Speciation of heavy metal ions as influenced by interactions with montmorillonite, Al hydroxide polymers and citrate

Promotor: dr. W.H. van Riemsdijk
hoogleraar bodemscheikunde en chemische grond- en gewasanalyse
Co-promotor: dr.ir. M.G.M. Bruggenwert
universitair hoofddocent bodemscheikunde

R.P.T. Janssen

Speciation of heavy metal ions as influenced by interactions with montmorillonite, Al hydroxide polymers and citrate

Proefschrift
ter verkrijging van de graad van doctor
in de landbouw- en milieuwetenschappen
op gezag van de rector magnificus,
dr. C.M. Karssen,
in het openbaar te verdedigen
op vrijdag 16 juni 1995
des namiddags te vier uur in de Aula
van de Landbouwuniversiteit te Wageningen.

The research reported in this thesis was funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Janssen, R.P.T.

Speciation of heavy metal ions as influenced by
interactions with montmorillonite, Al hydroxide polymers
and citrate / R.P.T. Janssen. - [S.I. : s.n.]
Thesis Landbouwuniversiteit Wageningen.
- With ref. - With summary in Dutch.
ISBN 90-5485-399-9
Subject headings: heavy metals / ion exchange

Abstract

Janssen, R.P.T., 1995. **Speciation of heavy metal ions as influenced by interactions with montmorillonite, Al hydroxide polymers and citrate.** Ph.D. thesis, Wageningen Agricultural University, the Netherlands, 127 pages.

Clay minerals, metal-hydroxides and organic matter can bind metal ions; moreover they also interact with each other. These mutual interactions influence the metal binding to a significant extent. In this study, the speciation of the heavy metal ions Zn and Pb was investigated in model systems consisting of various combinations of the clay mineral montmorillonite (Na saturated), Al hydroxide polymers and citric acid at pH 5.0, 6.0 and 6.6. A speciation model was developed to determine the distribution of Zn and Pb in these systems. pH had a pronounced effect on Zn and Pb binding. Zn and Pb binding to the clay/Al hydroxide polymer systems decreased with decreasing pH. The decrease of the pH led to a decrease of the cation exchange capacity and to a decrease of the affinity of the Al hydroxide polymers for metal ions. The decrease in metal ion binding was also influenced by increasing competition of Al^{3+}. The effect of the Al:clay ratio on metal binding was influenced by the pH. This is because the nature of the Al hydroxide is dependent on the Al:clay ratio at pH 5.0 and independent at pH 6.6. The available binding sites on the Al hydroxide polymers have a high affinity for Zn and Pb ions. Zn and Pb binding on the siloxane surface became relatively more important when the binding sites on the Al hydroxide polymers were nearly all occupied. Citrate sorption to clay/Al hydroxide polymer systems was strongly dependent on the conditions of formation of the systems. Citrate adsorbed to the edge faces of the clay platelets of aged clay/Al hydroxide systems. When citrate is present during the formation of clay/Al hydroxide systems, it was found that citrate was incorporated in the Al hydroxide polymers. At increased citrate:Al ratios, citric acid can perturb the formation or dissolve the Al hydroxide polymers. The distribution of Zn over the various species in a clay/Al hydroxide polymer/citrate system was calculated by using the speciation model. Only slightly less Zn was sorbed to the Al hydroxide polymers compared to the same systems without citrate. For high molar fractions of Zn bound to the exchange sites, binding of Zn to the Al hydroxide increased strongly in the presence of citrate, suggesting the formation of a coprecipitate or solid solution between Al- and Zn hydroxide and citrate. At increasing citrate:Al ratios, Zn sorption decreased strongly, due to Zn and Al complexation by citrate.

Addtional index words: Al interlayers, hydroxy Al, low molecular weight organic acids, Vanselow selectivity coefficient.

Stellingen

1. Cambier en Sposito (1991) hebben citraat adsorptie aan kleirandjes in synthetische klei/Al-hydroxyde systemen gemeten i.p.v. aan Al-hydroxyde zoals zij onterecht concluderen.

   Cambier, P. and G. Sposito. Interactions of citric acid and synthetic hydroxy-aluminum montmorillonite. Clays and Clay Minerals, 39, 158-166, 1991.
   Dit proefschrift.

2. De berekening van een niet constant oplosbaarheidsprodukt voor $Al(OH)_3$ in synthetische klei/Al-hydroxyde systemen door Cambier en Sposito (1991), lijkt te fungeren om de massabalansen kloppend te maken, maar is vermoedelijk chemisch niet reëel.

   Cambier, P. and G. Sposito. Interactions of citric acid and synthetic hydroxy-aluminum montmorillonite. Clays and Clay Minerals, 39, 158-166, 1991.
   Dit proefschrift.

3. De waarneming van Kozak and Huang (1971) dat de kationenomwisselingscapaciteit niet rechtevenredig daalt met de hoeveelheid gefixeerd aluminium, wordt niet veroorzaakt door sterische hindering van omwisselbare kationen, zoals zij veronderstellen, maar door binding aan het kleioppervlak van Al-hydroxyde polymeren welke verschillen in positieve lading.

   Kozak, L.M. and P.M. Huang. Adsorption of hydroxy-Al by certain phyllosilicates and its relation to K/Ca cation exchange selectivity. Clays and Clay Minerals, 19, 95-102, 1971.
   Dit proefschrift.

4. De verschillen in de typen reacties en complexeringsconstanten voor aluminium met citraat zoals vermeld in de literatuur, laten zien dat het kritiekloos gebruiken van een speciatieprogramma met bijbehorende database van evenwichtsconstanten niet zonder gevaar is.

   Dit proefschrift.

5. Synthetische klei/Al-hydroxyde systemen kunnen worden gebruikt om zware metalen uit afvalwaterstromen te verwijderen, en de mobiliteit van zware metalen in bodems te verlagen.

   Dit proefschrift.

6. De enorme hoeveelheid kleimineralen die wordt gebruikt als grondstof voor kattebakkorrels dient sterk te worden verminderd door composteerbaar materiaal te gebruiken. Hierdoor wordt minder huisvuil gestort of verbrand. Tevens wordt hierdoor het eenmalig gebruik van kleimineralen met hun unieke eigenschappen verminderd.

7. De voorgenomen vervanging van loodhoudende drinkwaterbuizen door koperen, is hoofdzakelijk gebaseerd op de overschrijding van de in de toekomst te verlagen norm van lood in drinkwater. Een eventuele verlaging van de drinkwaternorm voor koper, zou in de toekomst de vervanging van de koperen drinkwaterbuizen tot gevolg kunnen hebben.

8. Verontreiniging van de bodem met o.a. zware metalen tast de grond van ons bestaan aan.

9. Aangezien de lusten voor de autogebruiker zijn en de lasten voor het "autoloze" bevolkingsdeel, dient het openbaar vervoer gratis te zijn en worden betaald uit de opbrengsten van het autogebruik.

10. Indien de huidige snelheid van aantasting van het milieu zich voortzet, zal het aanpassingsvermogen van de mens sterk op de proef worden gesteld.

11. Van het zelf maken van wijn kun je twee keer genieten.

Stellingen behorend bij het proefschrift 'Speciation of heavy metal ions as influenced by interactions with montmorillonite, Al hydroxide polymers and citrate' van R.P.T. Janssen, Wageningen, 16 juni 1995.

Contents

CHAPTER 1

General Introduction

Heavy metals

In recent decades, growing concern about the quality of the natural environment has stimulated interest in the occurrence and behaviour of heavy metals in soils and natural waters. In the Netherlands legislation has been passed on the indicative levels of contamination. These levels of pollutants are mainly based on total concentrations in soils and waters. However, it has recently been realized that the ecotoxicity of pollutants and the soil quality are related to the availability of the pollutants in question, and therefore more research is now focusing on the speciation of heavy metals in soils, in order to elucidate the availability of heavy metal ions.

Heavy metals are those elements whose gravity density in solid state (20°C-25°C) exceeds 5000 kg/m^3. They are notorious for their toxicity. Two such heavy metals, zinc (Zn) and lead (Pb) are trace elements found in natural rock formations mainly as poorly soluble minerals. Their content in natural, unpolluted soils is usually low. In general, Zn occurs in soils in higher concentrations than Pb. Industry, agriculture and traffic enhance the Zn and Pb content in soil, especially in the upper horizons. Zn is more mobile than Pb.

Zn is an essential trace element for humans, animals and higher plants. For humans and animals Zn acts as a catalytic or structural component in numerous enzymes involved in energy metabolism and in transcription and translation (Kiekens, 1990). However, Zn becomes toxic when taken in excess. Zn is noncumulative in human beings. At high concentrations, Zn is principally phytotoxic, so concern is mainly directed towards its effects on crop yield and soil fertility.

As far as is known, Pb is not an essential trace element for humans, animals or plants. In human beings its uptake is possible by inhalation, via food and drink, and by absorption through the skin. Pb accumulates in humans and is mainly stored in liver, kidneys and bones. It is excreted very slowly through urine, faeces, sweat and hair. Long-term exposure to Pb may give rise to toxic effects affecting the kidneys, blood and the nervous system (Fergusson, 1990).

The main pollutant sources for Zn in soils are mining activities, the agricultural use of sewage sludge and composted materials and the use of fertilizers and pesticides (Kiekens, 1990). For Pb these sources are mining and smelting activities, agricultural use of sewage sludge and vehicle exhaust (Davies, 1990). Zn is widely used for many purposes. Pb is widely used in batteries, paints and as an antiknock additive in petrol. However, Pb emission by cars has been reduced by the substitution of other additives in petrol. Pb has been used by mankind from early times. It was used as a structural metal in ancient times, and for weather-proofing buildings. The Romans were the first of the ancient peoples to use Pb on a large scale and the fact that they had so much contact with Pb has prompted the suggestion that Pb poisoning among the leaders of the Roman Empire may have contributed to the empire's downfall (Waldron, 1980).

