more gradual increase in Cu retention from multi-contaminant solutions with pH. When

just Cu is present, retention by the Fe oxide increases from 25 to 100% in 2 pH units (pH 4 to 6) whereas with Pb as a competing ion, the same percentage increase requires 3 pH units (pH 3.8 to 6.9). The sorption edges for the other oxides are shifted upwards by 0.4 to 0.5 pH units, and are a little shallower for the Cu+Pb solutions (Figures 5.33c & d) as illustrated by the change in pH<sub>50</sub> (Table 5.5).

рН <sub>50</sub>	25 mmol /L		
	Cu (single metal)	Cu (Cu+Pb)	
Fe	4.2	4.6	
3FeAl	4.6	5.0	
FeAl	4.6	4.9	
Fe3AI	4.6	5.0	
AI	4.6	5.1	
Table 5.5	i. pH <sub>50</sub> (25 mmol Cu /L)	- oxides.	



Figure 5.33b. Oxides - retention of Cu (single metal solutions, 5 mmol /L).

Another interesting trend that can be observed from Figures 5.33c & d (25 mmol /L) is that the pH rise required for a change in Cu retention from 0 to 100% decreases with decreasing Fe/AI ratio; thus for the Cu+Pb solutions, the magnitude of pH shift is AI < Fe3AI < FeAI < 3FeAI < Fe (Figure 5.33c). The results for Cu retention from single metal solutions show a similar trend although the variation between the AI, Fe3AI and FeAI oxides is less clear. In general, as

the number of Fe sites is reduced (decreasing Fe/AI ratio), the Cu sorption edges become steeper and more parallel with the Cu precipitation curve. The presence of Pb seems to interfere with the *shape* of the Cu sorption edge for Fe rich oxides but only affects the *location* of the Cu sorption edge for low Fe/AI oxides.



Figure 5.33c. Oxides - retention of Cu (Cu+Pb solutions, 25 mmol /L).





The potentiometric titration data (Section 1.9, Chapter 4) suggest that the surface functional groups provided by the AI and Fe components have differing acid-base properties; similarly the batch test data are consistent with the surface sites having different affinities and hence complexation capacities for Cu and Pb. The similarity between the 25 mmol Cu /L retention curves for AI, Fe3AI, FeAI and 3FeAI suggest that Cu sorption on these oxides is predominantly by the same mechanism. The wider pH range needed for the Fe oxide to retain 100% of added Cu suggests that Fe sites require a larger rise in pH to form surface complexes with Cu, and is consistent with Cu having a lower affinity for Fe hydroxyl groups than for Al surface hydroxyls. The slightly shallower gradient retention curves as the Fe/AI ratio increases can therefore be explained by the presence of Fe surface sites which require a larger rise in pH to complex Cu ions than do the AI sites. The preceding discussion only applies at very high contaminant loading (25 mmol /L) since at lower Cu concentrations, the order of retention and shape of the sorption curves depends on the Fe/AI ratio; the higher the Fe/AI ratio, the more Cu will be retained (i.e. Fe > 3FeAI > FeAI > Fe3AI > AI).

The variation in Cu retention behaviour observed at high metal concentration could be explained by more than one type of surface site being provided by the AI component although two sorption mechanisms (i.e. surface complexation accompanied by surface precipitation) is also consistent with the data. Karthikeyan et al (1997) concluded that the apparently greater affinity shown by Cu for AI over Fe oxides was due to the AI oxide promoting surface precipitation more effectively than Fe oxides. Since retention by surface precipitation is not limited by the availability of surface complexation sites, this mechanism results in a greater proportion of Cu being sorbed at a given pH.

## CHAPTER 6 CONTAMINANT RETENTION - SYNTHETIC CLAYS

## 1. Single metal contaminant tests - Pb or Cu

## 1.1 Contaminant retention - Pb (single metal series)

Figure 6.1 shows the percentage of added Pb that is retained by the different synthetic clays as a function of pH for four Pb concentrations (0.5, 2.5, 5 and 25 mmol Pb /L). The order of Pb retention by the different clays changes with concentration but appears to be controlled by the Fe/Al ratio of the oxide component; at 0.5 mmol Pb /L (Figure 6.1a), the retention order (pH 4 to 5) is K-Fe > K-3FeAl > K-FeAl = Kaolinite > K-Fe3Al > K-Al. At pH 4, the K-Fe and K-3FeAl clays remove over 50% of the added Pb (K-Fe = 85%, K-3FeAl = 50%) in contrast to the other clays which retain less than 30% (Kaolinite, K-FeAl, K-Fe3Al), while the K-Al exhibits close to zero Pb accumulation capacity at this pH.



Figure 6.1a. Synthetic clays - 0.5 mmol Pb /L.

Complete removal of Pb from solution is achieved at pH 5 (K-Fe), pH 5.5 (K-3FeAl, K-FeAl), pH 6.3 (K-Fe3Al, K-Al) and pH 6.6 (Kaolinite). Comparison with the bulk precipitation data (Pb-ppt) suggests that adsorption is the dominant retention mechanism since precipitation in the absence of particles does not commence until pH 5 and removes only 60% of added Pb at pH 7.5. As noted in the discussion of the oxide retention results (Chapter 5), it is recognised that particle surfaces may act as nucleation sites and initiate precipitation at lower pH values than in the absence of solids by lowering the activation energy barrier (Stumm & Morgan, 1996), and also that distinguishing between adsorption, surface precipitation and bulk precipitation is not possible with the experimental methods available in this study.



Figure 6.1b. Synthetic clays - 2.5 mmol Pb /L.

In Figure 6.1b, the Pb concentration is 2.5 mmol /L and the order of Pb retention (pH 5) has reverted to what would be expected based on the oxide Pb retention data (Chapter 5) with K-Fe > K-3FeAl > K-FeAl > K-Fe3Al > K-Al > kaolinite. Since bulk precipitation is expected to remove less than 10% by pH 7.5, adsorption remains the dominant Pb retention mechanism. The retention curves for the different clays are closer than in Figure 6.1a while the pH range at which 100% of the Pb is retained is much narrower and has shifted to higher pH: pH 6 to 6.7 for the five synthetic clays and pH 7.2 for kaolinite.
At the higher concentration of 5 mmol /L (Figure 6.1c), the Pb retention order is unchanged below pH 5.2 but then becomes less clear at higher pH since the different curves are very close together. Kaolinite shows a maximum Pb removal of 75% at pH 7.5.



Figure 6.1c. Synthetic clays - 5 mmol Pb /L.



Figure 6.1d. Synthetic clays - 25 mmol Pb /L.

At 25 mmol /L (Figure 6.1d), the accumulation capacity of the synthetic clays and kaolinite has been exceeded and less than 50% of the added Pb is retained by pH 7.5; some additional data points were determined for higher pH to allow the

curves to be extended. The selectivity of the different clays is not clear since the curves overlap, but below pH 5.5 the expected order of increased retention with increased Fe/AI ratio appears to be followed while above pH 6.5 the lower Fe/AI ratio clays (K-FeAI, K-Fe3AI, K-AI) seem to be more effective at retaining Pb than the K-3FeAI and K-Fe clays. Kaolinite retains distinctly less Pb throughout the pH range studied.



Figure 6.2a. K-Fe, Pb retention.



Figure 6.2b. K-3FeAI, Pb retention.



Figure 6.2c. K-FeAl, Pb retention.



Figure 6.2d. K-Fe3AI, Pb retention.

Previous research suggests that the majority of sorption by kaolinite is through electrostatic attraction (Spark et al, 1995b; Yong et al, 1992b) within the diffuse double layer; increasing the ionic strength of the solution causes the double layer to be compressed (Mitchell & Madsen, 1987) and therefore less contaminant ions will be retained. The sharp reduction in Pb retention as the concentration (and hence ionic strength) increases to 25 mmol /L confirms that the driving force for

Pb retention on kaolinite is electrostatic attraction. Precipitation does not appear to contribute greatly to Pb retention within this pH range, presumably because soluble Pb complexes (e.g.  $PbOAc^{+}$ ,  $Pb(OAc)_{2}^{0}$ ) form in solution and inhibit the formation of insoluble Pb hydroxides such as  $Pb(OH)_{2}$  (s).

Figure 6.2 demonstrates the influence of Pb concentration on retention by each synthetic clay as a function of pH. The pH at which 50% of added contaminant is retained ( $pH_{50}$ ) has been used to assess the relative affinity of cations for different materials (Kinniburgh et al, 1976). Table 6.1 summarises the  $pH_{50}$  values for the different synthetic clays at different Pb concentrations.



Figure 6.2e. K-AI, Pb retention.

рH <sub>50</sub>	Pb concentration (mmol /L)						
	0.5	2.5	5	25			
K-Fe	3.5	3.8	4.6	>7.5			
K-3FeAI	3.9	4.4	5.1	>7.5			
K-FeAI	4.5	4.8	5.2	7.25			
K-Fe3AI	4.7	5.1	5.4	7.25			
K-AI	4.8	5.25	5.5	7.2			
Kaolinite	4.5	5.5	6.1	>7.5			
Table 6.1. p	H <sub>50</sub> - synthe	tic clays & Pb	·	•			



Figure 6.2f. Kaolinite, Pb retention.

The behaviour of K-Fe and K-3FeAI is similar (Figures 6.2a & b) with a clear upward shift in pH<sub>50</sub> as the Pb concentration increases. The sorption curves become shallower with increasing concentration and for 25 mmol /L the retention curves are broadly parallel to the bulk precipitation line shown in Figure 6.1d. K-FeAI (Figure 6.2c) shows similar trends although the 25 mmol /L curve becomes steeper above pH 6.5, approximately the pH at which bulk precipitation should begin. This similarity between the sorption and bulk precipitation curves could be due to either surface precipitation or surface-promoted bulk precipitation but differentiating these two mechanisms is not possible (and perhaps not even desirable ?) given the experimental techniques available in this study. Conversely, in the graphs for K-Fe3AI and K-AI (Figures 6.2d & e) only the 25 mmol /L curve is very shallow. The lower concentration curves remain steep and are quite close together both in terms of  $pH_{50}$  and  $pH_{100}$  (pH at which 100% retention occurs, Table 6.2). The kaolinite curves (Figure 6.2f) are shallow and have similar spacing to the K-Fe graphs although they are displaced to a higher pH than any of the synthetic clays.

pH <sub>100</sub>	Pb concentration (mmol /L)						
- Γ	0.5	2.5	5	25			
K-Fe	5.4	6.0	6.9	>7.5			
K-3FeAI	5.6	6.5	6.9	>7.5			
K-FeAI	5.6	6.6	6.8	>7.5			
K-Fe3AI	6.6	6.7	6.8	>7.5			
K-AI	6.3	6.7	7.2	>7.5			
Kaolinite	6.7	7.2	>7.5	>7.5			
Table 6.2. p	H <sub>100</sub> - synthe	etic clays & P	Ъ.	• • • • • • • • • • • • • • • • • • • •			

## 1.2 Contaminant retention - Cu (single metal series)

The influence of the adsorbing solid on the retention of Cu as a function of equilibrium pH is shown in Figure 6.3. Based on the oxide results (Chapter 5), the low Fe/Al synthetic clays would be expected to retain more Cu however this is not strictly followed. Table 6.3 shows the value of  $pH_{50}$  at different Cu concentrations based on the data presented graphically in Figure 6.3. At 0.5 mmol /L (Figure 6.3a), the retention order from pH 4 to 4.5 is K-FeAl > K-Fe3Al > K-Fe > K-Al > K-3FeAl > kaolinite. The bulk precipitation curve (Cu-ppt) shows that precipitation does not begin until pH 5.7 which is above the pH at which 100% of the added Cu is retained for all the clays except kaolinite (Table 6.4) suggesting that adsorption is the dominant retention mechanism.



Figure 6.3a. Synthetic clays - 0.5 mmol Cu /L.

pH <sub>50</sub>	Cu concentration (mmol /L)						
	0.5	2.5	5	25			
K-Fe	4.2	4.5	4.8	5.4			
K-3FeAI	4.4	4.9	5.1	5.6			
K-FeAI	4.0	4.5	4.7	5.1			
K-Fe3AI	4.1	4.5	4.7	5.1			
K-AI	4.4	4.8	4.8	5.0			
Kaolinite	4.7	5.4	5.5	5.9			
Table 6.3. p	H <sub>50</sub> - synthe	tic clays & Cu	J	· · · · · · · · · · · · · · · · · · ·			



Figure 6.3b. Synthetic clays - 2.5 mmol Cu /L.

At the higher concentration of 2.5 mmol /L (Figure 6.3b) the K-Fe, K-FeAI and K-Fe3AI lines overlap while the K-AI and K-3FeAI clays retain slightly less Cu up to pH 5. Above pH 5, K-AI retains more Cu than for the other clays since its sorption curve rises steeply. Kaolinite retains the lowest proportion of added Cu at all pH values and is close to the bulk precipitation curve.



Figure 6.3c. Synthetic clays - 5 mmol Cu /L.



Figure 6.3d. Synthetic clays - 25 mmol Cu /L.

The retention curves are slightly more widely spaced at 5 mmol /L (Figure 6.3c) with the low Fe/AI ratio clays (K-AI, K-Fe3AI and K-FeAI) showing steeper profiles and retaining more Cu than K-Fe and K-3FeAI while kaolinite accumulates the least Cu. Adsorption remains the most likely accumulation mechanism, at least below pH 5.5.

At 25 mmol /L (Figure 6.3d) the effect of Fe/AI ratio is more visible with K-AI = K-Fe3AI > K-FeAI > K-Fe > K-3FeAI > kaolinite. The curves for K-Fe, K-3FeAI and kaolinite are very close to the bulk precipitation line suggesting that surface or bulk precipitation is important. For the other synthetic clays, precipitation is probably a factor above pH 5.5, perhaps accounting for as much as half the retained Cu.

pH <sub>100</sub>	Cu concentration (mmol /L)						
	0.5	2.5	5	25			
K-Fe	5.6	6.2	6.5	6.5			
K-3FeAI	5.4	6.4	6.5	6.5			
K-FeAI	5.3	6.3	6.3	6.6			
K-Fe3AI	5.4	6.0	6.3	6.5			
K-AI	5.5	5.7	6.5	6.5			
Kaolinite	6.0	6.6	6.6	6.6			
Table 6.4. p	H <sub>100</sub> - synthe	etic clays & C	u.	·			



Figure 6.4a. K-Fe, Pb retention.