Interactions between heavy metals in soils and clay, hydroxides and organic matter

The bio-availability and transport of heavy metal ions to the groundwater is strongly related to the distribution of heavy metal ions over the solid and liquid phases of the soil. This distribution is determined by chemical reactions in the soil. The four main chemical reactions determining whether heavy metal ions are bound to the soil particles or present in the soil solution phase are:

1. adsorption and desorption processes
2. ion exchange
3. precipitation and dissolution reactions
4. complexation

Adsorption, desorption and ion exchange processes take place with the reactive components present in soils. These are:

1. clay minerals
2. hydroxides of Al, Fe and Mn
3. organic matter

In general, most of the heavy metal ions in soils are sorbed to these components and only a small fraction is present in the solution phase. As long as heavy metal ions are bound to the soil particles, there is no direct danger for uptake by humans (except for geophagy by children), animals and plants. However the mobility of heavy metal ions can increase strongly, e.g. because of complexation by soluble organic acids or acidification of soils by acid rain. Another consequence of acidification of soils is the increasing solubility and mobility of Al species. The Al species Al^{3+} is considered to be toxic to plants (Parker et al., 1989). It is of great practical interest and importance to have a better quantitative understanding of the interactions that influence the binding and mobility of heavy metal ions in soils. This is especially important for the regulation on soil and groundwater quality criteria, because the availability of the metal is closely related to ecotoxicity and soil quality.

The interpretation of heavy metal ion behaviour in soils is extremely complicated. A study of the behaviour of heavy metal ions in synthesized clay/organic matter/hydroxide systems can contribute to the proper description and interpretation of the behaviour of these metals in soils. In this thesis the synthesized system Zn and Pb (as examples of heavy metals), montmorillonite (as an example of a clay mineral), Al hydroxide and citric acid (as an example of a low molecular soluble organic matter) is studied. Al hydroxide binds irreversibly to the siloxane surface of clay minerals, forming layers of Al hydroxide polymers (Al interlayers) between the clay platelets (Zelazny and Jardine, 1989; Barnhisel and Bertsch, 1989). Al interlayered clay minerals are geographically widespread and are relevant in many soils (Barnhisel and Bertsch, 1989). They play an important role in the adsorption behaviour and capacity of metal binding in soils (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991). Low molecular weight organic acids such as citric acid are commonly present in the natural environment (Stevenson and Fitch, 1986) and can be exudeded from the roots of various plant species.

Heavy metal ions react to the reactive components clay minerals, Al hydroxyde and citric acid, in different ways. They bind reversibly on clay minerals via an ion-exchange reaction. This reaction can be described by an ion exchange equation. Heavy metal ions bind specifically to the reactive sites present on the Al hydroxide particles. The term specific sorption implies complexation (chemisorption) by singly coordinated OH groups present on the surface of the Al hydroxide particles. Specific sorption is pH dependent and accompanied by a release of protons. Heavy metal ions also form complexes with citric acid. This reaction can be described by complex formation constants. The interaction between metal ions and the mixture of clay, Al hydroxide and citric acid cannot be calculated from the weighted summation of the interaction for the individual components using binding models for each seperate component of the mixture. Mutual interactions between the components influence the metal binding to a significant extent. Since mixtures of soil components always occur in natural soil systems, the heavy metal ion adsorption to natural soil systems could be predicted much more accurately if more were known about where heavy metal ions adsorb, and to what extent.

It is to be expected that the bio-availability of the heavy metal ions is dependent on various factors, including the type of ion binding, pH and Al:clay ratio. More insight into the bio-availability of heavy metals will be gained when the distribution of the heavy metal ions over the different reactive phases is known.

The literature to date has focused on the behaviour of heavy metal ions on the interaction with Al hydroxide or clay minerals or organic matter. Only a few studies have focused on heavy metal binding to multi-component systems. Some studies have investigated the binding of heavy metal ions to clay/Al hydroxide systems. Harsh and Doner (1984) showed that Cu adsorption on a synthetic hydroxy-Al-montmorillonite complex was pH-dependent and that specific sites for Cu did exist. According to Keizer and Bruggenwert (1991) the Al hydroxide bound to a clay surface has a much greater affinity for heavy metal ions compared with free Al hydroxide. The interaction between clay and Al hydroxide polymers can increase the binding of heavy metal ions. This effect is due to a strong increase of the surface area of the Al hydroxide polymers and the reduction of the positive electric field emanating from the positively charged Al hydroxide particles, because of the interaction with the negatively charged clay particles. This enhances the binding of positively charged heavy metal ions.

Some studies have been done on the influence of low molecular organic acids (like citric acid), on clay/Al hydroxide systems. Citric acid (if present in ionic form it is called citrate) forms strong complexes with Al ions and may thus influence the properties and formation of the clay/Al hydroxide polymer system. Citrate can interact with clay/Al hydroxide polymer systems during the formation of these systems or with aged (i.e. already existing) systems.

Citrate may be incorporated in the Al interlayers during its formation (Goh and Huang, 1984 and 1986). It has also been shown that low molecular organic acids like citric and tannic acid, can perturb the formation of Al-interlayered clay minerals as a consequence of the formation of soluble Al-organic acid complexes (Buondonno et al., 1989; Goh and Huang, 1984 and 1986; Violante and Jackson, 1981). On the other hand citrate may also adsorb to aged Al interlayers (Cambier and Sposito, 1991). The latter authors suggest that citrate binds to Al interlayers at pH values between 4 and 5.5. For higher pH values they suggest that the Al hydroxide polymers desorb from the clay mineral and that a new citrate-containing phase is formed under these conditions. At increasing citrate concentrations the Al hydroxide polymers may dissolve.

It may be expected that the influence on the interactions of citrate with aged clay/Al hydroxide polymer systems and the formation of such systems depend on factors such as the pH, Al:clay ratio and Al:citrate ratio. A further study could shed more light on the interaction processes occurring in such systems. Moreover it could elucidate the competition between the possible sorption of citrate to Al hydroxide polymers on one hand and possible dissolution of Al hydroxide polymers induced by formation of soluble Al citrate complexes on the other hand.

To date, few detailed studies have been conducted on systems in which metal ions, Al ions, clay and citrate co-exist (Chairidchai and Ritchie, 1990 and

1992). Such a system is complex and numerous interactions may occur. Citric acid forms strong complexes not only with Al but also with heavy metal ions, and it may influence the properties and formation of the clay/Al hydroxide polymer system and thus the extent of heavy metal ion binding.

The four interactions that may occur in a system containing: clay, Al hydroxide polymers, citrate, Zn (as an example of a heavy metal ion) are:

a) Citrate may bind to the edge faces of the clay.
b) Citrate may form complexes with Zn and Al species in solution.
c) Citrate may form complexes with Al from the Al hydroxide polymers by forming soluble Al citrate complexes.
d) Citrate may form complexes with Zn, leading to a decrease in the Zn binding to the clay surface and Al hydroxide polymers.

Citrate influences the Zn sorption in two ways: by the formation of Zn-citrate complexes and by the fact that fewer Al hydroxide polymers are formed. Zn citrate complexation reduces the activity of Zn^{2+} and thus the binding of Zn^{2+} ions to the clay surface. Complexation of Al by citrate reduces the amount of Al hydroxide polymers which will also lead to a decrease in metal ion binding, because less reactive surface is available for binding.

To improve our quantitative understanding of the interactions that influence the binding, mobility and bio-availability of heavy metal ions in soils, it is important to be able to describe all observed reactions quantitatively. Since there is much uncertainty about the speciation of Al/citrate systems in solution (Pattnaik and Pani, 1961; Kwong and Huang, 1979; Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984; Gregor and Powell, 1986), the validity of the complexation models should be tested.

Aim and outline of this thesis

The research described in this thesis was based upon the questions discussed above. The binding of heavy metal ions in systems containing clay minerals (montmorillonite), Al hydroxide and also low molecular weight organic ligands (citric acid) was investigated. The aim of this study was to determine the effect of the interaction between montmorillonite, Al hydroxide and citric acid on the speciation of heavy metal ions (Zn and Pb). The heavy metal ions were distinghuished into heavy metal ions in solution, heavy metal ions forming part of the exchangeable ions on the clay surface and heavy metal ions specifically bound to the Al hydroxide polymers, in the presence and absence of citrate.

A methodology that allows for the speciation of metal ions in clay/Al hydroxide systems was developed and tested (chapter 2). It was applied to the binding of Zn and Pb (chapters 3 and 4). The results and consequences for the availability in soils are discussed.

The binding of citrate to clay/Al hydroxide polymer systems and the formation of such systems in the presence of citrate is described in chapter 5. In chapter 6 the effect of citrate on the Zn binding during the formation of clay/Al hydroxide systems is calculated and evaluated.

CHAPTER 2

Effect of Al hydroxide polymers on Ca, Zn and Pb exchange of Na montmorillonite

Abstract

When Al species react with Na montmorillonite at a pH of 5.0 or 6.6 and an Al/clay ratio up to 2.00 mol Al/kg clay, the Al hydroxide polymers (ALHO) formed were irreversibly sorbed on the clay mineral. Under the experimental conditions prevailing at pH 6.6, this reaction reduced the CEC by 0.25 eq per mole Al which was sorbed in the form of ALHO. At pH 5.0 the cation exchange capacity (CEC) reduction was not linearly dependent on the amount of ALHO sorbed; it varied from 0.27 to 0.42 eq per mole Al sorbed. Exchangeable Al^{3+} ions were negligible at pH 6.6. At pH 5.0 an important fraction of the exchangeable ions on the siloxane surface of the clay was formed by Al^{3+} ions. The exchange of Ca, Zn and Pb on Na montmorillonite from Clay Spur (Wyoming) was investigated in a chloride background medium (for Ca and Zn) or a nitrate background medium (for Pb) at pH 5.0 to pH 6.6 and at a total salt concentration of 0.01*M* monovalent anions. The Ca/Na exchange results were interpreted with two types of ion exchange equations, K_V (Vanselow selectivity coefficient) and K_N. For K_N, equivalent fractions are used for the exchangeable ions, whereas molar fractions are used for K_V. It was found that K_V was nearly a constant for $0.05 \leq M_{Ca} < 0.70$, whereas K_N increased with increasing M. Since the K_V is almost a constant, for these systems cation exchange is best described in terms of the Vanselow ion exchange equation. For Ca/Na, Zn/Na and Pb/Na exchange the average K_V for $0.05 \leq M < 0.70$ was found to be 1.2, 1.2 and 1.6 respectively, independent of pH. The exchange of Ca on Na montmorillonite/ALHO systems was investigated in a chloride background medium at pH 6.0 and a total salt concentration of 0.01*M* monovalent anions. Two loadings with Al (0.76 and 1.90 mol Al/kg clay) were studied, to ascertain if the exchange is dependent on the system's degree of condensation. The preference for Ca on the clay/ALHO (CALHO) system at pH 6.0 was greater than for the pure clay and independent of the loading of the clay with Al, and could be characterized by an average K_V of 2.0. It is shown that the K_V for Zn and Pb exchange on Na montmorillonite/ALHO systems could not be determined directly in this system. The effect of the presence of ALHO on the selectivity coefficient of Zn/Na and Pb/Na exchange was estimated by extrapolating the experimental results of Ca/Na, Zn/Na and Pb/Na exchange for pure clay and Ca/Na exchange for CALHO systems. The outcome of the estimated selectivity coefficients was tested by another independent method using experimental results for Zn and Pb sorption to CALHO systems (Chapters 3 and 4). It was found that the preference for Zn and Pb on the CALHO system was greater than for the pure clay and independent of the loading of the clay with Al. The exchange on the siloxane surface of the CALHO system could be well characterized by an average K_V that was equal to 2.0 for Zn/Na and to 2.6 for Pb/Na. These K_V were independent of the pH (in the range from 5.0 to 6.6).

8

This chapter is submitted for publication in *Environmental Science and Technology*. R.P.T. Janssen, M.G.M. Bruggenwert and W.H. van Riemsdijk; Effect of Al hydroxide polymers on Ca, Zn and Pb exchange of Na montmorillonite.

Introduction

Metal ions are known to bind to clay minerals via an ion exchange mechanism to the negatively charged siloxane surface that dominates the total surface area of the clay. The edge faces of clay minerals, which form a small fraction of the total surface area of the clay, bind metal ions via formation of surface complexes with reactive groups like for instance a hydroxyl group that is singly coordinated to an underlying Al ion of the clay structure. The binding to these sites may be affected by the negative electric field that emanates from the siloxane surface, the so called spillover effect (Secor and Radke, 1985).

Metal ions can also form surface complexes with reactive sites present on Al hydroxide polymers (Kinniburgh *et al.*, 1976; Micera *et al.*, 1986)(denoted as ALHO). The extent of this reaction depends amongst others on the electrostatic potential which is affected by the pH and by the available reactive surface area. The smaller the particle the higher the reactive surface area. However, small particles are thermodynamically unstable and tend to form larger particles decreasing their reactive surface area. Extremely small ALHO are known to interact strongly with clay minerals (Sawhney, 1960; Shen and Rich, 1962; Carstea, 1968). This interaction may stabilize these small particles. The strong interaction between the positively charged polymer particles and the negative field of the clay platelet may also influence the binding of heavy metal ions to the ALHO.

Another aspect of clay/ALHO systems (denoted as CALHO) is that they flocculate well, have a relatively high hydraulic conductivity when used as column material, which makes them potentially a suitable product to treat metal ion containing waste streams. The interaction between ALHO and clays occurs also in naturally soil systems. Either for the purpose of treating metal ion containing waste streams or for the purpose of a better understanding of metal ion behaviour in polluted soils it is of interest to have a better quantitative insight in the processes that influence the metal ion binding for such systems.

The presence of ALHO has a strong effect on the aggregation of Na montmorillonite. This change in spatial distribution influences the exchange reactions between the ions adsorbed on the siloxane surface of the clay and the ions in the solution phase (Barnhisel and Bertsch, 1989; Zelazny and Jardine, 1989). Also tactoid formation (packets of clay platelets) by di- and trivalent ions has an effect on the selectivity of cation exchange on the clay. Several studies have investigated the tactoid formation of clay by divalent ions most of them concerning Ca/Na exchange on clay minerals.

Blackmore and Miller (1961), Norrish and Quirk (1954) and Warkentin *et al.* (1957) studied the spatial structure of Na and Ca clay minerals. They concluded that the platelets of a pure Na clay are separated, whereas platelets of a pure Ca clay exist as packets of several platelets in parallel alignment called tactoids or quasi-crystals. When tactoids are formed in a mixture of Na and Ca ions 'demixing' of cations occurs (first shown by Glaeser and Méring, 1954). Shainberg and Otoh (1968) and Bar On *et al.* (1970) showed that Na^+ ions are concentrated on the external surfaces and Ca^{2+} ions on the internal surfaces of the tactoids. Tactoids consist of 4 to 8 platelets in a packet with a film of water 0.45 nm thick on each internal surface. Shainberg and Kemper (1966) calculated that the affinity of the internal surface for Ca is 2-4 times greater than that of the external surface.

Many studies on the Ca/Na and HM/Na exchange (HM= heavy metal ions) on clay minerals (Banin, 1968; Bolt, 1955; Glaeser and Méring, 1954; Maes *et al.*, 1973; Mc Bride, 1980; Schwertmann, 1962; Shainberg *et al.*, 1980; Sposito *et al.*, 1981, 1983a and 1983b; Sposito and Mattigod, 1979; Van Bladel *et al.*, 1972; Van Bladel and Gheyi, 1980; Wild and Keay, 1964) show that the selectivity coefficient is not a constant but changes with the fraction of Ca or HM adsorbed. This has been attributed to the tactoid formation of the clay mineral in the Ca or HM state (Banin, 1968; Mc Bride, 1980; Shainberg *et al.*, 1980).

Hydrolysis, polymerization and precipitation reactions of Al ions may give rise to different Al species (Al^{3+}, $AlOH^{2+}$, $Al_2(OH)_2{}^{4+}$, ... ALHO). The speciation is a function of Al concentration, pH and ionic strength. Since the pzc of amorphous $Al(OH)_3$ (Kinniburgh *et al.*, 1975) and gibbsite (Hiemstra *et al.*, 1987 and 1989) is high (9.4 and 10 respectively) the ALHO surface is positively charged under acid conditions. In the presence of clay minerals the positively charged Al species will sorb onto the siloxane surface. The speciation of the Al in the sorbed phase is a function of pH, ionic strength, type of competitive cations and total amount of Al present. At increasing pH the speciation shifts towards the ALHO and monomeric Al^{3+} represents a small to negligible fraction of the exchangeable cations that are bound to the clay surface. At decreasing pH the fraction of exchangeable monomeric Al^{3+} increases. ALHO binds strongly to the siloxane surface of phyllosilicate clay minerals, forming layers of ALHO between the clay platelets which are not exchangeable by competition with high concentrations of cations (Zelazny and Jardine, 1989; Barnhisel and Bertsch, 1989). The ALHO can only be removed by treatment with an acid or a strong complex-forming agent for Al (Barnhisel and Bertsch, 1989). The basal spacing of ALHO interlayered clay minerals is 1.4 nm. The mineral is resistant to collapse upon KCl treatment by the presence of the nonexchangeable Al polymers (Rich and Obenshain; 1955). The ALHO interlayered clay minerals are known to be common in acid to slightly acid soils. Rich (1968) gives the most favourable soil conditions for interlayer formation.

Many laboratory experiments have been done to synthesize Al interlayered clay minerals (Sawhney, 1960; Shen and Rich, 1962; Carstea, 1968). The chemical properties of the clay mineral may change when ALHO interlayers are present. The cation exchange capacity (CEC) is reduced by ALHO interlayers (Shen and Rich, 1962; Carstea, 1968; Sawhney, 1968; Keren *et al.*, 1977; Keren, 1980). Keren (1980) investigated the CEC reduction by ALHO interlayers under different experimental conditions. He concluded that low equilibrium pH values and slow rates of Al neutralization led to greater reductions in CEC. Barnhisel and Bertsch (1989) determined the composition of the ALHO from data reported by several researchers that show that the CEC of clays decreased as the result of sorption of ALHO. They invariably found a value of 2.7 for the OH/Al molar ratio in the range of amounts ALHO studied. Harsh and Doner (1985) observed a random distribution of hydroxy-Al "islands"in the interlayers of Wyoming montmorillonite. Whereas the hydroxy-Al in the interlayers of vermiculite occur as "atolls" (Dixon and Jackson, 1962; Frink, 1965). However the mechanism of Al interlayer sorption on clays is still not completely understood. In this chapter the effect of the Al:clay ratio on the CEC is studied for pH 5.0 and 6.6. Since the speciation of the Al in the sorbed phase is a function of pH, this may influence the compostion of the ALHO. One of the purposes of this study is to gain more insight in the chemical compostion of the ALHO as influenced by Al:clay ratio and pH.

Hydroxy-Al interlayers can also influence the selectivity of cation exchange reactions (Barnhisel and Bertsch, 1989; Zelazny and Jardine, 1989). Untill now the effect of synthetic ALHO interlayering on cation exchange has hardly been studied. Keizer and Bruggenwert (1991) studied the Ca/Cd exchange in a pure montmorillonite system and in a montmorillonite/ALHO complex system. Kozak and Huang (1971) studied K/Ca exchange in a pure Na montmorillonite system and in a Na montmorillonite/ALHO complex system. Both authors observed no difference between the selectivity coefficients in a pure clay system and a CALHO system. On the other hand Keren (1979) studied the effect of ALHO interlayers on the selectivity coefficient for Na/Ca exchange of the clay mineral montmorillonite. He observed an increase in the selectivity coefficient if Al interlayering is present. Keren (1979) suggested the tactoid formation by Al increased the selectivity of Ca on interior sites and decreased it for exterior sites. He observed also that the selectivity coefficient was rather independent of the composition for the CALHO system, whereas the selectivity coefficient for the pure clay changed greatly with the equivalent fraction of Na adsorbed. Unfortunately Keren (1979) studied Na/Ca exchange on the pure clay and CALHO at pH 7.5 and at a very high Al:clay ratio. This makes extrapolation of Keren's results to natural soil systems with a lower pH and Al:clay ratio difficult, since the Al speciation is a function of pH and possible also Al:clay ratio. Moreover specific Ca sorption on the ALHO interlayers at such a high pH can not be excluded and may have influenced the results (Kinniburgh *et al.*, 1975).