Figure 6.4 demonstrates the influence of Cu concentration on retention by each individual synthetic clay as a function of pH. The  $pH_{50}$  rises for each synthetic clay as the Cu concentration increases, however the difference in retention between 2.5 and 5 mmol /L is small, especially for K-AI (Figure 6.4e). Similarly the  $pH_{100}$  (100% Cu retention) values increase with Cu concentration and are generally close for 2.5, 5 and 25 mmol /L (Table 6.4).



Figure 6.4b. K-3FeAI, Pb retention.



Figure 6.4c. K-FeAI, Pb retention.

## 1.3 Discussion - metal sorption mechanisms

Figure 6.2 shows changes in the gradient of the Pb retention profiles with high Fe/AI ratio clays having generally shallower curves as Pb concentration increases. All of the Cu retention curves however, remain steep as the Cu concentration increases (Figure 6.4). This difference is likely due to the shape of

the bulk precipitation curves with Pb being very shallow for 2.5 mmol /L and above while Cu precipitation does not change much with concentration and remains steep.



Figure 6.4d. K-Fe3AI, Pb retention.



Figure 6.4e. K-Al, Pb retention.

Other researchers who have reported similar shifts in the adsorption edge and  $pH_{50}$  as the contaminant concentration increases have suggested that particle surfaces are composed of many groups of binding sites (Benjamin & Leckie, 1981). The strength with which each site type can bind metals may vary considerably leading to higher affinity sites being filled initially, with lower affinity sites following. As metals are sorbed by sites with decreasing affinity for particular cations, the adsorption edge shifts to higher pH since competition with protons interferes with metal sorption. As the pH increases, the concentration of protons decreases and metal retention progresses.



Figure 6.4f. Kaolinite, Pb retention.

The synthetic soils in this study contain sites from both their oxide and kaolinite components. As discussed in Chapter 5, the oxides will contribute both =AI-OH and =Fe-OH sites that have different affinities for Pb and Cu. Kaolinite surfaces have four different site types on which heavy metals may be sorbed: the plane of oxygen on the surface of the silica tetrahedral sheet (silanol groups); hydroxyl groups associated with the alumina octahedral sheet; and hydroxyl groups at the particle edge where the crystal lattice is broken which may be either =AI-OH or =Si-OH (Spark et al, 1995b). However the potentiometric titration results (Section

3.8, Chapter 4,) suggest that the oxides largely control the surface chemistry of these synthetic clays.

## 2. Mixed metal solution contaminant tests (Cu+Pb)

## 2.1 Contaminant retention - Pb versus Cu (Cu+Pb solutions)

In addition to the single metal batch tests, a series of experiments was conducted in which equimolar concentrations of Cu and Pb were added to the synthetic clays to evaluate the effect of competition on the retention of the individual heavy metals. The concentration of Cu and Pb was the same as that used in the single metal tests (0.5, 2.5, 5 or 25 mmol /L) to give a total metal concentration of 1, 5, 10 or 50 mmol Cu+Pb /L. The selectivity of the adsorbents for contaminants was expected to follow that found in the single metal series.



Figure 6.5a. K-Fe, Cu+Pb (0.5 mmol /L multi-contaminant solutions).



Figure 6.5b. K-Fe, Cu+Pb (2.5 mmol /L multi-contaminant solutions).



Figure 6.5c. K-Fe, Cu+Pb (5 mmol /L multi-contaminant solutions).

Figure 6.5 presents results from the batch tests containing both Cu and Pb onto K-Fe and demonstrates that the identity of the sorbing ion strongly influences retention selectivity while pH is also important. At the lowest concentration of 0.5 mmol /L (total metal = 1 mmol /L, Figure 6.5a), a considerably greater proportion

of Pb is retained than Cu at low pH, although by pH 5.5, 100% of both metals is retained.

As the concentration increases to 2.5 mmol /L (Figure 6.5b) the gap between the two metals is smaller but Pb is still preferentially sorbed over Cu. In Figure 6.5c (5 mmol Cu or Pb /L), Pb is removed in preference to Cu up to about pH 5.8, but at higher pH slightly more (10%) Cu than Pb is retained by the clay.



Figure 6.5d. K-Fe, Cu+Pb (25 mmol /L multi-contaminant solutions).

At the highest concentration (25 mmol Cu or Pb /L, Figure 6.5d) the accumulation capacity of the clay is greatly exceeded with only 40% of Pb and 75% of Cu being retained at pH 7.5. Again, more (35%) Cu than Pb is sorbed above pH 5.8, possibly reflecting the greater propensity of the Cu to precipitate than Pb (see Figure 5.2).



Figure 6.6a. K-3FeAI, Cu+Pb (0.5 mmol /L multi-contaminant solutions).

The pattern of heavy metal retention is similar in the lower Fe/Al ratio clay, K-3FeAl, although the preference for Pb over Cu at 0.5 mmol /L is less marked than with K-Fe (Figure 6.6a).



Figure 6.6b. K-3FeAI, Cu+Pb (2.5 mmol /L multi-contaminant solutions).



Figure 6.6c. K-3FeAI, Cu+Pb (5 mmol /L multi-contaminant solutions).

Slightly more Cu than Pb is retained by K-3FeAl from 2.5 mmol /L solutions (Figure 6.6b) above pH 5.6. Figure 6.6c (5 mmol /L) shows Cu being clearly preferred above pH 5.7 and 100% Pb retention not occurring within the pH range studied.



Figure 6.6d. K-3FeAI, Cu+Pb (25 mmol /L multi-contaminant solutions).

In contrast to the K-Fe results, for 25 mmol Cu or Pb /L, K-3FeAl retains approximately 35% more Cu than Pb at pH 7 while equal amounts are sorbed below pH 5.3 (Figure 6.6d). Maximum removal of Cu (55 to 60%) is similar for both K-Fe and K-3FeAl at this high concentration but less Pb is retained by K-3FeAl (30%) than K-Fe (35%).



Figure 6.7a. K-FeAI, Cu+Pb (0.5 mmol /L multi-contaminant solutions).



Figure 6.7b. K-FeAI, Cu+Pb (2.5 mmol /L multi-contaminant solutions).

The K-FeAl clay shows a preference for Cu over Pb at all concentrations (Figures 6.7a to d) although at concentrations above 2.5 mmol /L, approximately equal proportions of Cu and Pb are retained below pH 4.5.



Figure 6.7c. K-FeAI, Cu+Pb (5 mmol /L multi-contaminant solutions).



Figure 6.7d. K-FeAI, Cu+Pb (25 mmol /L multi-contaminant solutions).

The greatest difference between K-FeAI and the higher Fe/AI ratio clays (K-Fe, K-3FeAI) is when 25 mmol /L is added. Figure 6.7d shows that virtually all of the

added Cu is retained at pH 7 while less than 30% Pb is sorbed. This can be partly linked to the different precipitation behaviour of Cu and Pb but as was discussed with the single metal solutions (Figures 6.1 & 6.3), the nature of the particle surface also plays an important role.



Figure 6.8a. K-Fe3Al, Cu+Pb (0.5 mmol /L multi-contaminant solutions).



Figure 6.8b. K-Fe3AI, Cu+Pb (2.5 mmol /L multi-contaminant solutions).



Figure 6.8c. K-Fe3Al, Cu+Pb (5 mmol /L multi-contaminant solutions).



Figure 6.8d. K-Fe3AI, Cu+Pb (25 mmol /L multi-contaminant solutions).

The K-Fe3AI (Figure 6.8) and K-AI (Figure 6.9) clays show similar selectivity for Cu over Pb at all concentrations suggesting that the AI component preferentially retains Cu over Pb and that the Fe component, although appearing to prefer Pb over Cu, has a lower metal accumulation capacity. A mechanistic explanation for this remains to be found since it appears to contrast with the results of the oxide

batch tests (Chapter 5) in which Fe oxides, while preferring Pb to Cu, still retained more Cu than any of the Al rich oxides, except at the highest metal loading.



Figure 6.9a. K-AI, Cu+Pb (0.5 mmol /L multi-contaminant solutions).



Figure 6.9b. K-AI, Cu+Pb (2.5 mmol /L multi-contaminant solutions).

Although kaolinite retains less Cu or Pb than any of the synthetic clays, it shows a similar pattern of behaviour to K-3FeAl (Figure 6.10). Kaolinite retains more Pb

than Cu at 0.5 mmol /L, approximately equal amounts at 2.5 mmol /L and considerably more (40%) Cu than Pb for 5 mmol /L. At 25 mmol /L, only a small proportion of either Cu (35%) or Pb (10%) are removed from solution reflecting the limited accumulation capacity of this material (Figure 6.10d).

The pH at which 50% of added Cu or Pb is retained (pH<sub>50</sub>) is tabulated in Table 6.5. For 0.5 mmol Pb /L, the selectivity order based on the pH<sub>50</sub> is K-Fe > K-3FeAl > K-FeAl > K-Fe3Al > kaolinite > K-Al, however for Cu the order is K-Al = K-Fe3Al = K-FeAl > K-Fe > K-3FeAl > kaolinite. For 2.5 and 5 mmol /L, the pH<sub>50</sub> order for Pb is less clear although kaolinite shows the lowest affinity and K-Fe has a distinctly higher selectivity. Since the accumulation capacity of all the clays is exceeded for 25 mmol /L, it is not possible to extract pH<sub>50</sub> values for Pb from the data although based on the maximum retention at pH 7.5, the order is K-Fe > K-FeAl = K-Fe3Al > K-3FeAl > K-Al > kaolinite.



Figure 6.9c. K-AI, Cu+Pb (5 mmol /L multi-contaminant solutions).

For 2.5 mmol Cu /L, the  $pH_{50}$  order is K-FeAl > K-Al = K-Fe3Al > K-Fe > K-3FeAl > kaolinite while at 5 mmol Cu /L the order is linked to the Fe/Al ratio with low Fe clays (K-Al, K-Fe3Al, K-FeAl) retaining more than higher Fe clays (K-3FeAl, K-Fe); kaolinite remains the least retentive material. At the highest concentration

studied (25 mmol Cu /L) the Fe/Al ratio more clearly controls the selectivity with the order being K-Al = K-Fe3Al > K-FeAl > K-3FeAl > K-Fe >> kaolinite.



Figure 6.9d. K-AI, Cu+Pb (25 mmol /L multi-contaminant solutions).

pH <sub>50</sub>	Pb (C	Pb (Cu+Pb) conc. (mmol /L)				Cu (Cu+Pb) conc.			
	0.5	2.5	5	25	0.5	2.5	5	25	
K-Fe	<4.0	4.3	5.2	40%, 7.5	4.5	5.1	5.5	6.7	
K-3FeAI	4.0	5.2	5.6	30%, 7.5	4.7	5.4	5.7	6.5	
K-FeAI	4.4	5.1	5.7	35%, 7.5	<4.2	4.4	5.1	5.6	
K-Fe3Al	4.7	5.3	5.9	35%, 7.5	<4.4	4.8	5.0	5.4	
K-AI	4.9	5.6	5.6	25%, 7.5	<4.2	4.8	4.9	5.4	
Kaolinite	4.8	5.8	7.4	15%, 7.5	5.4	5.6	5.9	45%, 7.5	
Table 6.5. pH <sub>50</sub> - synthetic clays - Cu+Pb.									



Figure 6.10a. Kaolinite, Cu+Pb (0.5 mmol /L multi-contaminant solutions).



Figure 6.10b. Kaolinite, Cu+Pb (2.5 mmol /L multi-contaminant solutions).

Table 6.6 lists the pH at which 100% retention occurs ( $pH_{100}$ ) and demonstrates that retention selectivity and capacity is a function of the sorbing substrate, metal identity and concentration. At all concentrations, the  $pH_{100}$  is located at a lower pH for Cu than for Pb except for 0.5 mmol Pb /L with K-Fe. The lower Fe/Al ratio clays show greater selectivity for Cu at all concentrations while kaolinite retains the smallest proportion of added contaminants. The Pb results are less clear at low metal concentrations (0.5, 2.5, 5 mmol /L), but at high metal loading (25

mmol /L) the higher Fe/Al ratio clays retain a greater percentage of added Pb than Cu.



Figure 6.10c. Kaolinite, Cu+Pb (5 mmol /L multi-contaminant solutions).

<b>pH</b> <sub>100</sub>	Pb (Cu+Pb) conc. (mmol /L)				Cu (Cu+Pb) conc. (mmol /L)				
-	0.5	2.5	5	25	0.5	2.5	5	25	
K-Fe	5.5	7.1	80%,	<b>40%</b> ,	6.7	7.1	90%,	75%,	
			pH 6.5	pH 7.5			pH 6.5	pH 7.5	
K-3FeAl	7.0	7.1	90%,	30%,	7.0	7.1	6.9	65%,	
			pH 6.9	pH 7.5				pH 7.5	
K-FeAI	6.0	7.0	85%,	35%,	6.0	6.2	6.4	7.3	
			pH 6.7	pH 7.5					
K-Fe3AI	6.4	7.3	80%,	35%,	5.7	6.1	6.4	7.0	
			pH 6.6	pH 7.5				ļ	
K-AI	6.4	85%,	50%,	25%,	5.7	6.1	90%,	7.2	
		pH 6.7	pH 5.6	pH 7.5			pH 5.6		
Kaolinite	7.5	6.7	55%,	15%,	7.5	6.8	95%,	40%,	
			pH 7.5	pH 7.5	]		pH 7.5	pH 7.5	
Table 6.6	Table 6.6. pH <sub>100</sub> - synthetic clays - Cu+Pb.								