The present study was undertaken to determine the effect of ALHO on Ca/Na exchange for a series of exchanger compositions, in systems loaded with 0.00, 0.76 and 1.90 mol Al/kg clay at pH 6.0 and a total salt concentration of 0.01*M* monovalent anions. Two loadings of the clay with Al were studied, since the exchange may be dependent on the degree of condensation of the system.

We also studied the effect of the presence of ALHO on Zn/Na and Pb/Na exchange. In contradistinction to Ca, HM ions can sorb in a CALHO system not only to the siloxane surface of the clay competing with Na^+ ions but they also bind to the ALHO by specific sorption (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991). Since the two processes are chemically different it is important to be able to discriminate the total observed adsorption into the two different parts (Chapters 3 and 4).

With an ion exchange equation for the exchange of HM with Na^+ on the siloxane surface of CALHO, it is possible to calculate the amount of HM sorbed on the clay surface and "speciate" the HM in the system among HM in solution, HM that forms part of the exchangeable ions on the clay surface and HM that is specifically bound to the ALHO. In order to be able to apply this concept, an appropriate ion exchange equation should be selected and the ion exchange coefficient should be known. The selectivity coefficient for the exchange of HM for Na^+ on the clay surface in CALHO is needed.

It is not possible to determine the exchange coefficient directly in a CALHO system at pH 6.0, since HM ions bind as well to the clay surface as to the ALHO (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991). The sorption of HM ions on the ALHO is accompanied with a change in the charge of the ALHO (Kinniburgh *et al.*, 1975 and 1976; Micera *et al.*, 1986), decreasing the cation exchange capacity (CEC) of the clay which further complicates the determination of an ion exchange coefficient.

In this chapter we have estimated the effect of the presence of ALHO on the selectivity coefficient of HM/Na exchange by extrapolation of the experimental results of Ca/Na and HM/Na exchange for pure clay and Ca/Na exchange for CALHO. Therefore we studied the exchange of Zn and Pb on pure Na montmorillonite. The outcome of the estimated selectivity coefficients was tested by another independent method using the experimental results for Zn and Pb sorption to CALHO systems (Chapters 3 and 4).

Experimental

Preparation of the stock clay suspension

Montmorillonite clay from Clay Spur, Wyoming obtained from Ward's Natural Science Establishment, was used for all experiments. The montmorillonite was suspended in deionized water and passed through a 63 μm sieve. The suspension was then saturated with Na by four washings with 1*M* NaCl. Subsequently the clay suspension was washed several times with deionized water to remove the excess salt. A 2 μm fraction was obtained by gravity sedimentation at constant temperature. The clay suspension was centrifuged at 2300 g for 20 minutes; the clear supernatant was decanted. The electrolyte concentration of the concentrated clay suspension was further lowered by dialyzing the clay suspension. After dialysis the total electrolyte concentration in the solution of the clay suspension was determined by measuring the Na concentration and was found to be 0.0115*M*. The clay suspension contained 2.63% clay. The CEC of the clay was measured by measuring the amount of Na desorbed from the clay by 0.0033*M* $La(NO_3)_3$ and was found to be 0.95 eq/kg clay.

Ca sorption on clay and CALHO systems

Various pure clay and CALHO systems were prepared as follows. A certain amount of the stock clay suspension was pipetted to 500 mL bottles (the suspensions would finally contain 10.52 g clay/L). Deionized water was added to adjust the volume to 125 mL, which is half of the final volume. Then 0.100*M* $AlCl_3$ solution was added to the suspensions at the rate of 0.00, 0.76 and 1.90 mol/kg clay. Subsequently 0.1*M* NaCl was added until these suspensions contained 0.01*M* Na in solution. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.300*M* NaOH or 0.100*M* HCl was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 5.0 or 6.0 was reached. The suspensions were shaken for seven days. The pH of the suspensions were measured regularly and if necessary adjusted until a pH of 5.0 or 6.0 was reached again. In order to obtain a salt level of approximately 0.01*M*, the CALHO suspensions were subject in this seven days period of the following procedure. The bottles were filled up to the rim with deionized water (ca.500 ml) and stand overnight. The next day the above clear solution was removed to have left a CALHO suspension with a total salt level of approximately 0.01*M*. The bottles were filled up again to the rim with deionized water if the salt level was still higher than 0.01*M*. Finally an 0.01*M* NaCl solution was added to the CALHO suspensions to obtain a total salt level of nearly 0.01*M*. The next day the above clear solution was removed. The final volume of 250 mL was obtained by using a balance. Subsequently after seven days 20 mL CALHO (0.76 mol Al/kg clay or 1.90 mol Al/kg clay) or clay were under constant stirring pipetted into a bottle for the Ca/Na experiments. Then 20 mL of a solution containing $0.005M$ $CaCl_2$ and $0.010M$ NaCl were pipetted to the suspensions (clay content 5.26 g/L) and titrated with $0.010M$ NaOH or $0.100M$ HCl until a pH of 5.0 or 6.0 was reached. The suspensions were shaken for about 20 hours and the pH of the suspensions were measured and if necessary adjusted to the same pH. The final volumes were determined by using a balance. Under constant stirring 30 mL of each suspension was pipetted into a centrifuge tube and centrifuged at 37,000 g for the pure clay and at 10,000 g for the CALHO for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solutions. The Na, Ca and Al concentrations in the supernatant solutions were determined.

Zn and Pb sorption on clay

For the Zn/Na and Pb/Na experiments 1 mL clay suspension and 9 mL deionized water were pipetted directly into a centrifuge tube. Subsequently 20 mL of a solution containing $0.010M$ $ZnCl_2$, $Pb(NO_3)_2$ and $0.010M$ NaCl (for Zn) or $0.010M$ $NaNO_3$ (for Pb) were pipetted to the suspensions (clay content 0.92 g/L) and titrated with $0.010M$ NaOH or $0.100M$ HCl until a pH was reached. The suspensions were shaken for about 20 hours and the pH of the suspensions were measured and if necessary adjusted to the same pH. The final volumes were determined by using a balance. The suspensions were centrifuged at 10,000 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solution. The Na and Pb or Zn concentrations in the supernatant solutions were determined.

Extraction with $La(NO_3)_3$

To the clay residue in the centrifuge tubes, 50 mL $0.0033M$ $La(NO_3)_3$ was added. The suspensions were shaken for two hours. The extraction time is long enough to achieve equilibrium since a rapid attainment of equilibrium is reached in ion exchange processes (Inskeep and Baham, 1983; Garcia-Miragaya and Page, 1976). Then the suspensions were centrifuged at 10,000 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear extract solutions. The Na, Ca, Al and Pb or Zn concentrations in the extracts were determined. The efficiency to exchange mono-, bi and trivalent ions by La^{3+} can easily be estimated since the selectivity coefficients for La exchange are known (Bruggenwert and Kamphorst, 1979). From simple ion exchange calculations it followed that the amount of La^{3+} (0.17 mmol/50 mL or 0.1 mmol/30 mL) is enough to remove essentially all Na^+, Pb^{2+} and Zn^{2+} ions attached to the clay surface in exchangeable form (total surface charge per centrifuge tube: 0.20 meq or 0.03 meq). To exchange all Ca^{2+} from the clay surface (total surface charge per centrifuge tube: 0.20 meq) a second amount of

50 mL 0.0033*M* $La(NO_3)_3$ was added to the clay residues in the centrifuge tubes. The suspensions were shaken and centrifuged. The Ca concentrations in the extracts were determined. In most cases the excess of La^{3+} over Al^{3+} in the extract is such that essentially all exchangeable Al^{3+} will be replaced by La^{3+}. However for the pH 5.0 experiments not all exchangeable Al^{3+} will be extracted and a correction is necessary (as explained in the section results and discussion).

X-ray diffraction patterns

XRD patterns were prepared from the pure clay and the clay loaded with three amounts of ALHO (0.80, 1.20 and 2.00 mol Al/kg clay). The CALHO systems were prepared in the same way as described above. The systems were titrated to a pH of 6.0 and were aged for two weeks. The pH of the suspensions were measured regularly and adjusted until a pH of 6.0 was reached again. The ALHO species in the complex increased the basal spacing of montmorillonite from 1.17 to 1.22, 1.29 and 1.36 nm at 295 K for the systems loaded with 0.80, 1.20 and 2.00 mol Al/kg clay respectively. This indicates that Al interlayers were formed for the highest loading of the clay with Al. For the two lower loadings probably an incomplete interlayering was obtained due to the low amount of Al added. The X-ray diffraction patterns of the oriented K-saturated minerals were obtained with a Philips PW 1820/PW 1710 diffractometer with a CoKα radiation (0.17889 nm) equipped with a monochromator.

Analysis

Na, Ca, Pb, Zn and Al were analysed by ICP-AES (Spectro Analytical Instruments) in the supernatant and La extract.

Chemical speciation calculations

Chemical speciation in the equilibrium solution was calculated using the program ECOSAT (Keizer and Van Riemsdijk, 1994). The adapted Davies equation was used to calculate the activity coefficients. The ECOSAT program used: the equilibrium constants for hydrolysis products of Ca, Na, Al, Zn and Pb (Lindsay, 1979); Ca, Na, Al, Zn, Pb chloride and nitrate complexes (Lindsay, 1979); the solubility product of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965).

Results and Discussion

The CEC of clay/Al hydroxide polymers (CALHO)

The cation exchange capacity (CEC) is expected to be reduced by the positively charged Al hydroxide polymers (denoted as ALHO) that are bound to the negatively charged clay surface. We determined the CEC by exchanging the cations associated with the clay surface with trivalent La ions. From simple ion exchange calculations we knew that the concentration of La was high enough to replace all monovalent and bivalent exchangeable ions on the clay surface. The efficiency to exchange trivalent Al could be estimated easily, because monomeric Al^{3+} and La^{3+} have approximately the same preference for the clay (Bruggenwert and Kamphorst, 1979). In most cases the excess of La^{3+} over Al^{3+} in the extract was such that essentially all exchangeable Al^{3+} was replaced by La^{3+}. The only instance of not all exchangeable Al being extracted was in the pH 5.0 experiments. Here, a correction (never more than 30%) was necessary. We determined the CEC of the clay/ALHO (denoted as CALHO) materials for four ratios of ALHO polymer to clay at pH 5.0 and pH 6.6. Apart from Al and H, Na was the only cation in the system. The La extraction at pH 6.6 revealed Na^+ as the only exchangeable cation. All the Al was thus present in the form of non-exchangeable ALHO. This result is what we expected, because the concentration of Al^{3+} in a solution at pH 6.6 in equilibrium with $Al(OH)_3$ is extremely low, and it cannot compete effectively with the Na^+ ions which are present in a large excess. Assuming a solubility constant of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965), the excess of Na^+ over Al^{3+} was roughly a factor $10^{8.8}$. It may be assumed that the released Na ions originate from the negative clay surface only, and not from the positive ALHO surface (Sprycha, 1989). Under these conditions the CEC of the clay can be calculated from the extracted amounts of Na^+ ions.

The CEC measured in this way at pH 6.6 as a function of the amount of Al in the system that is present as Al fixed (i.e. non-exchangeable ALHO) is shown in Figure 1a. The reduction of the CEC is linearly dependent on the amount of ALHO per unit amount of clay. This strongly suggests that all the ALHO present was sorbed to the clay. The ALHO would have had no effect on the CEC if it had been present as a separate phase. The results also indicate that the nature of the ALHO formed is independent of the degree the clay is loaded with ALHO in the range of loadings studied. The average charge of the ALHO, expressed per Al atom, can be derived from the slope of the curve. It was 0.25+ per Al atom, suggesting an average OH/Al mole ratio of 2.75 for the ALHO component.

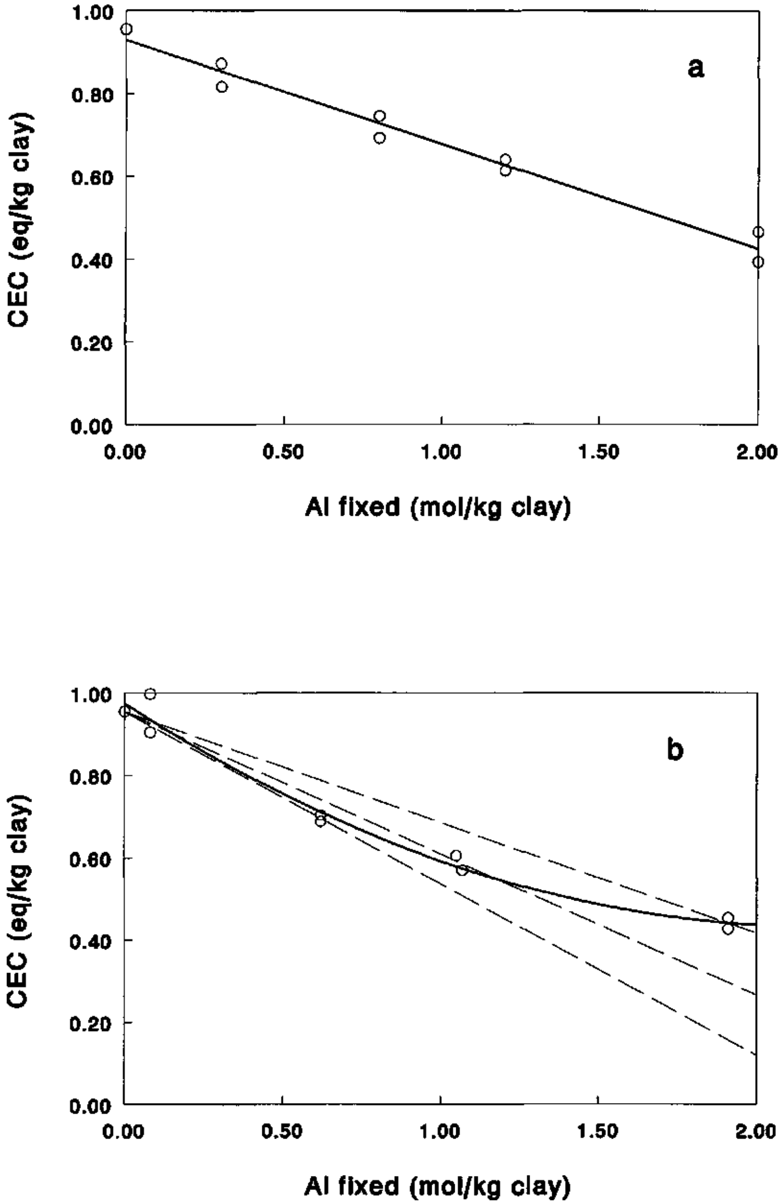

Figure 1 Relation between the CEC and the amount of Al fixed to the clay as ALHO at pH 6.6 (Figure 1a) and at pH 5.0 (Figure 1b).

At pH 5.0 the situation is different. The concentration of monomeric Al^{3+} in solution could be estimated from the solubility product of the ALHO which has been estimated to be 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965). Although the concentration of Al^{3+} in solution was only $10^{-6}M$, because of its trivalent charge this concentration was high enough to compete effectively with Na^+ for the exchange sites. As a result, part of the Al was present as exchangeable ions and part as ALHO polymers attached to the clay particles. In addition to monomeric Al^{3+}, monomeric $AlOH^{2+}$ is also relevant in the solution phase. However, on the basis of ion exchange calculations using a Donnan approach and assuming a concentration of $2.5M$ in the Donnan phase (Bolt, 1979), we did not expect $AlOH^{2+}$ to be significant as an exchangeable ion under these conditions.

Both Al ions as well as Na ions were detected in the La extract; this shows that both Na^+ and Al^{3+} were present in exchangeable form. The amount of Al^{3+} sorbed was determined from the composition of the La extract, assuming that during the extraction no secondary Al hydroxide precipitate was formed. The experiments at pH 6.6 showed that treatment with La^{3+} does not lead to Al being released if it is present as ALHO. This indicates that no ALHO was dissolved in the La extract or removed from the clay surface by La^{3+}.

As indicated above the La concentration used was not high enough to remove all the Al^{3+} that was in exchangeable form at pH 5.0. For the system with the smallest addition of Al the CEC remained large, and most of the Al was present as exchangeable Al^{3+}. For larger Al loadings, only a relatively small fraction of the total Al was present in exchangeable form. The amount of exchangeable Al^{3+} present was estimated from the measured Al^{3+} and estimated La^{3+} concentration in the extract and assuming that the selectivity coefficient for La^{3+}/Al^{3+} exchange is one (Bruggenwert and Kamphorst, 1979). The correction was never larger than 30%. The CEC of the clay was calculated from the amount of Na^+ plus Al^{3+} determined as exchangeable ions, based upon the La extraction and the calculated Al^{3+} correction.

The amount of ALHO attached to the clay was calculated by subtracting the exchangeable Al and the Al present in solution from the total amount of Al added to the system. Figure 1b shows the CEC measured in this way at pH 5.0, as a function of the amount of Al in the system that is present as ALHO fixed to the clay. The reduction of the CEC is not entirely linearly dependent on the amount of ALHO per unit amount of clay (unlike the case at pH 6.6: see Figure 1a). The inverse relation between CEC and ALHO suggests that the ALHO polymers strongly interact with the clay surface. The measured Al concentrations in the supernatant which were very low, showed that indeed no separate ALHO phase was present in the supernatant. The clay without ALHO polymers for the salt level used resulted in a rather stable suspension which did not flocculate significantly overnight.

The average positive charge of the ALHO present could be calculated for each loading from the slope of the three dashed lines in Figure 1b. The average charge per Al atom present as ALHO was inversely related to the amounts of ALHO present and was 0.42+, 0.34+ and 0.27+ for 0.62, 1.06 and 1.91 mol Al/kg clay respectively. As expected, the average charge at pH 5.0 was always higher than the constant average charge of 0.25+ of the ALHO at pH 6.6. At constant pH and ionic strength, the surface charge density of the ALHO can be expected to be approximately constant. The non-linear behaviour of the curve would then result from a difference in size of the ALHO, which should be smaller for lower Al loadings in order to explain the change in the observed slope.

Ca/Na exchange for pure clay and CALHO at pH 6.0

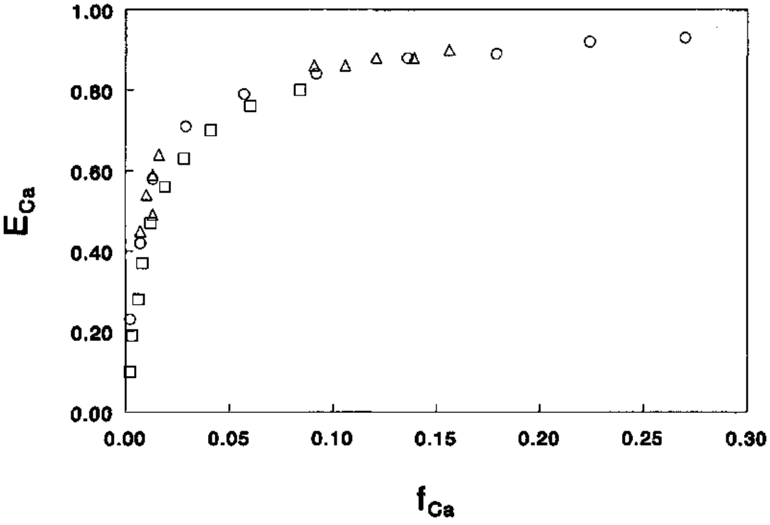

Figure 2 Isotherms for Ca/Na exchange on pure montmorillonite (□), and montmorillonite loaded with 0.76 mol Al/kg clay (△), and 1.90 mol Al/kg clay (○) at pH 6.0.