Figure 6.10d. Kaolinite, Cu+Pb (25 mmol /L multi-contaminant solutions).

2.2 Contaminant retention - Pb (single metal) versus Pb (Cu+Pb solutions)



Figure 6.11a. K-Fe, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).

The effect of competing ions on the retention of Pb and Cu can be clarified by comparing the retention of each metal from single metal solutions with the results

from the Cu+Pb solutions. It should be remembered that while the concentration of Pb (or Cu) is the same in both single metal and Cu+Pb solutions, the multicontaminant solutions (Cu+Pb) contain twice the total metal concentration than is present in the single metal solutions; thus the ionic strength is higher and overall competition is greater.



Figure 6.11b. K-Fe, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).

Figure 6.11a illustrates that while K-Fe retains slightly more Pb from single metal solutions than from Cu+Pb solutions, the difference is very small for 0.5 mmol Pb /L.

As the concentration of Pb increases however, the difference is more substantial with 10 to 15% more retention by K-Fe from solutions containing only Pb at 2.5 and 5 mmol Pb /L (Figures 6.11b & c). This is interesting since the bulk precipitation data suggest greater precipitation (5 to 20%) should occur from the Cu+Pb than single metal solutions, although this is not expected to commence until pH 5.5 to 6 when most Pb has already been removed from solution. For 25 mmol Pb /L (Figure 6.11d) there is no observable competition effect, presumably since the Pb retention capacity is exceeded at this concentration.



Figure 6.11c. K-Fe, Pb retention (5 mmol /L Pb & Cu+Pb solutions).



Figure 6.11d. K-Fe, Pb retention (25 mmol /L Pb & Cu+Pb solutions).



Figure 6.12a. K-3FeAI, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.12b. K-3FeAI, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).

K-3FeAI demonstrates similar behaviour to K-Fe although greater Pb retention from single metal solutions is observed for all concentrations with the increase being 5% from 0.5 and 25 mmol Pb /L (Figures 6.12a & d), and 15 to 20% from 2.5 and 5 mmol Pb /L (Figures 6.12b & c).



Figure 6.12c. K-3FeAI, Pb retention (5 mmol /L Pb & Cu+Pb solutions).



Figure 6.12d. K-3FeAI, Pb retention (25 mmol /L Pb & Cu+Pb solutions).

The same trend can be observed for the K-FeAl clay although the difference between the single Pb and Cu+Pb solutions is more variable and depends on pH as well as concentration, particularly for 2.5 and 5 mmol Pb /L (Figures 6.13b & c).



Figure 6.13a. K-FeAI, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.13b. K-FeAI, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).

At a concentration of 25 mmol Pb /L, there is a larger gap between the two types of solution with up to 20% more Pb being retained by K-FeAl from single metal solutions at pH 7.5 (Figure 6.13d).



Figure 6.13c. K-FeAI, Pb retention (5 mmol /L Pb & Cu+Pb solutions).

For K-Fe3AI, competing ions seem to have very little influence on retention for 0.5 mmol Pb /L (Figure 6.14a), but increasing the concentration widens the gap between the two types of solution so that at 2.5 mmol /L, about 15% more Pb is retained from single metal solutions above pH 5.5 (Figure 6.14b). For 5 mmol Pb /L, the maximum competition effect (35%) occurs above pH 5.5 (Figure 6.14c) while at 25 mmol Pb /L, the presence of Cu clearly interferes with Pb retention, particularly above pH 6 (Figure 6.14d).



Figure 6.13d. K-FeAi, Pb retention (25 mmol /L Pb & Cu+Pb solutions).



Figure 6.14a. K-Fe3Al, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).

The experimental results for K-AI are less conclusive, with an apparent increase in Pb retention in the presence of Cu at < pH 4.7 for 0.5 mmol Pb /L (Figure 6.15a) and a slight increase in Pb sorption from single metal solutions at higher pH. For concentrations of 2.5 and 5 mmol Pb /L (Figures 6.15b & c), approximately 10% more Pb is retained from single metal than multi-contaminant solutions.



Figure 6.14b. K-Fe3Al, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.14c. K-Fe3Al, Pb retention (5 mmol /L Pb & Cu+Pb solutions).

Figure 6.15d (25 mmol Pb /L) shows an increasing effect of competition for Pb retention by K-AI at high contaminant concentrations as the pH rises above 6.5 (additional data points were established for > pH 7.5).



Figure 6.14d. K-Fe3AI, Pb retention (25 mmol /L Pb & Cu+Pb solutions).



Figure 6.15a. K-AI, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).


Figure 6.15b. K-Al, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.15c. K-AI, Pb retention (5 mmol /L Pb & Cu+Pb solutions).



Figure 6.15d. K-Al, Pb retention (25 mmol /L Pb & Cu+Pb solutions).

The kaolinite data continue the same trend with competing Cu ions lowering Pb retention by less than 10% at low concentration (0.5 mmol Pb /L, Figure 6.16a). Although Cu suppresses Pb sorption by 10 to 20% for 2.5 and 5 mmol Pb /L (Figures 6.16b & c), it has very little effect at 25 mmol Pb /L (Figure 6.16d), probably due to the very low accumulation capacity of kaolinite for heavy metals at this high contaminant concentration.



Figure 6.16a. Kaolinite, Pb retention (0.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.16b. Kaolinite, Pb retention (2.5 mmol /L Pb & Cu+Pb solutions).



Figure 6.16c. Kaolinite, Pb retention (5 mmol /L Pb & Cu+Pb solutions).



Figure 6.16d. Kaolinite, Pb retention (25 mmol /L Pb & Cu+Pb solutions).

# 2.3 Contaminant retention - Cu (single metal) versus Cu (Cu+Pb solutions)

The retention of Cu in the presence of Pb is illustrated for the different synthetic clays and kaolinite in Figures 6.17 to 6.22.



Figure 6.17a. K-Fe, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).

Figure 6.17 shows that for K-Fe, competition with Pb causes greater suppression of Cu sorption than was observed for Pb. While the influence is small for 0.5 mmol /L (10%, Figure 6.17a), approximately 35 to 40% less Cu is retained from Cu+Pb solutions above pH 5 for 2.5 and 5 mmol /L (Figures 6.17b & c).



Figure 6.17b. K-Fe, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.17c. K-Fe, Cu retention (5 mmol /L Cu & Cu+Pb solutions).

At the highest concentration (25 mmol Cu /L, Figure 6.17d), the effect of competition is even more striking. At pH 6, 50% more Cu is retained from single metal solutions than from Cu+Pb solutions; at higher pH, the bulk precipitation data suggest that retention is by precipitation. For the mixed Cu+Pb tests however, more Cu remains in solution above pH 6 than expected from the bulk precipitation data.



Figure 6.17d. K-Fe, Cu retention (25 mmol /L Cu & Cu+Pb solutions).



Figure 6.18a. K-3FeAI, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.18b. K-3FeAI, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).

The results for K-3FeAl are shown in Figure 6.18 and similar trends are observed to those seen for K-Fe. For 0.5, 2.5 and 5 mmol Cu /L (Figures 6.17a to c), the greatest impact of competing ions appears to be in the pH 5 to 5.5 range with 20 to 40% more Cu retained from single metal solutions than from those containing both Cu and Pb; above pH 6, bulk precipitation decreases soluble Cu to very low levels.



Figure 6.18c. K-3FeAI, Cu retention (5 mmol /L Cu & Cu+Pb solutions).

For 25 mmol Cu /L, the K-3FeAl results are similar to K-Fe with greatly suppressed retention of Cu in the presence of Pb (Figure 6.18d). Again, bulk precipitation in the absence of clay removes more Cu from Cu+Pb solutions than is observed when K-3FeAl is present.



Figure 6.18d. K-3FeAI, Cu retention (25 mmol /L Cu & Cu+Pb solutions).



Figure 6.19a. K-FeAI, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).

Figure 6.19 presents results for K-FeAI; at low concentration of added metals (0.5 mmol Cu /L, Figure 6.19a) Pb does not appear to affect the retention of Cu. However at intermediate metal concentrations (2.5 and 5 mmol Cu /L, Figures 6.19b & c), the presence of Pb lowers Cu retention by 15 to 20% from pH 4.5 to 5.5 while at higher pH, all the added Cu is retained.



Figure 6.19b. K-FeAI, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.19c. K-FeAI, Cu retention (5 mmol /L Cu & Cu+Pb solutions).

In contrast to the high Fe/Al ratio clays (K-Fe, K-3FeAl), complete retention of Cu by K-FeAl is observed even at 25 mmol Cu /L (Figure 6.19d) although above pH 5.7 the sorption curve overlaps the bulk precipitation curve. Sorption of Cu from single metal solutions is approximately 5 to 30% greater than from multi-contaminant solutions with the largest difference being found from pH 5 to 5.5.



Figure 6.19d. K-FeAI, Cu retention (25 mmol /L Cu & Cu+Pb solutions).

K-Fe3AI retains the same proportion of added Cu from 0.5 mmol /L solutions both with and without competing ions (Figure 6.20a) whereas increasing the metal concentration to 2.5 mmol /L causes Cu retention from single metal solutions to be enhanced by approximately 25% relative to sorption from Cu+Pb solutions for pH 4.5 to 5.2 (Figure 6.20b).



Figure 6.20a. K-Fe3Al, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).

For 5 mmol /L, about 30% more Cu is retained from single metal solutions in the pH range 4.7 to 5.5 (Figure 6.20c) and the shape of the Cu+Pb curve is a little shallower than the single metal curve. The retention curve for Cu from single metal solutions containing 25 mmol /L has essentially the same shape as that for Cu from Cu+Pb solutions but the latter is shifted to a higher pH by about 0.4 pH units (Figure 6.20d). As a result, about 30% more Cu is sorbed from single metal than from multi-contaminant solutions. For this synthetic clay, over 80% of the added Cu (single metal and Cu+Pb solutions) is retained before the bulk precipitation pH suggesting that this material has a high capacity for Cu adsorption.



Figure 6.20b. K-Fe3AI, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.20c. K-Fe3AI, Cu retention (5 mmol /L Cu & Cu+Pb solutions).



Figure 6.20d. K-Fe3Al, Cu retention (25 mmol /L Cu & Cu+Pb solutions).

K-AI demonstrates different Cu retention behaviour to the other synthetic clays with respect to competition with Pb ions. Figure 6.21a shows that about 15% more Cu is retained from Cu+Pb solutions than from single metal solutions while at 2.5 and 5 mmol Cu /L it is not possible to differentiate between the two systems (Figures 6.21b & c). At least 90% of added Cu from 0.5, 2.5 & 5 mmol /L solutions is retained prior to the bulk precipitation pH (pH 5.6) allowing the conclusion that this synthetic clay has a very high capacity to adsorb Cu since the presence of Pb does not appear to interfere with Cu retention.



Figure 6.21a. K-Al, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.21b. K-AI, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.21c. K-AI, Cu retention (5 mmol /L Cu & Cu+Pb solutions).

At 25 mmol Cu /L (Figure 6.21d) competition for sorption sites from Pb depresses Cu retention by K-Al from mixed Cu+Pb solutions by about 25% compared to single metal solutions from pH 4.6 to 5.3; this suggests that the preference shown by surface sites for Cu over Pb no longer controls Cu retention. It is possible that sorption of Pb inhibits the surface precipitation of Cu on Al sites (proposed in Chapter 5) by blocking these surface sites and interfering with the development of solid solutions consisting of Al(OH)<sub>3</sub> and Cu(OH)<sub>2</sub>. However, adsorption is still expected to be the dominant retention mechanism since over 80% of added Cu is removed from solution before the bulk precipitation pH (pH 5.7) is attained.



Figure 6.21d. K-Al, Cu retention (25 mmol /L Cu & Cu+Pb solutions).



Figure 6.22a. Kaolinite, Cu retention (0.5 mmol /L Cu & Cu+Pb solutions).

The shape of the kaolinite retention curves for Cu from single and mixed (Cu+Pb) solutions is similar to the higher Fe/AI ratio synthetic clays. For 0.5, 2.5 and 5 mmol Cu /L the Cu retention curves from both solutions are broadly parallel with the single metal curves but are located about 0.25 pH units below the Cu+Pb mixed solutions and there is therefore approximately 15 to 20% greater sorption in the absence of Pb (Figures 6.22a to c).



Figure 6.22b. Kaolinite, Cu retention (2.5 mmol /L Cu & Cu+Pb solutions).



Figure 6.22c. Kaolinite, Cu retention (5 mmol /L Cu & Cu+Pb solutions).

For 0.5 mmol Cu /L (Figure 6.22a), over 90% of the added Cu is retained from both solutions before bulk precipitation begins, while increasing the concentration causes the retention curves to be shifted closer to the precipitation edge. Both the 2.5 and 5 mmol /L Cu+Pb sorption edges overlap the bulk precipitation curves (no clay present) when 75% and 60% respectively of added Cu remains in solution (Figures 6.22b & c).



Figure 6.22d. Kaolinite, Cu retention (25 mmol /L Cu & Cu+Pb solutions).

At 25 mmol Cu /L, very little Cu removal by kaolinite occurs until about pH 5.3 and only about 50% of Cu added from single metal solutions is retained by pH 5.8 where the kaolinite retention and bulk precipitation curves join (Figure 6.22d); complete Cu removal occurs at about pH 6.5. This contrasts with the Cu+Pb solutions where the presence of Pb reduces Cu removal relative to the single metal solutions while the presence of kaolinite appears to suppress Cu removal relative to bulk precipitation data.

The suppression of Cu sorption relative to bulk precipitation from 25 mmol /L Cu+Pb solutions observed for K-Fe, K-3FeAI and kaolinite was unexpected and is difficult to explain. It is possible that as Pb is sorbed from the Cu+Pb solutions, the ratio of acetate to dissolved metal increases and promotes the formation of additional soluble complexes (e.g.  $Cu(OAc)_2^0$ ,  $Cu(OAc)_3$ ) that inhibit the precipitation of  $Cu(OH)_2$ . This metal loading corresponds to a very high acetate concentration of 100 mmol /L and additional research into the aqueous speciation of Cu in the presence of acetate is necessary to explain these results; unfortunately this is beyond the scope of the current thesis.

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Soluble sulphate and acetate concentrations were not measured during the batch tests but it is possible that adsorbed sulphate undergoes ion exchange with acetate and subsequently forms stable soluble complexes with metal ions; adsorption of acetate ions may also lower the affinity of the surface for metals. In the absence of dissolved sulphate and acetate measurements it is not possible to further investigate this possibility. Clarification of these high contaminant concentration test results requires additional batch tests to be conducted using a non-complexing ion such as nitrate but this work is beyond the scope of the current thesis.

## CHAPTER 7 MODELLING - CONTAMINANT RETENTION

Geochemical speciation models can be used to predict the distribution of contaminant species in different environmental compartments (e.g. dissolved, adsorbed, precipitated) as a result of changes in the concentration of contaminant, pH, ionic strength and other variables. If these models can be properly calibrated, and the bonding mechanisms correctly described, it should be possible to predict the fate of contaminants under various remediation scenarios.

This thesis was designed primarily as an experiment-based study, however it was thought useful to apply a simple surface complexation model to the results to demonstrate the potential benefits and pitfalls for such models in predicting the fate of contaminants in the environment. The modelling approach was necessarily simplistic and a systematic optimisation of the model parameters was not undertaken; this alone would be worthy of several Ph.D. theses. It should be emphasised that although a *quantitative* model was applied, the modelling results presented here are intended only to provide some qualitative insight into possible reaction mechanisms. There remains considerable debate in the literature (e.g. Sposito, 1984, Yong et al. 1992b; Baeyens & Bradbury, 1997; Bradbury & Baeyens, 1997; Morel, 1997; Schroth & Sposito, 1998) as to the relative importance of the possible different surface hydroxyl groups, e.g. ferrol (=FeOH), aluminol (=AIOH) and silanol (=SiOH). Even within these broad divisions, there is expected to be variability in the acid-base behaviour and reactivity towards contaminants, and accurate measurement of such variability was not possible with the experimental techniques available for this thesis. In the following discussion the oxide surface has therefore been considered as having an average reactivity which incorporates contributions from both Fe and AI surface hydroxyl groups; while it is acknowledged that this is an simplification of reality, a similar approach has been used for natural materials by other researchers with some success (Fu & Allen, 1992; Wang et al, 1997; Meima & Comans, 1998).

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## 7.1 Geochemical modelling - MINTEQA2

The theoretical basis for speciation modelling is that thermodynamic databases can be used to find the species that will form at equilibrium such that the system has the lowest Gibbs Free Energy (Mangold & Tsang, 1991; Macdonald, 1994). Most work has been undertaken with *equilibrium* models in which the kinetic rate of reactions is not accounted for, and while this can lead to problems with some reactions (e.g. redox), it is seen as a reasonable assumption for experiments such as the 24 hour batch tests used in this thesis (Dzombak & Morel, 1990).

MINTEQA2 is a geochemical speciation model that can be used to calculate the equilibrium distribution of chemical species among dissolved, adsorbed and precipitated phases under specified environmental conditions (Allison et al, 1991). The system being considered is described in terms of a set of independent components for which total concentrations are provided; the thermodynamic database limits conditions to 25°C and 1 atmosphere. Other solution conditions such as the pH may be fixed or calculated, and it is possible to specify the formation or exclusion of certain species (e.g. particular solids). The set of components is chosen so that every species can be written as the product of a reaction involving only components. MINTEQA2 then solves the multi-component equilibrium problem by simultaneously solving the non-linear mass action expressions and linear mass balance relationships (Allison et al, 1991).

The basic procedure used by MINTEQA2 for calculating the equilibrium distribution of species is the *equilibrium constant method* (Macdonald, 1994):

- 1. Calculate aqueous phase equilibrium
  - 1.1 Guess initial activities of all components in the system (e.g. activities of Cu<sup>2+</sup>, Pb<sup>2+</sup>, OAc<sup>-</sup>).
  - 1.2 Calculate species activities using mass action equations.
  - 1.3 Use estimated species activities to compute concentrations of each individual component.

- 1.4 Compare concentrations of components to values input by the user.
- 1.5 If the difference between the calculated and input concentrations is greater than a specified tolerance level, the program returns to step 1.1 and makes a different guess of the component activities.
- 1.6 Once the calculated and input concentrations are sufficiently close, the program checks to see if any species are oversaturated and so should be allowed to precipitate.
- 2. Calculate overall equilibrium
  - 2.1 Over-saturated species are allowed to precipitate as the solid phase which has the highest saturation index (several solid phases may be possible but initially only the least soluble will be allowed to form).
  - 2.2 Recalculate aqueous phase concentrations to take account of the loss of precipitated species.
  - 2.3 Based on these new aqueous concentrations, check degree of saturation (over or under) of solid phases and allow either dissolution or precipitation.
  - 2.4 Once overall equilibrium is reached (change in concentration less than specified tolerance level), the model has converged and the concentrations of different species (aqueous, solid, adsorbed) are provided.

Adsorption is modelled as an aqueous phase complexation reaction in which the surface is treated as a ligand with which components can react. The user must specify the components and species involved in possible adsorption reactions as well as the equilibrium constants for these reactions (see Equation 7.1).

## 7.2 Surface complexation modelling

The surface complexation modelling approach assumes that the reaction of ions (e.g.  $H^+$ ,  $OH^-$ ) with surface hydroxyl groups is analogous to the formation of soluble complexes (Dzombak & Morel, 1990; Stumm & Morgan, 1996). In

addition to this chemical reaction (*co-ordination*), sorbing ions must pass through the interfacial electric field at the surface and these secondary electrostatic effects must be incorporated through assigning surface charge to the sorption reactions (Dzombak & Morel, 1990). All surface complexation models are based on four main concepts (Davis & Kent, 1990):

- 1. Sorption takes place at specific co-ordination sites.
- 2. Sorption reactions can be described quantitatively by mass law equations.
- 3. Surface charge results from the sorption reactions themselves.
- 4. The effect of surface charge on sorption can be taken into account by applying a correction factor derived from the electric double layer theory to mass law constants for surface reactions.

Several geometric models of the interfacial region have been proposed such as the diffuse double layer, constant capacitance, and triple layer models; the differences between these are illustrated in Figure 7.1 (adapted from Westall & Hohl, 1980; Davis & Kent, 1990).

Each model can be reduced to a set of simultaneous equations that can be solved numerically; regardless of the geometric model used, the following equations must be solved:

- 1. Mass law equations for all possible surface reactions.
- 2. Mole balance equations for surface sites. If more than one type of surface site is proposed, then a mole balance equation is needed for each type of surface site.
- 3. Equation for the computation of surface charge.
- 4. A set of equations representing the constraints imposed by the specific geometric model chosen for the double layer structure.



Figure 7.1. Schematic drawing illustrating the decay of electric potential with distance from the surface for the diffuse double layer, constant capacitance and triple layer models (adapted from Westall & Hohl, 1980; Davis & Kent, 1990).

The	differences	between	the	three	most	popular	geometric	models	are
sumi	marised in Ta	<b>ble 7</b> .1.							

The different geometric interpretation of the oxide/water interface leads to each model requiring a different number of modelling parameters, particularly with respect to the location and degree of hydration of sorbed ions, and the spatial distribution of solution counter-ions. The ability of a particular model (e.g. DDLM vs. CCM) to represent experimental data does not necessarily mean that the physical representation of the solid/solution interface is accurate; the model is simply of the correct mathematical form (Westall & Hohl, 1980).

Although many possible surface complexation reactions can be envisaged, it is generally accepted that the simplest mechanism that can effectively describe the experimental data should be utilised (Dzombak & Morel, 1990; Herbelin & Westall, 1996). Spectroscopic or other direct measurements of the molecular structure of the soil-solution interface were not available to support the inclusion of bidentate or tertiary complexes in this study, and so the following reaction was used to model the experimental results with the diffuse double layer model (DDLM):

#### Equation 7.1

$$= XOH + Me^{2*} = = XOMe^* + H^* \qquad K_{=XOMe^*}^{\text{int}} = \frac{\{\equiv XOMe^*\}\{H^*\}}{\{\equiv XOH\}\{Me^{2*}\}}$$

where  $Me^{2+}$  represents a metal cation, e.g.  $Cu^{2+}$  or  $Pb^{2+}$ , and  $\equiv XOH$  is a surface hydroxyl group.

The effect of pH on the speciation of surface hydroxyl groups was discussed in Chapter 4. The degree of protonation and the sorption of other ions determines the net charge ( $\sigma_0$ ) on the particle surface, which in turn affects the surface potential ( $\Psi_0$ ). For the diffuse double layer model, MINTEQA2 relates the net surface charge to the surface potential in accordance with Equation 7.2 (Allison et al, 1991):

## Equation 7.2

$$\sigma_o = 0.1174 \sqrt{I} \sinh\left(\frac{Z\Psi_o F}{2RT}\right)$$

where Z = valence of the electrolyte, I = ionic strength, F = Faraday Constant, R = Ideal Gas Constant, T = absolute temperature.

The non-linear least squares optimisation program, FITEQL Version 3.2 (Herbelin & Westall, 1996), was used to estimate the equilibrium constants for the surface complexation of metal ions with surface hydroxyl groups. Activity corrections were included by providing the computer model with solution and surface complexation constants that had been corrected already for ionic strength.

In addition to metal-surface complexation, it is also necessary to consider solution complexation reactions since these will affect the speciation of metal ions (e.g.  $Cu^{2+}_{(aq)}$ ,  $CuOH^{+}_{(aq)}$ ,  $Cu(OH)^{0}_{2}_{(aq)}$ ) and hence the concentration (or more correctly, *activity*) of contaminant species available for reaction with the surface. The aqueous equilibrium constants used in this study were taken from the MINTEQA2 database (Allison et al, 1991), Morel & Hering (1993) or Stumm & Morgan (1996). However since these literature constants are for I = 0M (activity coefficient = 1), they must be corrected for use at different ionic strengths to take account of non-ideal behaviour. Ionic strength and activity coefficients were calculated using MINTEQA2 (Allison et al, 1991) and the Davies equation (Equation 7.3) for I less than or equal to 0.1M:

#### Equation 7.3

$$\log \gamma_{I} = -AZ_{I}^{2} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.24I \right)$$

where  $\gamma_i$  = activity coefficient of species i; A = constant dependent on dielectric constant and temperature; I = ionic strength (Allison et al, 1991).

Table 7.2 lists the conditional aqueous complexation equilibrium constants used; these are *conditional* since they are valid only for the ionic strength and metal concentration shown.

log K	values	CuOH <sup>+</sup>	<b>PbOH</b> <sup>+</sup>	HOAc	CuOAc*	Cu(OAc) <sub>2</sub>	PbOAc <sup>+</sup>	Pb(OAc) <sub>2</sub>			
mmol											
/L	0	-8.00	-7.71	4.76	2.22	3.63	2.87	4.08			
0.5	0.0005	-8.02	-7.73	4.74	2.18	3.56	2.83	4.01			
2.5	0.0025	-8.05	-7.76	4.71	2.12	3.49	2.77	3.94			
5	0.005	-8.07	-7.78	4.69	2.09	3.43	2.74	3.88			
25	0.023	-8.13	-7.84	4.63	1.97	3.25	2.62	3.70			
Table	Table 7.2. Aqueous equilibrium constants used (log K).										

## 7.3 FITEQL

FITEQL is a computer program that can be used to determine equilibrium constants from experimental data (Dzombak & Morel, 1990). The chemical system being investigated is defined in terms of a series of species and components. All chemical entities relevant to the problem are defined as species (Herbelin & Westall, 1996). The set of components is chosen so that every species can be written as the product of a reaction involving only components, and no component can be obtained from a reaction involving other components. The program is designed to calculate the optimal values of equilibrium constants and/or total component concentrations based on experimental data for component concentrations and known equilibrium constants. The basic procedure for determining equilibrium constants (e.g. K<sub>aXOMe+</sub>, Equation 7.1) using FITEQL is summarised below (adapted from Dzombak & Morel, 1990):

- 1. Input the chemical equilibrium model by specifying species and components.
- 2. Input the total component concentrations, known K values and guesses for unknown K values.
- 3. Input experimental equilibrium data for total and free concentrations.
- 4. Calculate the equilibrium concentrations given the input K values and experimental (fixed) free concentrations.
- Compute the difference between the calculated and experimental component concentrations (residuals); the program is designed to minimise the sum of squares of these residuals.
- 6. Test for convergence using the sum of squares of residuals; if it is less than a certain value, the program ends.

- 7. If convergence has not been achieved, the program returns to step 4 with new estimates of the unknown K values.
- 8. Once convergence is achieved, output the optimum values for the unknown parameters (K), the standard deviations associated with these parameters, and the sum of squares of residuals.

Complete details of the FITEQL program are presented in the users manual (Herbelin & Westall, 1996) and the program has been extensively reviewed by Dzombak & Morel (1990).

FITEQL provides several measures by which the validity of the optimised parameters can be evaluated. The two main indicators of the goodness of fit are the overall variance, V, and the standard deviation for each adjustable (unknown) parameter. The goodness of fit of the proposed model to the data can be assessed by the proximity of V to 1. Since the overall variance depends on the experimental error estimates which are rarely known with any degree of certainty, values of V between 0.1 and 20 indicate a reasonably good fit (Herbelin & Westall, 1996). Due to unavoidable experimental errors and the level of accuracy of atomic absorption spectrophotometers, values of the overall variance of up to 100 have been used by previous researchers with reasonable success (Dzombak & Morel, 1990). In the current thesis, the overall variance for each adjustable parameter is provided along with the value of each parameter (Tables 7.4 and 7.5).