In Figure 2 the results are given for Ca/Na exchange for pure clay and CALHO at pH 6.0 and a total salt concentration of 0.01*M* monovalent anions. The only exchangeable ions present on the exchange complex are Ca^{2+} and Na^{+}, since exchangeable Al^{3+} was negligible at this pH. Exchangeable Ca^{2+} and Na^+ were determined in the La extract. No Al was found in the extract and therefore we concluded it is a binary system in terms of ion exchange. The results are presented in dimensionless form. The E_{Ca} equals the moles of charge attributed by exchangeable Ca divided by the CEC. The actual CEC of the various systems depends on the amount of ALHO present. The CEC can be derived from Figure 1a and for clay systems loaded with 0.76 and 1.90 mol Al/kg clay equals: 0.72 and 0.45 eq/kg clay respectively (see also Table 1). The f_{Ca} equals the equivalent fraction of the cations in solution that is compensated by Ca ions. The results indicate that Ca is strongly preferred by the clay and even more preferred by the CALHO. The results can be interpreted with one of the various ion exchange models found in literature. The exchange reaction can be written as:

$$Na_2\text{-clay} + Ca^{2+} \longleftrightarrow Ca\text{-clay} + 2Na^+ \qquad (1)$$

One frequently used ion exchange model uses the charge fraction, E, for the adsorbed ions in the definition of the exchange coefficient and ion activities for the ions in the bulk solution phase. The exchange coefficient for reaction (1) is defined as:

$$K_N = \frac{E_{Ca} \times (Na^+)^2}{E_{Na}^2 \times (Ca^{2+})} \qquad (2)$$

This K_N can be related to the thermodynamic exchange constant according to the derivation given by Kielland (1935) and refined by Argersinger *et al.* (1950) and Gaines and Thomas (1953). Equation (2) is often referred to as the Gaines-Thomas ion exchange model.

In the Vanselow model (1932) mole fractions (M) are used instead of charge fractions. The ion exchange coefficient for reaction (1) according to the Vanselow model therefore equals:

$$K_V = \frac{M_{Ca} \times (Na^+)^2}{M_{Na}^2 \times (Ca^{2+})} \qquad (3)$$

The values of K_N and K_V can be calculated for each point of the ion exchange isotherm. The results for the pure clay are shown in Figure 3. Both K_V and K_N increase with increasing M_{Ca}. However, K_V is only slightly dependent on the exchanger composition. It appears that K_N is more dependent on tactoid formation than K_V and that ideality in cation-exchanger phases is best studied

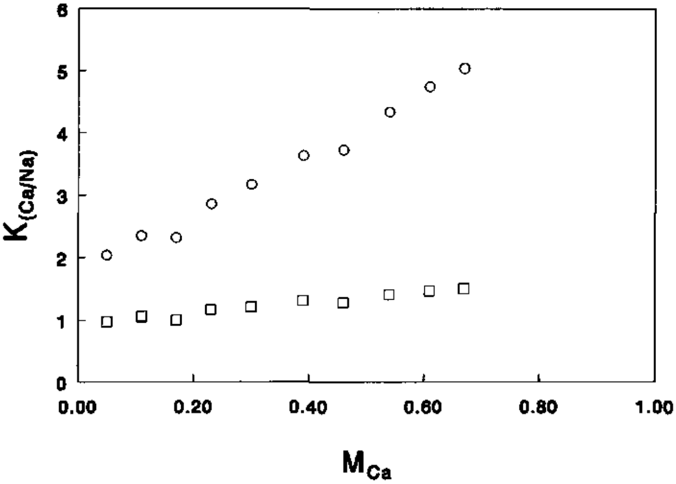

Figure 3 Dependence of the Vanselow selectivity coefficient (□) and the K_N (○) for Ca/Na on the molar fraction of exchangeable Ca on pure montmorillonite.

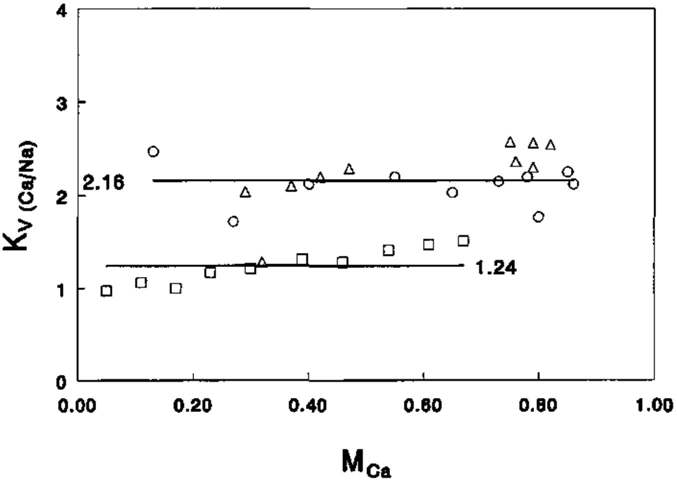

Figure 4 Dependence of the Vanselow selectivity coefficient for Ca/Na on the molar fraction of exchangeable Ca on pure montmorillonite (□) and montmorillonite loaded with 0.76 mol Al/kg clay (△), and 1.90 mol Al/kg clay (○).

in terms of the Vanselow selectivity coefficient (Sposito and Mattigod, 1979).

The near constancy of K_V over a wide range of ion exchange conditions means that the ion exchange behaviour can best be approximated with the Vanselow model. The calculated Vanselow exchange coefficients for the CALHO systems are shown in Figure 4, together with the results for the pure clay. The results show that the Vanselow model also yields a reasonably constant K_V for the CALHO systems, independent of the amount of ALHO, and that the preference for Ca is increased in the range measured. The measured CEC (Table 1) does not change systematically with the amount of exchangeable Ca for a given ALHO loading of the clay. The greater preference for Ca in CALHO systems is probably not caused by specific adsorption of Ca to the ALHO. In the case of specific adsorption, we would have expected K_V to increase concomitantly with the amount of ALHO present and the CEC to decrease with increasing M_{Ca}. The increase in the preference for Ca is probably caused by the clay in the CALHO system having a different structure. Apparently, increasing the amount of ALHO affects the remaining CEC only, not the structure.

Table 1 Relation between the CEC (in eq/kg clay) of CALHO systems for two Al loadings and the molar fraction of Ca bound to the clay surface at pH 6.0.

M_{Ca}	CEC (eq/kg) CALHO: 0.76 mol Al/kg clay	M_{Ca}	CEC (eq/kg) CALHO: 1.90 mol Al/kg clay
0	0.69	0	0.44
0.29	0.70	0.13	0.44
0.32	0.71	0.27	0.44
0.37	0.71	0.40	0.45
0.42	0.71	0.55	0.44
0.47	0.72	0.65	0.45
0.75	0.73	0.73	0.45
0.76	0.74	0.78	0.45
0.79	0.74	0.80	0.45
0.79	0.71	0.85	0.45
0.82	0.72	0.86	0.46
mean ± s.d.	0.72 ± 0.01		0.45 ± 0.01

Zn/Na and Pb/Na exchange for pure clay and CALHO

Heavy metal ions (HM) like Zn and Pb behave differently from Ca ions in CALHO systems. In addition to ion exchange on the siloxane surface, binding to the ALHO may also take place via formation of ion-specific surface complexes in the case of HM (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991). The formation of a complex between metal ions and the surface of the ALHO (without clay) enhances the positive charge of the ALHO, since metal binding to hydroxide surfaces is accompanied by a substoichiometric release of protons (Kinniburgh *et al.*, 1975 and 1976; Micera *et al.*, 1986). In other words, the molar ratio between proton release and metal binding is less than two. Measuring the CEC of CALHO systems by extraction with La^{3+} ions, is no longer a reliable method either because it is uncertain to what extent La extraction will lead to a release of metal ions bound to the ALHO. This makes it more complicated to calculate the selectivity coefficient for HM/Na exchange in CALHO systems directly. One way to estimate the selectivity coefficient of HM/Na exchange in CALHO is to use the experimental results on Ca/Na and HM/Na exchange for pure clay and Ca/Na exchange for CALHO. Below, we have followed this approach for Zn/Na exchange.

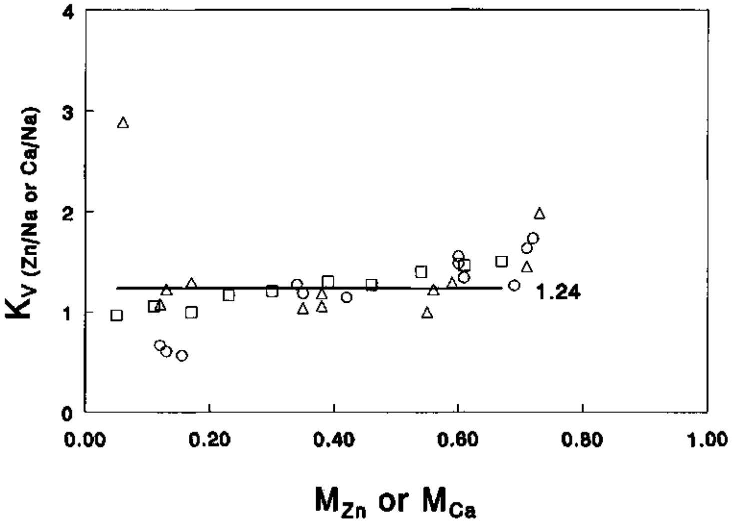

Figure 5 Dependence of the Vanselow selectivity coefficient for Ca/Na exchange at pH 6.0 (□) and for Zn/Na exchange at pH 5.0 (△) and pH 6.6 (○) on the molar fraction of exchangeable Ca and Zn on pure montmorillonite.

Figure 5 shows the selectivity coefficient (K_V) for Ca and Zn exchange with Na at a total salt concentration of 0.01*M* monovalent anions for the pure clay. The data for Ca/Na exchange are the same as presented in Figures 3 and 4. The amounts of exchangeable Zn^{2+} and Na^+ were determined in the La extract. The Zn/Na exchange was measured at pH 5.0 and 6.6 as shown in the figure. In this pH range no dependence of K_V on pH was observed. No $Zn(OH)_2$ precipitate was formed in any of the Zn systems, since the log IAP calculated in the equilibrium solution was always less than the log K_{so} for $Zn(OH)_2$ (Smith and Martell, 1981). The results indicate that the Vanselow selectivity coefficients for Ca/Na or Zn/Na were essentially the same within the experimental accuracy. The average values are 1.24 ± 0.16 for Ca/Na exchange and 1.23 ± 0.24 for Zn/Na exchange. That Ca and Zn have approximately the same preference for montmorillonite in ion exchange reactions is supported by the results of Van Bladel *et al.* (1993), who observed an almost non-preferential exchange for Zn/Ca exchange of Camp Berteau montmorillonite. Using data from Maes (1973), Sposito and Mattigod (1979) calculated a K_V of 1.49 for Zn/Na exchange on that montmorillonite. This value is slightly higher than the K_V we found for montmorillonite, but the small difference might be due to differences in the type of clay used.

Using these results we can now estimate the exchange coefficient for Zn/Na exchange for a CALHO. Since a pure clay shows no difference in preference for Ca or Zn it may be assumed that the same holds for the CALHO system. This assumption implies that the presence of CALHO on the clay has the same effect on Zn/Na exchange as on Ca/Na exchange. We therefore estimated the Vanselow selectivity coefficient for Zn/Na exchange for CALHO to be 2.16.

The method of estimating the K_V of Ca/Na for Zn does not work for Pb because Pb shows a greater preference for the clay compared with Ca (Figure 7). We therefore need another independent method to estimate the exchange coefficient for CALHO type systems. Let us first test the method for Zn/Na exchange for CALHO, since this enables us to compare the outcome of both estimation methods. We will use the experimental results for Zn sorption to CALHO systems from Chapter 3, to estimate the exchange coefficient for Zn/Na for a CALHO system. The data are for ion exchange at pH 5.0 and pH 6.6 for clays loaded with four amounts of ALHO. The salt concentration was 0.01*M* monovalent anions. The ion exchange is a ternary process at pH 5.0 and effectively a binary process at pH 6.6. For a ternary exchange reaction the ion exchange equation (3) can be rewritten as:

$$\frac{1-M_{Al}-M_{Na}}{M_{Na}^2}=K_V\times\frac{(Zn^{2+})}{(Na^+)^2} \qquad (4)$$

The mole fraction of exchangeable ions can be expressed as:

$$M_i=\frac{q_i}{\Sigma q_i}=\frac{q_i}{Q_t} \qquad (5)$$

where q_i is the amount adsorbed in exchangeable form of ion i expressed in mol/kg and Q_t is the total amount of adsorbed ions (mol/kg). Combining equations (4) and (5) results in:

$$\frac{1-\frac{q_{Al}}{Q_t}-\frac{q_{Na}}{Q_t}}{\frac{q_{Na}^2}{Q_t^2}}=K_V\times\frac{(Zn^{2+})}{(Na^+)^2} \qquad (6)$$

The amount of Zn ions adsorbed in exchangeable form equals:

$$q_{Zn}=Q_t-q_{Al}-q_{Na} \qquad (7)$$

The CEC in eq/kg of the clay system follows from:

$$CEC=\Sigma z_i\times q_i \qquad (8)$$

where z_i is the charge of the exchangeable ion i. Note that the actual value of the CEC depends on how much ALHO is bound to the clay and also on how much Zn is bound to the ALHO via formation of surface complexes. The values of q_{Al} and q_{Na} follow from the La extraction. The activities of Zn^{2+} and Na^+ follow from measurement of the concentrations in solution. It follows that Q_t can be calculated from equation (6) if K_V is known. From equations (7) and (8), the value of q_{Zn} and the CEC can then be calculated. For pH 6.6 equations (4) to (8) still apply, the only difference being that M_{Al} and q_{Al} can be neglected.

It could be argued that it is still impossible to derive the value of K_V since Q_t cannot be determined unequivocally from the La extraction procedure, because it is not known a priori how much the La extraction procedure extracts HM that was previously bound to the ALHO. It is still possible, however, to use equations (4) to (7) to estimate the value of K_V, bearing in mind that the amount of q_{Zn} calculated using a chosen value of K_V can never exceed the amount of Zn extracted by the La extraction procedure. This test gives an upper limit to a realistic value of K_V. We also expect that the K_V for the CALHO will be greater than (or equal to) the value of K_V for the pure clay system. Another estimation of the lower limit for HM exchange could be the value that is determined for Ca/Na exchange for the CALHO.

We first used this procedure to estimate the value of K_V for Zn/Na exchange at pH 5.0. The amounts of exchangeable Na^+ and Al^{3+} (corrected for the amount not extracted with La^{3+}, see the section on the CEC of CALHO) were determined in the La extract. Using the previous estimate of 2.2 for K_V resulted in values of q_{Zn} that were larger than what was extracted with La. This indicates that this is a slight overestimate. Most calculated values for q_{Zn} (denoted in the figure as Zn-CEC) corresponded very well with the amount extracted with La at pH 5.0 if a value of 2.0 was used for K_V, as Figure 6 shows. Thus in the range of Al loadings studied a realistic estimate for the value of K_V for Zn/Na exchange in CALHO is 2.0, independent of the Al loading.

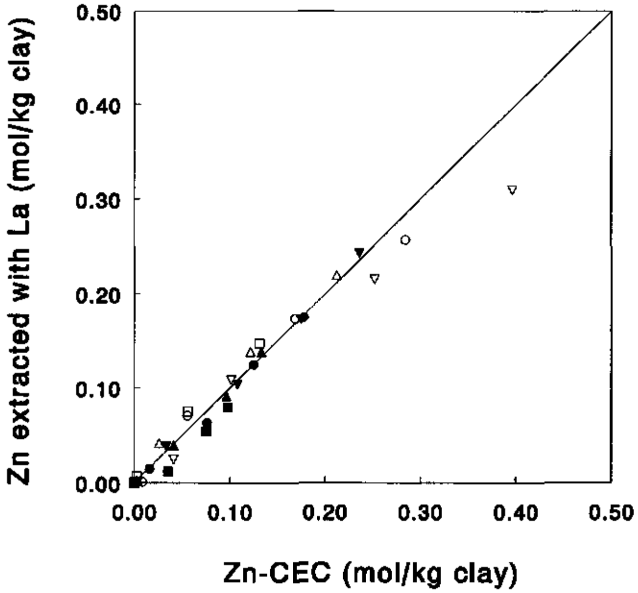

Figure 6 The amount of Zn extracted from CALHO systems with $La(NO_3)_3$ vs. the calculated amount of Zn sorbed on the clay surface (Zn-CEC) at pH 5.0 and 6.6. The loadings in mol Al/kg clay are: ▽/▼ = 0.30 ; ○/● = 0.80 ; △/▲ = 1.20; □/■ = 2.00. Closed symbols indicate the experiments at pH 5.0, open symbols the experiments at pH 6.6.

This implies that the average K_V for Ca/Na exchange is also equal to 2.0, since the K_V values for Zn/Na and Ca/Na exchange for pure clay systems are equal. Reducing the average K_V for Ca/Na exchange from 2.2 to 2.0 may be reasonable, since the K_V was measured mainly with data points in the range $M_{Ca}>0.25$ (Figure 4). The K_V for $M_{Ca}\leq0.25$ is probably lower, reducing the average K_V. This result also shows that the K_V is independent of the pH in the range 5.0 to 6.0, since the K_V for Ca/Na exchange found in a CALHO system at pH 6.0 is also valid for Zn/Na exchange at pH 5.0. Furthermore, Figure 6 indicates that the La procedure does not extract any Zn that is bound to the ALHO under these conditions. Keizer and Bruggenwert (1991) also concluded that a La extraction does not remove any Zn that is specifically bound to the ALHO at pH 5.0. The results we obtained for the systems at pH 6.6 using K_V= 2.0 are also shown in Figure 6. They indicate that a reasonable estimate of the value of K_V can be obtained with this new procedure.

The results of Pb/Na exchange for the pure clay were measured at pH 5.0, 5.5 and 6.0 at a total salt concentration of 0.01*M* monovalent anions (Figure 7).

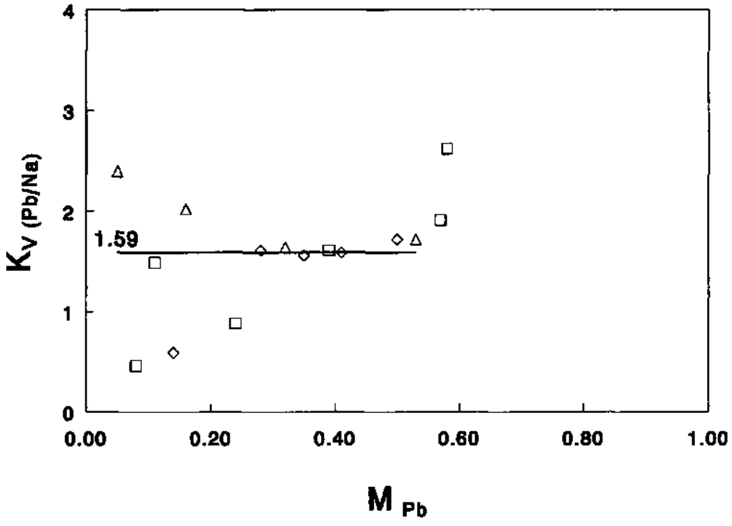

Figure 7 Dependence of the Vanselow selectivity coefficient for Pb/Na exchange at pH 5.0 (△), pH 5.5 (◇) and pH 6.0 (□) on the molar fraction of exchangeable Pb on pure montmorillonite.