The magnitude of the experimental error estimates affects the overall variance and hence the goodness of fit obtained with FITEQL. The difficulty in evaluating the error in individual data points when investigating titration or sorption by oxides and soils has led to most researchers setting the error estimate in pH measurements at  $\pm 0.04$  pH units and so the relative error equals 0.1 (Dzombak & Morel, 1990). The relative experimental error associated with atomic absorption spectrophotometer measurements has been estimated at 2 to 10% and so a relative error estimate for free or bound sorbate measurements was set at 0.01 (Herbelin & Westall, 1996). FITEQL was used to estimate the equilibrium constants for the protonation and de-protonation of surface hydroxyl groups from the potentiometric titration tests at 0.01M and 0.1M, as discussed in Chapter 4. The program was also used to extract equilibrium constants for the surface complexation of Cu and Pb from the contaminant batch equilibrium tests that were conducted for four different metal concentrations (0.5, 2.5, 5 and 25 mmol /L). Since the equilibrium constants were intended for use in modelling adsorption (surface complexation), only values below pH 5 were used for the FITEQL runs since retention of Cu and Pb at higher pH values may have included contributions from bulk precipitation.

The equilibrium constants estimated by FITEQL are in theory *intrinsic* values after activity corrections have been taken into account, and therefore they should not be affected by the conditions of the experiment (e.g. 0.1M or 0.01M ionic strength). In practice however, there is some variation and so a number of values for the equilibrium constants are obtained. The issue of selecting the "best estimate" or "optimal" value of the equilibrium constants has been extensively reviewed by Dzombak & Morel (1990) and their recommended approach was utilised here. After eliminating those values with a high overall variance (greater than 100), a weighting factor was used on the remaining log K values that took into account the standard deviation calculated by FITEQL for that data set. The weighting factor (w<sub>i</sub>) is:

#### Equation 7.4

$$w_{i} = \frac{(1/\sigma_{\log K})_{i}}{\sum (1/\sigma_{\log K})_{i}}$$

where  $(\sigma_{\log K})_i$  is the standard deviation calculated by FITEQL for the *i*th data set. The magnitude of  $\sigma_{\log K}$  is a function of both the quantity of data in a particular data set and the variability in the data. Greater quantities of data and lower variability lead to a smaller standard deviation. The best estimate for log K is therefore given by:

## **Equation 7.5**

 $\log K = \sum w_i (\log K)_i$ 

The values of log  $K_{a1}$  and log  $K_{a2}$  reported in Table 4.7 (section 1.9.2, Chapter 4) were calculated in accordance with equations 7.4 and 7.5 and are shown here as Table 7.3. The total concentration of sites, Tot [XOH], has been recalculated since the batch tests contained 33.3 g oxide /L compared to the 5 g /L used in the potentiometric titrations.

Oxide	log K <sub>a1</sub>	log K <sub>a2</sub>	Tot [XOH] (mmol /L)	N <sub>s</sub> (sites / nm <sup>2</sup> )
Fe	2.15	-6.44	4.425	0.234
3FeAl	2.68	-6.87	6.612	0.344
FeAI	3.71	-7.63	8.141	0.366
Fe3Al	3.52	-6.82	1.190	0.788
AI	3.05	-7.02	1.178	0.822
Table 7.3	. FITEQL	paramet	ers.	

The parameters extracted by FITEQL from the batch test experimental data, and subsequently used with the MINTEQA2 model are summarised in Tables 7.4 and 7.5. The metal-surface complexation constants (log K) presented in these tables were obtained from metal concentrations of 0.5, 2.5 and for some data sets, 5 mmol /L, before the weighting procedure described previously was applied. FITEQL did not converge for any solution where the concentration was equal to 25 mmol /L.

	0.5 mM		2.5 mM		5 mM		Optimum log K <sub>xopb</sub>	Surface precipitation	
Oxide	log K <sub>XOPb</sub> *	V	log K <sub>XOPb</sub>	V	log K <sub>XOPb</sub>	V		log K <sub>PbFe</sub>	log K <sub>PbAl</sub>
Fe	1.30	0.01	1.13	0.03	•	-	1.14	3.64	n.a.
3FeAl	0.17	0.7	0.10	0.6	0.42	42	0.28	2.78	10.66
FeAI	0.13	0.3	-0.16	12	-0.01	42	-0.06	2.44	10.32
Fe3Al	-0.60	0.4	-0.91	0.8	-0.88	58	-0.87	1.63	9.51
AI	-1.37	40	-1.71	0.6	-1.09	40	-1.34	n.a.	9.04
Table 7 "-" = no	.4. FITEQ	L para	meters fo a. = not a	r Pb so Ipplicab	rption. le.		<u> </u>	•	<u> </u>

	0.5 mM		2.5 mM		5 mM		Optimum log K <sub>xocu</sub> *	Surface precipitation	
Oxide	log K <sub>xocu</sub> t	V	log K <sub>xocu</sub> t	V	log K <sub>xocu</sub> *	V		log K <sub>cufe</sub>	log K <sub>CuAl</sub>
Fe	-0.32	1	-0.05	1.7	0.49	57	-0.09	2.41	n.a.
<b>3FeAI</b>	-0.61	2	-0.66	5	-0.48	88	-0.57	1.93	9.81
FeAl	-0.72	0.1	-0.91	17	-0.83	142	-0.85	1.65	9.53
Fe3AI	-0.91	2	-1.30	71	-1.30	315	-1.25	1.25	9.13
AI	-1.32	0.3	-1.29	35	-1.24	226	-1.30	n.a.	9.08
Table 7 n.a. = n	.5. FITEQ ot applica	L para ble.	meters for	Cu so	rption.	•• -	•		•

## 7.4 Surface precipitation

If the solute (metal) concentration is high, then surface precipitation of the metal must be considered in addition to simple surface complexation. Surface precipitation can occur at a pH below that required for bulk precipitation since metal ions adsorbed to surface hydroxyl groups act as nucleation points for the growth of precipitates (Farley et al, 1985). As a general rule, surface precipitation should be included within the model when the dissolved metal concentration is greater than one-tenth of its solubility or half the total surface site concentration (Dzombak & Morel, 1990). The total surface site concentration in the oxide-contaminant tests varies from  $1.178 \times 10^{-2}$  (Al) to  $4.425 \times 10^{-3}$  (Fe) mol /L (Table 7.3) while the metal concentration ranges from  $5\times10^{-4}$  to  $2.5\times10^{-2}$  mol /L. In all cases, the metal concentration is expected to be high enough for bulk precipitation above approximately pH 5, while the metal/surface site ratio is greater than half for metal concentrations above  $2.5\times10^{-3}$  mol /L (2.5 mmol /L).

The inclusion of surface precipitation as a possible retention mechanism within the model is achieved through Equations 7.10 to 7.12; the assistance of Dr. Jeannet Meima (Netherlands Institute of Applied Geoscience TNO - National Geological Survey) in modifying the MINTEQA2 database to incorporate surface precipitation is gratefully acknowledged.

## 7.5 Reactions considered for modelling sorption

The following reactions were used to describe sorption for both surface complexation and surface precipitation; if insufficient contaminant is present for

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surface precipitation to occur then Equation 7.10 reduces to surface complexation (Equation 7.1), and equations 7.11 and 7.12 do not apply. Surface complexation is expected to dominate retention until the surface sites are "full", because if all the retained metal can be accounted for by adsorption processes then surface precipitation does not need to be invoked as a retention mechanism.

Surface hydrolysis (protonation/de-protonation):

#### Equation 7.6

$$XOH + H^+ + e^{-F\Psi/RT} = XOH_2^+$$
  $K_{a1} = \frac{[XOH_2^+]}{[XOH][H^+](e^{-F\Psi/RT})}$ 

#### Equation 7.7

$$XOH - H^+ - e^{-F\Psi/RT} = XO^ K_{a2} = \frac{[XO^-](e^{-F\Psi/RT})[H^+]}{[XOH]}$$

The exponential term ( $e^{-F\psi/RT}$ ) is necessary since the activities of ions close to the charged surface are different from those further away as a result of the electrical work needed to move ions across the potential gradient present between the charged surface and the bulk solution. The exponential Boltzmann expression (Equation 7.8) is used to express this activity difference which is related to the ion charge, Z, and the electrical potential,  $\psi$ , near the surface (Allison et al, 1991):

#### **Equation 7.8**

 $\{X_{y}^{Z}\} = \{X^{Z}\} [e^{-i\Psi rRT}]^{Z}$ 

where Z = charge of ion X;  $\{X_s^Z\}$  = activity of an ion X of charge Z near the surface;  $\{X^Z\}$  = corresponding activity of X in bulk solution outside the influence of the charged surface;  $e^{-F\psi/RT}$  = Boltzmann factor.

Solution complexation:

## **Equation 7.9**

$$Me^{2*} + H_2O = MeOH^* + H^*$$
  $K_{MeOH^*} = \frac{\{MeOH^*\}\{H^*\}}{\{Me^{2*}\}}$ 

Adsorption and surface precipitation:

## **Equation 7.10**

$$= XOH + Me^{2*} + H_2O = X(OH)_3(s) + = MeOH_2^*$$
$$K = K_{=MeOH_1}^{int} \cdot K_{ipX} = \frac{\{=MeOH_2^*\}\{H^*\}\{X(OH)_3(s)\}}{\{=XOH\}\{Me^{2*}\}\{H,O\}}$$

#### Equation 7.11

$$= XOH + X^{3*} + 3H_2O = X(OH)_3(s) + = XOH + 3H^*$$

$$K = 1/K_{ypX} = \frac{\{X(OH)_3(s)\}\{=XOH\}\{H^*\}^3}{\{=XOH\}\{X^{3*}\}\{H_2O\}} = \frac{\{X(OH)_3(s)\}\{H^*\}^3}{\{X^{3*}\}\{H_2O\}}$$

## Equation 7.12

$$=MeOH_{2}^{*} + Me^{2*} + 2H_{2}O = Me(OH)_{2}(s) + =MeOH_{2}^{*} + 2H^{*}$$
$$K = 1/K_{spMe} = \frac{\{Me(OH)_{2}(s)\}\{H^{*}\}^{2}}{\{Me^{2*}\}}$$

 $K_{spX}$  and  $K_{spMe}$  refer to the bulk solubility products of  $X(OH)_3$  (s) and  $Me(OH)_2$  (s) respectively.

Equation 7.10 mathematically describes the surface precipitation of the heavy metal,  $Me^{2^+}$ ; surface precipitation is considered to be equivalent to the formation of a solid solution (i.e. a solid phase containing both X(OH)<sub>3</sub> (s) and Me(OH)<sub>2</sub> (s)) in which the mole fraction of Me(OH)<sub>2</sub> is initially small relative to the oxide, X(OH)<sub>3</sub>. As more Me<sup>2+</sup> is removed from the solution in accordance with equations 7.10 and 7.12, the mole fraction of Me(OH)<sub>2</sub> (s) increases and therefore the

solubility of the surface precipitated contaminant (in the solid solution) approaches that of a pure  $Me(OH)_2$  bulk precipitate. This is because the solubility of the salt that represents the major component of a mixed solid is only slightly affected by the formation of a solid solution, however the solubility of the minor component is significantly reduced when its mole fraction is small (Stumm & Morgan, 1996). This explains why a surface precipitate is formed even though the solution is undersaturated with respect to the heavy metal contaminants.

## 7.6 Modelling results

The current thesis was designed primarily to be experimental in nature and since MINTEQA2 proved unable to adequately predict the precipitation of Pb in the absence of particles (see Chapter 5), the model was only applied to a sub-set of the experimental results; the amorphous oxides with single metal solutions (Cu or Pb). Furthermore the experimental data available was not suitable for the model to be applied in a *quantitative* manner; therefore the model interpretation presented here is intended to provide only an indication of likely reaction mechanisms from a *qualitative* perspective. It is recommended that future work include a more comprehensive modelling procedure including a systematic variation of each of the model parameters so as to optimise the model for the experimental system. The synthetic clays were excluded from the modelling process since the experimental program was not designed to distinguish between the contribution to surface charge from the pH-dependent and the permanently charged functional groups.

It is acknowledged that the modelling procedure presented in this Chapter is a relatively simple application of the surface complexation / surface precipitation model without the exhaustive optimisation that would be necessary if it was intended to apply the results to systems other than those for which experimental data are available. However, as will be discussed below, even this simple approach allows certain conclusions to be drawn regarding the need to consider the surface precipitation model when contaminant concentrations are high. Furthermore, the surface precipitation model has not been widely reported in the literature, particularly for oxides other than pure amorphous Fe oxides (Dzombak

& Morel, 1990) and incinerator ash (Meima & Comans, 1998). This is believed to be the first application of this model to systems containing amorphous AI and mixed Fe-AI oxides.

An initial effort to use MINTEQA2 to reproduce the experimental data was attempted by assuming retention by surface complexation and/or bulk precipitation. The equilibrium constants extracted with FITEQL were input to MINTEQA2 at the appropriate metal concentration. The input parameters for each oxide are tabulated in Tables 7.3 to 7.5. The results of these modelling efforts are presented in Figures 7.2 to 7.13.

The surface complexation model was increasingly less effective at predicting contaminant retention as the metal concentration increased, and surface precipitation was therefore introduced in accordance with the method of Dzombak & Morel (1990) and Meima & Comans (1998).

7.6.1 Lead



Figure 7.2a. Pb retention by Fe oxide - MINTEQA2 results (0.5 mmol /L).

Figure 7.2a shows the predicted retention of Pb by the Fe oxide from a 0.5 mmol /L solution. Two values were used for the surface complexation constant,  $K_{Pb}$ , and both appear to fit the data adequately. However it should be noted that under

the experimental conditions investigated, virtually all of the added Pb was retained which makes it difficult to assess the true effectiveness of the model in reproducing the data. The two values used for  $K_{Pb}$  are the value calculated by FITEQL from the 0.5 mmol /L data alone (log  $K_{Pb}$  = 1.299), and the average from the 0.5 and 2.5 mmol /L FITEQL runs (log  $K_{Pb}$  = 1.1365). MINTEQA2 predicts that all retention is by adsorption (surface complexation).



Figure 7.2b. Pb retention by Fe oxide - MINTEQA2 results (2.5 mmol /L).

In Figure 7.2b, the Pb concentration has increased to 2.5 mmol /L. The surface complexation model (ads+ppt) underestimates retention compared with the experimental data. Until pH 6.7, adsorption accounts for all Pb retained, with bulk precipitation beginning above this pH. When the surface precipitation model was applied to this system, retention was overestimated by about 5% below pH 4.5. The surface precipitation model appears to more accurately reproduce the experimental data for this system.

Figure 7.2c presents the MINTEQA2 results for 5 mmol Pb /L on Fe oxide. At this concentration, surface complexation significantly underestimates retention (> 30%), even when bulk precipitation is included. The surface precipitation model however, is again relatively successful at predicting Pb accumulation by the Fe oxide; the model underestimates retention by about 10% below pH 5, and accurately calculates 100% retention at pH 5.5.


Figure 7.2c. Pb retention by Fe oxide - MINTEQA2 results (5 mmol /L).



Figure 7.2d. Pb retention by Fe oxide - MINTEQA2 results (25 mmol /L).

At the highest Pb concentration (25 mmol /L, Figure 7.2d), neither model is particularly successful at predicting metal retention. The surface precipitation model is closer to the experimental data but is displaced by approximately 0.5 pH units.

Figure 7.3 presents the results of the MINTEQA2-generated curves for the retention of Pb by the 3FeAl oxide. Figure 7.3a shows that at 0.5 mmol /L, the model appears to be useful although there is insufficient experimental data to determine the effectiveness below pH 4.5. The impact of small variations in the surface complexation constant,  $K_{Pb}$  is shown with the FITEQL-calculated value

for 0.5 mmol /L (log  $K_{Pb}$  = 0.1666) giving similar results to the average constant calculated from 0.5, 2.5 and 5 mmol /L (log  $K_{Pb}$  = 0.2832).



Figure 7.3a. Pb retention by 3FeAl oxide - MINTEQA2 results (0.5 mmol /L).



Figure 7.3b. Pb retention by 3FeAl oxide - MINTEQA2 results (2.5 mmol /L).

In Figure 7.3b the surface complexation model underestimates Pb retention by 3FeAI from 2.5 mmol /L solutions by about 20% (at pH 4.5) although 100% retention is fairly accurately predicted at ca. pH 6. As the concentration increases to 5 mmol /L, bulk precipitation becomes significant in contaminant accumulation (Figure 7.3c) as shown by the difference between the "ads" and "ads+ppt" curves above pH 6.2. However the surface complexation model is less effective at

predicting Pb retention, at least using the parameters extracted with FITEQL in the current study. The surface precipitation model was applied to these two concentrations of Pb but was ineffective at reproducing the experimental data with 100% retention being predicted at all pH values.



Figure 7.3c. Pb retention by 3FeAI oxide - MINTEQA2 results (5 mmol /L).



Figure 7.3d. Pb retention by 3FeAI oxide - MINTEQA2 results (25 mmol /L).

Figure 7.3d compares the predictive ability of the surface complexation and surface precipitation models for 3FeAI at a metal concentration of 25 mmol /L. Whilst the surface complexation model produces a poor fit to the experimental data, the surface precipitation model provides a reasonably good fit to the data.



Figure 7.4a. Pb retention by FeAI oxide - MINTEQA2 results (0.5 mmol /L).



Figure 7.4b. Pb retention by FeAI oxide - MINTEQA2 results (2.5 mmol /L).

The model-generated curves presented in Figure 7.4 for FeAI are similar to those for the 3FeAI oxide. At 0.5 mmol Pb /L, the surface complexation model effectively represents the data; at 2.5 and 5 mmol /L, this model underestimates retention as a function of pH with the predicted curves being displaced by ca. one pH unit; and the surface precipitation model predicts 100% retention throughout the pH range studied.



Figure 7.4c. Pb retention by FeAl oxide - MINTEQA2 results (5 mmol /L).

At higher concentration however (25 mmol /L, Figure 7.4d), while the surface complexation model continues to be ineffective, the surface precipitation approach provides a reasonably good estimate of the retention of Pb by the oxide.



Figure 7.4d. Pb retention by FeAl oxide - MINTEQA2 results (25 mmol /L).



Figure 7.5a. Pb retention by Fe3Al oxide - MINTEQA2 results (0.5 mmol /L).

The Fe3AI oxide modelling results show a similar pattern to the other two mixed oxides (Figure 7.5). The shape of the predicted curves is quite accurate for Pb concentrations of 2.5 and 5 mmol /L but the experimental data lie about 0.5 pH units lower than the MINTEQA2 predictions (Figures 7.5b & c).



Figure 7.5b. Pb retention by Fe3Al oxide - MINTEQA2 results (2.5 mmol /L).

The surface precipitation model overestimates Pb retention by Fe3Al from 25 mmol /L solutions between pH 4.7 and pH 6.5 (Figure 7.5d) while the surface complexation model underpredicts retention below pH 6. The surface

complexation model suggests that the majority of retention is through bulk precipitation rather than adsorption/complexation.



Figure 7.5c. Pb retention by Fe3Al oxide - MINTEQA2 results (5 mmol /L).



Figure 7.5d. Pb retention by Fe3Al oxide - MINTEQA2 results (25 mmol /L).



Figure 7.6a. Pb retention by Al oxide - MINTEQA2 results (0.5 mmol /L).

For the Al oxide, the surface complexation model appears to accurately reproduce the experimental data by predicting adsorption for 0.5 and 2.5 mmol /L (Figures 7.6a & b). The average value of  $K_{Pb}$  (average of 0.5, 2.5 and 5 mmol /L FITEQL estimates) produced a closer fit to the data than the  $K_{Pb}$  estimated for the individual systems.



Figure 7.6b. Pb retention by Al oxide - MINTEQA2 results (2.5 mmol /L).



Figure 7.6c. Pb retention by Al oxide - MINTEQA2 results (5 mmol /L).

However at 5 mmol /L, the surface complexation model underestimates Pb retention throughout the pH range with the curve being displaced by about one pH unit (Figure 7.6c). At the highest concentration (25 mmol /L, Figure 7.6d), there is quite a large variation in the experimental data but it would appear that the surface complexation model underestimates retention below pH 6. The surface precipitation approach overestimates Pb accumulation at 25 mmol /L and predicts 100% retention at all pH values for lower Pb concentrations.



Figure 7.6d. Pb retention by AI oxide - MINTEQA2 results (25 mmol /L).

## 7.6.2 Surface speciation - Pb

Figure 7.7 shows the surface speciation of Pb species calculated using MINTEQA2 and the surface precipitation model at 25 mmol /L for each of the oxides. Of the two surface species invoked for the Fe oxide (Figure 7.7a), surface complexation (=FeOPb<sup>+</sup>) dominates below pH 4.6 but as the pH increases above pH 5.5, over 80% of Pb retained is present as the surface precipitate, =Pb(OH)<sub>2</sub> (s).



Figure 7.7a. Fe - Pb surface speciation, 25 mmol /L.



Figure 7.7b. 3FeAI - Pb surface speciation, 25 mmol /L.



Figure 7.7c. FeAI - Pb surface speciation, 25 mmol /L.

When the mixed Fe-Al oxides are considered, additional species should be present due to the presence of surface functional groups on both the Fe and Al oxide components (e.g.  $\equiv$ FeOPb<sup>+</sup> or  $\equiv$ AlOPb<sup>+</sup>). However, in extracting the equilibrium constants for metal retention by the oxides, a single type of surface complex,  $\equiv$ XOMe<sup>+</sup> (e.g. a mixture of  $\equiv$ FeOPb<sup>+</sup> and/or  $\equiv$ AlOPb<sup>+</sup>), was assumed to form and so it was not possible to distinguish between complexation by surface Fe and Al hydroxyl groups. The equilibrium constants extracted with FITEQL are therefore *average* constants for the whole oxide surface. This is reflected in the mathematical formulation of the model used in MINTEQA2, and so it is sensible to attempt only to distinguish between the proportion of contaminants retained by surface precipitation ( $\equiv$ Me(OH)<sub>2</sub>).

Figure 7.7b predicts that a similar dominant retention mechanism occurs for 3FeAI as with Fe, with surface complexation dominating below pH 4.7 and surface precipitation becoming more important at higher pH values. For the FeAI oxide, Figure 7.7c shows that the pH at which surface precipitation is the dominant retention mechanism has shifted to a slightly higher pH (ca. pH 5.8). The proportion of Pb retained by surface precipitation gradually increases relative to the contribution from surface complexation.



Figure 7.7d. Fe3Al - Pb surface speciation, 25 mmol /L.

In Figure 7.7d, Pb retention by the Fe3AI oxide suggests that surface precipitation does not become dominant until above pH 5, while the contribution from surface complexation appears to fall to a relatively constant value (ca. 35%) by pH 6.3.



Figure 7.7e. Al - Pb surface speciation, 25 mmol /L.

Figure 7.7e presents the predicted surface speciation for Pb on the Al oxide. Surface precipitation does not become dominant until ca. pH 5.5 while the relative contributions of surface precipitation and complexation remain constant above pH 6 at approximately 60% and 40% respectively. The pH at which surface precipitation becomes the dominant retention mechanism increases as the Fe/AI ratio decreases with Fe (pH 4.6) < 3FeAI (pH 4.7) < FeAI (pH 4.8) < Fe3AI (pH 5.1) < AI (pH 5.3). Surface precipitation is therefore predicted to be more important as the Fe/AI ratio increases.

## 7.6.3 Copper

Figure 7.8 shows the results of applying the MINTEQA2 surface complexation and surface precipitation models to the retention of Cu by the Fe oxide. At low Cu concentration (0.5 mmol /L, Figure 7.8a), the surface complexation model appears to represent the data fairly well, predicting adsorption throughout the pH range studied; however it should be noted that there are insufficient data points at low pH to fully evaluate the effectiveness of the model. Using the average equilibrium constant (log K<sub>Cu</sub> = 0.0914) derived from the 0.5, 2.5 and 5 mmol /L experiments provided a slightly better fit than the K<sub>Cu</sub> value obtained from the 0.5 mmol /L data alone (log K<sub>Cu</sub> = -0.3211).



Figure 7.8a. Cu retention by Fe oxide - MINTEQA2 results (0.5 mmol /L).



Figure 7.8b. Cu retention by Fe oxide - MINTEQA2 results (2.5 mmol /L).

As the concentration increases to 2.5 mmol /L (Figure 7.8b), the surface complexation model underestimates retention by ca. 25% at pH 4; all retention is predicted to be by adsorption rather than bulk precipitation. Conversely the surface precipitation model overestimates retention by about 15% at pH 4.



Figure 7.8c. Cu retention by Fe oxide - MINTEQA2 results (5 mmol /L).

Increasing the Cu loading causes the surface complexation model to become even less effective with Figure 7.8c predicting a much more shallow increase in retention until bulk precipitation commences; at pH 5, retention is underestimated by about 35%. The surface precipitation model provides a much closer fit to the experimental data, particularly above pH 4.5.



Figure 7.8d. Cu retention by Fe oxide - MINTEQA2 results (25 mmol /L).

At the highest contaminant concentration of 25 mmol /L, both models underestimate Cu retention by the Fe oxide, with the surface complexation model predicting about 15% retention until pH 5.5 after which there is a rapid increase due to bulk precipitation (Figure 7.8d). The curve generated by the surface precipitation model is very similar in shape to the experimental data but is off-set to a higher pH by approximately 0.5 pH units. It may be concluded from these predictions that the surface precipitation model incorporates the correct retention mechanisms but that some of the parameters used are incorrect.



Figure 7.9a. Cu retention by 3FeAI oxide - MINTEQA2 results (0.5 mmol /L).



Figure 7.9b. Cu retention by 3FeAl oxide - MINTEQA2 results (2.5 mmol /L).

When the models are applied to the mixed 3FeAl oxide (Figure 7.9), the surface complexation model shows a similar level of success as with the Fe oxide. Thus, the model is fairly effective at 0.5 mmol /L (Figure 7.9a), underestimates retention at intermediate concentrations (2.5 & 5 mmol /L, Figures 7.9b & c) and is displaced to higher pH by more than one pH unit at high Cu concentration (25 mmol /L, Figure 7.9d).



Figure 7.9c. Cu retention by 3FeAI oxide - MINTEQA2 results (5 mmol /L).



Figure 7.9d. Cu retention by 3FeAI oxide - MINTEQA2 results (25 mmol /L).

Varying the equilibrium constant,  $K_{Cu}$ , from the average value (from the 0.5, 2.5 & 5 mmol /L data) to the values calculated from the individual systems makes very little difference to the effectiveness of this model. Unfortunately attempts to apply the surface precipitation model to the 2.5 and 5 mmol /L systems were unsuccessful with 100% retention being predicted throughout the pH range. However Figure 7.9d shows the success of the surface precipitation model when the Cu concentration is 25 mmol /L, at least above pH 4.5. At lower pH values, the increased solubility of Al interferes with the model calculations and Cu retention is underestimated.



Figure 7.10a. Cu retention by FeAl oxide - MINTEQA2 results (0.5 mmol /L).



Figure 7.10b. Cu retention by FeAl oxide - MINTEQA2 results (2.5 mmol /L).



Figure 7.10c. Cu retention by FeAl oxide - MINTEQA2 results (5 mmol /L).

The effectiveness of the models in predicting the retention of Cu by the FeAl oxide is very similar to that discussed in the previous paragraph for the 3FeAl oxide (Figure 7.10). The small variation in the equilibrium constant,  $K_{Cu}$ , as the concentration changes meant that the average value was as effective at reproducing the experimental data as the value calculated for each concentration.



Figure 7.10d. Cu retention by FeAI oxide - MINTEQA2 results (25 mmol /L).

At 25 mmol /L (Figure 7.10d), the surface precipitation model is again quite successful in representing the experimental results for the FeAl oxide above pH 4.5.



Figure 7.11a, Cu retention by Fe3Al oxide - MINTEQA2 results (0.5 mmol /L).

Figure 7.11 shows that the Fe3Al - Cu system can be modelled more successfully than the higher Fe/Al ratio oxides, at least for Cu concentrations below 25 mmol /L, particularly when the value of  $K_{Cu}$  used was extracted only from the 0.5 mmol /L (log  $K_{Cu} = -0.9147$ ).



Figure 7.11b. Cu retention by Fe3AI oxide - MINTEQA2 results (2.5 mmol /L).

The surface complexation model predicts a somewhat shallower increase in retention with pH for 5 mmol /L (Figure 7.11c) with adsorption being the dominant mechanism rather than bulk precipitation.



Figure 7.11c. Cu retention by Fe3Al oxide - MINTEQA2 results (5 mmol /L).

The surface precipitation model is more useful than the surface complexation model for 25 mmol /L (Figure 7.11d) but significantly overestimates retention below pH 4.5. This is due to the increased concentration of AI in the system, and since AI becomes increasingly soluble below this pH, surface precipitation is not predicted to occur since the AI component of the oxide is calculated to dissolve,

thus eliminating the AI surface functional groups for the purposes of calculating surface precipitation as  $=Cu(OH)_2$  (s).



Figure 7.11d. Cu retention by Fe3Al oxide - MINTEQA2 results (25 mmol /L).

Due to the manner in which the model reactions are set up, the apparent dissolution of the AI component only affects the formation of the = $Cu(OH)_2$  (s) species while the = $AIOCu^+$  remains available for retaining Cu. Obviously such mathematical niceties will not be observed in nature, which serves to underline the need to be circumspect when utilising models for predicting the behaviour of natural systems.



Figure 7.12a. Cu retention by AI oxide - MINTEQA2 results (0.5 mmol /L).

Modelling the retention of Cu by the Al oxide is reasonably effective using the surface complexation model at Cu concentrations of 0.5 (Figure 7.12a) and 2.5 mmol /L (Figure 7.12b).



Figure 7.12b. Cu retention by Al oxide - MINTEQA2 results (2.5 mmol /L).

At 5 and 25 mmol /L however, the model underestimates the degree to which Cu retention increases with pH (Figures 7.12c & d). The surface precipitation model was only useful for the 25 mmol /L system since it predicted 100% retention at all pH values for lower contaminant concentrations. While the model-generated curve (Figure 7.12d) appears to intersect the experimental data at about pH 4.8, it does not seem to fully predict very rapid increase in Cu accumulation with increasing pH, and below pH 4.5, the surface precipitation model shows approximately 50% retention of Cu even at pH 3. Consideration of the surface complexation curve in Figure 7.12d suggests that the retention mechanism is a type of precipitation since the experimental data is broadly parallel to the bulk precipitation curve shown. It is suggested that although the surface precipitation model does not accurately reproduce the experimental data, this is due to errors in the choice of equilibrium constants rather than the mechanism of retention being incorrect.



Figure 7.12c. Cu retention by Al oxide - MINTEQA2 results (5 mmol /L).



Figure 7.12d. Cu retention by Al oxide - MINTEQA2 results (25 mmol /L).

## 7.6.4 Surface speciation - Cu

Figure 7.13 presents the surface speciation of Cu predicted by MINTEQA2 using the surface precipitation model. The results are very similar to those for Pb (Figure 7.7) with a greater proportion of contaminant being retained as the surface precipitate,  $=Cu(OH)_2$  (s), rather than as the adsorbed species,  $\equiv XOCu^+$  (where X is Fe or Al), as the Fe/Al ratio increases.



Figure 7.13a. Fe - Cu surface speciation - 25 mmol /L.



Figure 7.13b. 3FeAI - Cu surface speciation - 25 mmol /L.

The pH at which the surface precipitate becomes more important than the adsorbed species tends to increase as the Fe/AI ratio decreases; thus, Fe (pH 4.6) < 3FeAI (pH 4.7) < FeAI (pH 4.9) < Fe3AI (pH 5.2) < AI (pH 5.7). For all the oxides containing Fe, there is a gradual decrease in the concentration of the  $\equiv$ XOCu<sup>+</sup> species as the pH increases; however for the AI oxide, the proportion of Cu retained as  $\equiv$ XOCu<sup>+</sup> reaches a constant minima slightly above the pH at which surface precipitation becomes dominant.



Figure 7.13c. FeAI - Cu surface speciation - 25 mmol /L.



Figure 7.13d. Fe3AI - Cu surface speciation - 25 mmol /L.

The predicted surface speciation of Cu can be summarised as follows: at low pH, surface hydroxyl groups show a high reactivity towards Cu resulting in adsorption (surface complexation); as the pH increases, surface precipitation begins to occur and this mechanism competes effectively with adsorption causing an increased proportion of accumulated Cu to be retained in the form =Cu(OH)<sub>2</sub> (s).



Figure 7.13e. Al - Cu surface speciation - 25 mmol /L.

## 7.7 Recommendations for future sorption modelling

The success of the surface complexation and surface precipitation models in reproducing the experimental results was varied. There are several possible reasons to explain why the models were unable to represent the results.

As discussed in Section 1.1, Chapter 5, MINTEQA2 was unable to accurately reproduce the bulk precipitation of Pb (-acetate) in the absence of soil. The introduction of additional ligands in the form of surface active oxide particles is expected to further limit the effectiveness of MINTEQA2 in characterising the system. Improving the ability of MINTEQA2 to model Pb-acetate requires further study that is unfortunately beyond the scope of this thesis.

One aspect that was not addressed during the experimental program is the dissolution of the oxides at lower pH values. Aluminium becomes increasingly soluble below pH 5 (Stumm & Morgan, 1996) and consequent partial dissolution of the AI component of the oxides may lower the available surface area, as well as affect the number and reactivity of  $\equiv$ AIOH surface hydroxyl groups. Future work should measure the degree of dissolution of the oxides during the batch tests and thus assess how this affects the surface properties and contaminant retention capabilities of these amorphous oxides.



Finally, the mathematical construction of the surface precipitation equations in this study was necessarily simplistic and made no distinction between the precipitation of Cu (or Pb) onto Fe or Al oxides. Previous researchers have concluded that Al oxides may be more efficient in promoting the surface precipitation of Cu than Fe oxides (Karthikeyan et al, 1997) and hence cause more Cu to be retained at a given pH; this is an area that requires further study.

# CHAPTER 8 CONCLUSION

#### 1. Physicochemical properties of the amorphous oxides

Five amorphous oxides were synthesised with different proportions of Fe and AI to reflect the variation encountered in natural systems. In addition to the "pure" aluminium ("AI") and iron ("Fe") end-members, three mixed oxides were prepared: "Fe-3AI" (Fe/AI molar ratio = 0.3), "Fe-AI" (Fe/AI molar ratio = 1), "3Fe-AI" (Fe/AI molar ratio = 3). The molar concentration ((moles Fe + moles AI) / g of oxide) was approximately equal for all five synthetic oxides.

#### 1.1 Oxide structure

All of the amorphous oxides had very large specific surface areas compared to kaolinite clay. The Fe/Al ratio provided a clear influence on this property with high Fe/Al ratio oxides (Fe, 3FeAl) having significantly greater surface areas than low Fe/Al oxides (Fe3Al, Al). However, the maximum surface area was found at Fe/Al = 1 (FeAl). Attempts to calculate the surface area of the mixed oxides using the values from the pure end-members (Fe, Al) and the oxide composition were acceptable for 3FeAl and Fe3Al oxides but significantly underestimated that measured for the FeAl oxide. The particle size distribution results suggested that there is a general trend whereby increasing the Fe/Al ratio is accompanied by a finer particle size however this relationship was not clear, particularly for the silt and clay-sized particles.

The physicochemical properties of the oxides were used to propose a molecular structure in which  $SO_4^{2-}$  anions act as bridges between  $AI^{3+}$  and  $Fe^{3+}$  ions (e.g. - Fe-O-S(O<sub>2</sub>)-O-AI-) during the precipitation of solids although adsorbed  $SO_4^{2-}$  ions also inhibit the formation of larger crystals. The oxide structure is considered to develop as an open (porous) structure of loosely linked small particles with the most open structure being found at Fe/AI ratio = 1. At this Fe/AI ratio, the presence of equal concentrations of Fe and AI prevents either from controlling the structure of the oxide resulting in particles whose surfaces are a mixture of Fe and AI oxide. The formation of Fe-O-AI chains reduces the bond strength of

Al-O groups and further limits the development of regular oxide crystals. At Fe/Al ratio = 0.3 (Fe3Al), the specific surface area was not significantly different from the Al oxide suggesting that the mixed oxide structure is controlled by the Al component. Similarly the specific surface area of 3FeAl (Fe/Al = 3) was close to the Fe oxide meaning the Fe component controls the structure.

## 1.2 Oxide surface charge

Oxide surface charge, as estimated by ion exchange experiments, was very dependent upon pH. Cation exchange capacity increased from near zero at <pH 4.5-6 to 0.25 meq /g at >pH 7 with a general order of Fe > 3FeAl > Al > Fe3Al > FeAl (pH 6.3 to 7). The oxide points of zero charge (as calculated from ion exchange experiments) could be divided into two groups: Fe/Al less than or equal to 1 (Al, Fe3Al, FeAl;  $pH_{ZPC} = 6.2 - 6.4$ ) and Fe/Al > 1 (3FeAl, Fe;  $pH_{ZPC} = 5.3 - 5.8$ ).

Potentiometric titrations were also used to investigate the oxide surface charge. Differences in the surface charge density of the oxides allow their division into three groups based on the Fe/AI ratio: high (Fe, 3FeAI), medium (FeAI) and low (Fe3AI, AI). At high pH, decreasing the Fe/AI ratio causes the surface charge density to become more negative; at low pH, the surface becomes more positive with decreasing Fe/AI ratio. Therefore surface hydroxyl groups on the low Fe/AI ratio oxides appear to be more sensitive to pH changes (more easily protonated and de-protonated) than the oxides containing a higher proportion of Fe.

The computer model, FITEQL, was used to extract equilibrium constants for the protonation and de-protonation of the surface hydroxyl groups as well as the total concentration of these groups. Although subsequent modelling with MINTEQA2 was not completely successful at reproducing the experimental data, it was sufficiently accurate as to allow some confidence in the conceptual model of the solid : solution interface. Assuming the MINTEQA2 results are valid, the uncharged surface species, =XOH, is dominant below pH 7 for all the oxides; the positively charged species,  $=XOH_2^+$ , is only important below pH 4 to 5; and at higher pH, the de-protonated surface species,  $=XO^-$ , is prevalent.

## 2. Physicochemical properties of the synthetic clays

Synthetic clays were formed by the addition of pre-precipitated Fe-Al oxides to kaolinite so as to investigate the influence of small proportions of oxide on the surface properties and contaminant retention behaviour of kaolinite.

The presence of approximately 10% (by weight) of amorphous oxide significantly enhanced the specific surface area of the synthetic clays relative to kaolinite, however this increase did not correspond well to the surface area calculated from the amount of each oxide and kaolinite present. These calculations, which assumed no interaction between the oxide and kaolinite components, underestimated the measured surface area for K-Fe, K-3FeAI and K-Fe3AI; it was concluded that one possible cause of this disparity was the breakdown of aggregated oxide particles during the preparation process when the oxides and kaolinite were mixed in suspension for 24 hours. This mixing may have resulted in the exposure of greater amounts of oxide surface than was present in the oxides alone, and have cancelled out any reduction in surface area that might have been caused by the oxides covering the kaolinite surface or binding together adjacent clay particles.

## 2.1 Synthetic clay surface charge

The kaolinite showed the largest cation exchange capacity below pH 7.8 while at higher pH, the CEC for the synthetic clays rapidly increased and exceeded the kaolinite. The kaolinite carries a small permanent negative charge from isomorphous substitution, but the oxides appear to largely mask this at low pH when they are positively charged (and so have zero CEC), suggesting that the oxides cover much of the kaolinite surface. The cation exchange capacity varied considerably with pH, although to a lesser degree than was observed for the oxides alone.

Although the measurement of zero point of charge appeared to be influenced by the method of estimation (results differed between the ion exchange experiments

and the potentiometric titrations), there is a general increase in the  $pH_{ZPC}$  as the Fe/AI ratio of the synthetic clays increases with K-Fe > K-3FeAI > K-FeAI > K-Fe3AI > K-AI.

Attempts to calculate the equilibrium constants for the protonation and deprotonation of surface hydroxyl groups from potentiometric titrations and using FITEQL were less successful than for the oxides. This was attributed to the use of a single site type to describe the surface reactive groups; while it may be possible to use a single **average** surface hydroxyl group to represent the oxide surface, kaolinite contains at least three different types of surface sites including both permanently charged and pH-dependent groups and so the modelling approach was too simplistic.

## 3. Contaminant precipitation - no oxides or clay

The geochemical speciation model, MINTEQA2, was used to reproduce the experimental results for the precipitation of Cu and/or Pb from contaminant solutions in the absence of oxides or clay. As expected, precipitation removed 100% of the Cu over a narrow pH range; excluding tenorite (CuO) from the MINTEQA2 calculations improved the model fit with copper hydroxide (Cu(OH)<sub>2</sub>) forming instead.

An unexpected result was the low degree of Pb removal in the absence of oxides or clay. MINTEQA2 predicted complete precipitation over a narrow pH range for all concentrations of Pb (100% removal by pH 7) while the experimental data showed ca. 70% removal by pH 7.5 from 0.5 mmol /L solutions and less than 10% removal of Pb from 2.5, 5 and 25 mmol /L at pH 7.5. It was concluded that the low degree of precipitation could be due to kinetic limitations since the precipitation test was run over 24 hours which may not have been sufficient time, while MINTEQA2 is an equilibrium model and does not take account of reaction rates. Alternatively the reaction constants for Pb-acetate complexes may be inaccurate and the formation of soluble Pb-acetate complexes (e.g. PbOAc<sup>-</sup>, Pb(OAc)<sub>2</sub><sup>0</sup> (aq)) may inhibit precipitation. A further possibility is that the experimental methodology utilised may have been insufficiently sensitive to remove very small colloidal particles of precipitated Pb from the supernatant solution prior to analysis by atomic absorption spectrophotometry; this measurement technique does not distinguish between dissolved and colloidal metals.

## 4. Contaminant retention - oxides

The ability of the soils to retain Pb and/or Cu from metal solutions as a function of pH was studied by the use of 24 hour suspension tests with four different total metal concentrations. Increasing the Fe/Al ratio enhanced the ability of the oxides to retain Pb and Cu; "pure" Fe oxide retained the greatest mass of Pb and Cu at all pH values. At all Pb concentrations the Fe/Al ratio determined the order of contaminant retention with Fe > 3FeAl > FeAl > Fe3Al > Al. Retention of Cu at low to medium concentrations (0.5 to 5 mmol /L) followed the same pattern but at higher concentration (25 mmol /L) only Fe oxide showed a distinctly greater adsorption capacity. These amorphous oxides were shown to have a considerably greater capacity (measured as Pb or Cu retained per unit mass) than kaolinite for contaminant accumulation at all pH values and metal concentrations.

#### 4.1 Single metal solutions - oxides

In single metal systems (i.e. either Cu or Pb) at medium metal concentration (2.5 mmol /L), the Al oxide accumulated more Cu than Pb; for Fe/Al ratio = 0.3 (Fe3Al), approximately equal amounts of Pb and Cu were retained; further increasing the Fe/Al ratio (FeAl, 3FeAl, Fe) caused greater Pb than Cu to be retained. At higher metal concentration (25 mmol /L) more Cu than Pb was retained by the Al, Fe3Al and FeAl oxides while at Fe/Al ratio > 1 (3FeAl, Fe) Pb continued to be more efficiently removed from solution. The preference shown by Cu for Al-rich oxides, and Pb for Fe-rich oxides is in agreement with the principle of hard and soft Lewis acids and bases; Al oxide acts as a harder base than Fe oxide so should prefer harder metals (acids), i.e. Cu instead of Pb; similarly the softer base, Fe oxide, would be expected to preferentially bind with softer metals, i.e. Pb rather than Cu.

The high proportion of heavy metal cations retained when the net surface charge was positive suggests the formation of specifically adsorbed surface complexes in which chemical covalent bonds prevail over physical ionic (electrostatic) bonds. The majority of added metals were retained below the pH at which precipitation of Pb and Cu hydroxides was observed, further supporting the proposed formation of surface complexes. The high contaminant accumulation capacity exhibited by the amorphous oxides compared to kaolinite is due to their large surface area and the reactive nature of their surface hydroxyl groups. Remobilisation of these heavy metals from natural soils and sediments is less likely than if ion exchange is the main retention mechanism.

## 4.2 Mixed metal solutions - oxides

Batch tests were also conducted with solutions containing both Cu and Pb at equal concentrations to investigate the effect of competition between contaminants on accumulation by oxides. The Fe oxide retained more Pb than Cu for a given pH at all metal concentrations demonstrating the importance of the identity of the sorbing ion on contaminant retention. The 3FeAI oxide also preferred Pb to Cu at all metal loadings but the differences in the proportion retained was less marked. The FeAI oxide preferentially sorbed Pb over Cu at low to medium metal concentrations (0.5 to 5 mmol /L) but at high concentrations (25 mmol /L), more Cu was retained than Pb above pH 4.5. The Fe3AI oxide continued this trend with more Cu being retained than Pb when the metal concentration was greater than 0.5 mmol /L. The AI oxide showed a clear preference for Cu over Pb at all pH values from 0.5 and 2.5 mmol /L solutions and above pH 4.3 and pH 4.8 for 5 and 25 mmol /L solutions.

In summary, for high Fe/AI ratio oxides (Fe, 3FeAI), Pb was preferentially retained over Cu at all concentrations. For low to intermediate Fe/AI ratios (FeAI, Fe3AI) Cu was selectively sorbed over Pb at high concentration (25 mmol /L) and higher pH (> pH 5) while at low concentration (0.5 mmol /L) or low pH (< pH 5 for 5 or 25 mmol /L), Pb showed a stronger affinity for the surface. The AI oxide (no Fe present) retained more Cu than Pb for all concentrations although Pb was

preferred to Cu below pH 4.8 when the contaminant loading was very high (25 mmol /L).

When the multi-contaminant solution results were compared to the single metal batch tests, it was observed that the presence of Pb appeared to interfere with the **shape** of Cu sorption curves on Fe-rich oxides, but only with the **location** of Cu sorption edges on Al-rich oxides. It may be concluded from these results that the nature of the surface hydroxyl group (Al versus Fe) exerts a significant influence on the retention of contaminants in addition to the previously recognised importance of the identity of the heavy metal ion.

## 5. Contaminant retention - synthetic clays

A similar series of batch suspension tests was conducted for kaolinite and the synthetic clays (kaolinite to which oxides had been added).

## 5.2 Single metal solutions - synthetic clays

Pb retention by the different synthetic clays was influenced by their Fe/AI ratio and broadly followed that expected from the oxide experiments. The retention capacity of kaolinite was substantially enhanced by the presence of the oxides, particularly at higher metal concentrations where the kaolinite alone did not remove all of the added Pb by pH 7.5; this was explained by the greater surface reactivity of the oxide functional groups which can form surface complexes with contaminants as opposed to the kaolinite which primarily retains metals by ion exchange mechanisms. At low metal concentration (0.5 mmol /L) however, kaolinite was more effective at removing contaminants from solution than the low Fe/AI clays (K-Fe3AI, K-AI).

Retention of Cu followed a more complex pattern than Pb with low Fe/Al synthetic clays (K-FeAl, K-Fe3Al, K-Al) sorbing a greater proportion of added Cu at a given pH than the higher Fe/Al ratio clays (K-Fe, K-3FeAl), particularly at higher metal concentrations; the presence of oxides enhanced Cu accumulation relative to kaolinite alone. Bulk precipitation appeared to play a more important

role with retention curves for the high Fe/AI ratio clays and kaolinite closely following precipitation in the absence of particles.

## 5.2 Mixed metal solutions - synthetic clays

These results did not follow that expected from the single metal tests. K-Fe and K-3FeAI retained more Pb than Cu at low concentrations and lower pH values. but as the contaminant loading increased, a greater proportion of added Cu than Pb was accumulated. K-FeAI sorbed approximately equal amounts of Cu and Pb below pH 4.5, but at higher pH and high metal concentrations, significantly more Cu than Pb was removed from solution. K-Fe3AI and K-AI continued this trend and it was concluded that the AI component appeared to dominate the interaction with metals. This contrasted with the results from the oxide retention tests in which Fe oxides, while preferring Pb to Cu, still retained more Cu than any of the Al rich oxides, except at the highest metal loading. One possible explanation is that the method of mixing the oxides and kaolinite to produce the synthetic clays resulted in the AI rich oxides undergoing a greater degree of dissolution and reprecipitation since AI(III) is more soluble than Fe(III); the accessible surface area in the AI rich clays was therefore enhanced and the number of surface hydroxyl groups available for interaction with metals was increased. Since AI surface aroups (≡AIOH) have previously been shown to enhance the retention of Cu over Pb, competition between these two metals for retention was shifted in favour of Cu.

Kaolinite retained less contaminants than any of the synthetic clays but showed similar behaviour to K-3FeAl with more Pb being sorbed than Cu at low concentrations, and a gradual shift towards preference for Cu as the concentration increased; this was likely due to the greater bulk precipitation of Cu than Pb at higher metal loading.

An unexpected result was observed at 25 mmol (Cu+Pb) /L for K-Fe, K-3FeAl and kaolinite in which Cu sorption was less than that found in the bulk precipitation tests conducted in the absence of clay. Possible explanations include an increase in the ratio of dissolved acetate to dissolved Cu relative to

the bulk precipitation tests as Pb was removed from solution by sorption; this could encourage the formation of soluble Cu-acetate complexes and inhibit the precipitation (surface or bulk) of Cu. Another possibility is that ion exchange occurs between sorbed sulphate and dissolved acetate; the resultant increase in dissolved sulphate concentration may encourage the formation of soluble Cu-sulphate species while sorbed acetate may inhibit Cu retention. Since the concentrations of dissolved sulphate and acetate were not measured as part of the experimental program, it is not possible to confirm this speculation. Additional research into the influence of dissolved anion concentrations on the retention of Cu and Pb by particulate material is recommended to clarify the mechanisms controlling contaminant accumulation.

#### 6. Contaminant retention modelling

FITEQL was used to extract equilibrium constants for the surface complexation and surface precipitation of Cu or Pb from single metal solutions by the oxides and these were then utilised to generate sorption curves with MINTEQA2. The diffuse double layer surface complexation model was reasonably successful at reproducing the experimental results at low concentrations (0.5 mmol /L) but underestimated retention at higher metal loading (25 mmol /L). Adsorption was predicted to be dominant at lower pH and metal concentrations with bulk precipitation becoming more important as the pH and contaminant levels increased. The surface precipitation model was more effective at predicting contaminant retention for 25 mmol /L solutions, particularly for Cu and as the Fe/Al ratio decreased.

The generally good agreement between the shape of the model-generated curves and the experimental data suggests that the surface precipitation model incorporates the correct mechanism(s) for metal retention at higher contaminant concentrations; however the location of the curves is off-set for some systems, presumably due to inaccurate estimates of the equilibrium constants and other model parameters. The absolute value of the equilibrium constants for surface binding of metals did not appear to significantly affect the modelling results suggesting that other parameters such as the concentration, type and variability
of surface hydroxyl groups may be more critical to a successful description of the system.

The model-predicted surface speciation of Cu and Pb can be summarised as follows: at low pH, surface hydroxyl groups retain some of the dissolved metals by adsorption (surface complexation); as the pH increases, surface precipitation begins to occur and this mechanism competes effectively with adsorption causing an increased proportion of accumulated contaminant to be retained in the form = $Me(OH)_2$  (s).

#### 7. Contribution to knowledge

The experimental program extended previous work by systematically varying the Fe/AI ratio of amorphous oxides that had been precipitated from sulphate salts. Most previous work has involved synthesising oxides from non-interacting salts such as nitrate or chloride since these are expected to have a small influence on oxide properties. This study deliberately utilised the sulphate salts since naturally occurring oxides, particularly in waters draining mine-waste areas, tend to be high in sulphates.

This thesis has demonstrated that the Fe/AI ratio of amorphous oxides significantly affects their physicochemical properties including the specific surface area and surface charge density. The Fe/AI ratio strongly influences the retention of Cu and Pb as a function of pH and contaminant concentration; both the nature of the sorbing solid (i.e. proportion of Fe or AI), and the identity of the contaminant (i.e. Cu versus Pb) have been identified as important factors.

The surface precipitation model was applied to metal retention by amorphous Al and mixed Fe-Al oxides for the first time; although only a limited modelling exercise was conducted, this research suggests that further application of this model would be beneficial in the study of highly contaminated natural systems.

## 8. Recommendations for future work

### 8.1 Oxide solubility and structure

One aspect that was not addressed during this experimental program was the degree of oxide dissolution at lower pH values. Partial dissolution of the AI component of the oxides may lower the available surface area, affect the number and reactivity of  $\equiv$ AIOH surface hydroxyl groups, while dissolved AI<sup>3+</sup> ions could compete with heavy metals for surface sorption sites. Furthermore dissolved AI<sup>3+</sup> and Fe<sup>3+</sup> ions form highly stable aqueous acetate complexes and therefore if acetate does indeed influence metal retention as suggested in this thesis, variable dissolution of the oxides could exert a considerable effect on the overall retention of Pb and Cu. Future work should measure the degree of dissolution of the oxides during the batch tests and assess how this affects the surface properties and contaminant retention capabilities of these amorphous oxides. Investigation of the oxide structure proposed in this thesis would be useful.

## 8.2 Contaminant experiments

It is recommended that additional work be conducted with acetate salts of Pb since these compounds have not been widely studied despite their common presence in natural systems. Such future work should investigate the effect of reaction rates on precipitation and compare precipitation with that from other non-complexing salts such as nitrate. It would be beneficial to repeat the contaminant experiments using the nitrate salts of Cu and Pb to clarify the extent to which complexation by dissolved acetate interferes with the retention of metals by the surface. Conducting the contaminant retention experiments in a constant ionic strength medium would assist further elucidation of the mechanisms involved, and would aid in future modelling work. Furthermore, the molecular level mechanisms of contaminant retention could be explored using techniques such as X-ray absorption spectroscopy which was beyond the scope of the current experimental program.

# 8.3 Modelling

Future work should include a more comprehensive application of the surface complexation and surface precipitation models including a systematic variation of each of the model parameters so as to optimise the model for the experimental system. The synthetic clays were excluded from the modelling process since the experimental program was not designed to distinguish between the contribution to surface charge from the pH-dependent and the permanently charged functional groups. Since particles in the natural environment contain a variety of materials, with divergent surface properties, the relative importance of the different surface hydroxyl groups requires further clarification.

MINTEQA2 was unable to accurately reproduce the bulk precipitation of Pb (as acetate) in the absence of soil, and had variable success in predicting contaminant retention by the oxides. The ability of MINTEQA2 to model complex solutions requires further study, particularly with the increasing application of this, and similar geochemical models, to the prediction of contaminant fate and transport in natural systems. Modelling is often now used as the basis for judging the acceptability of various remedial options and regulatory authorities must have confidence that such risk assessments are based on sound science.

The mathematical construction of the surface precipitation equations in this study was necessarily simplistic and made no distinction between the precipitation of Cu (or Pb) onto Fe or Al oxides. Clarification of the reactivity of different surface hydroxyl groups (e.g. =AlOH versus =FeOH) would be very useful in determining whether an average equilibrium constant for the whole surface is an acceptable simplification.

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