We determined the amounts of exchangeable Pb^{2+} and Na^{+} in the La extract. Unfortunately, the quality of the data is not very good, so there is some scatter.

In the pH range from 5.0 to 6.0 no pH-dependent K_V was observed. The experiments were designed so that the concentrations of Pb added were low enough for the systems to be always undersaturated with respect to $Pb(OH)_2$ (Sillén and Martell, 1964). This reduced the likelihood of $Pb(OH)_2$ being precipitated. The average K_V is 1.59 ± 0.4 which is higher than the K_V for Ca/Na exchange of pure clay (1.23 ± 0.16). It may therefore be expected that the increase of K_V for Pb/Na exchange for a CALHO system is equal to the ratio of the K_V for Ca/Na exchange in CALHO and the pure clay (2.0/1.24= 1.61). The value of K_V for Pb/Na exchange in CALHO was estimated to be 2.6 (= 1.61*1.59).

Keizer and Bruggenwert (1991) suggested that Pb binding to ALHO is negligible at pH 5.0. This gives us the oppurtunity to test the value of K_V for Pb/Na exchange in CALHO systems in an independent way, using the experimental results of Pb sorption to CALHO systems from Chapter 4. In this chapter the results of the Pb sorption to CALHO systems for clay loaded with four amounts of ALHO at pH 5.0 and 6.0 and a total salt concentration of 0.01*M* monovalent anions are described. In the case of Pb sorption to CALHO

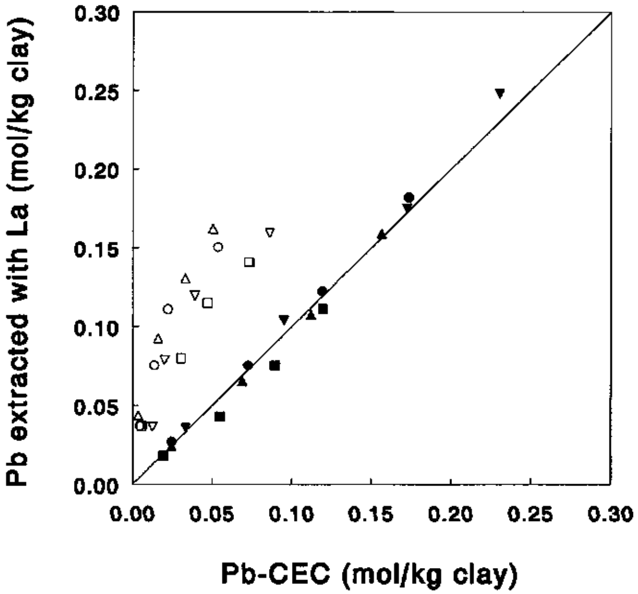

Figure 8 The amount of Pb extracted from CALHO systems with $La(NO_3)_3$ vs. the calculated amount of Pb sorbed on the clay surface (Pb-CEC) at pH 5.0 and 6.6. The loadings in mol Al/kg clay are: ▽/▼ = 0.30 ; ○/● = 0.80 ; △/▲ = 1.20; □/■ = 2.00. Closed symbols indicate the experiments at pH 5.0, open symbols the experiments at pH 6.0.

at pH 5.0, the La extraction should be approximately equal to the amount of exchangeable Pb (and to the total amount of Pb sorbed). We determined the amounts of exchangeable Na^+ and Al^{3+} (corrected for the amount not extracted with La^{3+}, see the section on the CEC of CALHO) in the La extract. Using the value of 2.6 for the K_V resulted in perfect agreement between the amount calculated for q_{Pb} (denoted as Pb-CEC)(using equations 4 to 7) and the amount of Pb extracted by La^{3+} (see Figure 8). This confirms that the value of K_V for Pb/Na exchange in CALHO is 2.6. Furthermore the K_V is independent of Al loading in the range Al loadings studied (see Figure 8). Using the same value for K_V for the data at pH 6.0, showed that the La extraction always results in a larger amount of Pb extracted than calculated as q_{Pb} (Pb-CEC). This suggests that in this case Pb bound to the ALHO is also extracted with La.

The Zn-CEC and Pb-CEC were calculated in CALHO systems at pH 5.0 (Figures 6 and 8) using the newly determined K_V values. We assumed a ternary system, since Al^{3+} sorbs on the siloxane surface. Figure 9 shows the adsorption

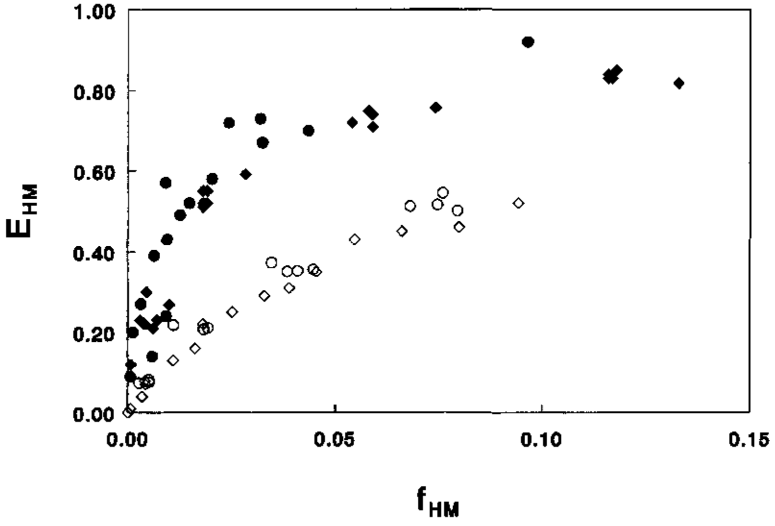

Figure 9 Isotherms for Zn/Na (◇ and ◆) and Pb/Na (○ and •) exchange on pure montmorillonite at pH 5.0 to 6.6, and montmorillonite loaded with Al at pH 5.0. Closed symbols indicate the experiments of the pure clay, open symbols the experiments of the clay loaded with Al.

isotherms of Zn and Pb onto Na clay at pH 5.0 to 6.6 and CALHO at pH 5.0, at a total salt concentration of 0.01*M* monovalent anions, where E_{HM} and f_{HM} are the equivalent fractions of HM^{2+} of the CEC and in the solution phase respectively. The results indicate that Zn and Pb are strongly preferred by the clay and the CALHO. At first sight, the adsorption of Zn and Pb to the clay seems stronger than the adsorption onto the CALHO. This is in contrast with the conclusion that the K_V increases when the clay is loaded with Al. The apparent increased preference of Zn and Pb on the pure clay is caused by Al^{3+} adsorption in CALHO systems reducing the amount of Zn^{2+} and Pb^{2+} sorbed on the siloxane surface. The sharp decrease in the preference of Zn and Pb in CALHO systems shows that a considerable part of the exchangeable ions is accounted for as Al^{3+} ions.

Finally, we can conclude that the K_V of divalent/Na exchange is greater in CALHO than in the pure clay. We found the value of K_V for Ca/Na, Zn/Na and Pb/Na exchange on CALHO to be 2.0, 2.0 and 2.6 respectively. The K_V was slightly dependent on the exchanger composition but independent of the Al loading and pH in the pH range from 5.0 to 6.0.

Acknowledgement

The authors would like to thank Mr. J.D.J van Doesburg for his help in characterizing the CALHO samples. This work was partly funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

CHAPTER 3

Ion binding of Zn by montmorillonite Al hydroxide polymer systems

Abstract

The binding of Zn to Na montmorillonite/Al hydroxide polymer systems containing 0.30, 0.80, 1.20 and 2.00 mol Al/kg clay was investigated in a chloride background medium at pH 5.0 and 6.6 and a total salt concentration of 0.01*M* monovalent anions. Zn ions can bind to these systems by becoming part of the charge compensation of the siloxane surface and by binding to the Al hydroxide polymers (ALHO) present on the clay surface. The contribution of these processes to the total binding was estimated by using an ion exchange model. The pH had a very strong effect on the Zn binding. At pH 6.6 the presence of ALHO on the clay led to more Zn binding than in a pure clay system. This is the result of Zn ions being bound to the ALHO (Zn-ALHO). At pH 5.0, the total Zn binding was less to the CALHO than to the pure clay. There are three reasons for this: the affinity of ALHO for Zn ions decreases strongly with decreasing pH; the CEC of the siloxane surface decreases with pH, due to the increasing positive surface charge of the ALHO; and Al^{3+} adsorption to the clay surface becomes important and competes with Zn^{2+} for exchange sites. The effect of the Al:clay ratio on Zn binding was influenced by pH. At pH 6.6 Zn binding to the ALHO, expressed per mole ALHO, was independent of the Al:clay ratio. This is because the nature of the ALHO is independent of the degree of loading of the clay with ALHO at pH 6.6. The plateau of the binding curve showed that 0.12 mole Zn-ALHO per mole ALHO was bound. On the other hand, Zn binding to the ALHO at pH 5.0, expressed per mole ALHO, was dependent on the Al:clay ratio. This is because at pH 5.0 the nature of the ALHO depends on the degree of loading of the clay with ALHO. With increased loading of the clay with ALHO, the average charge per Al atom decreased and the amount of Zn binding to the ALHO per mole ALHO increased. The plateaus of the binding curves ranged between 0.01 to 0.05 mole Zn-ALHO per mole ALHO. The results of the speciation calculations showed the difference in Zn ion binding the ALHO (Zn-ALHO) and siloxane surface (Zn-CEC). The available binding sites on ALHO had a very high affinity for Zn ions. The maximum amount of Zn bound to ALHO was reached already at low Zn concentrations. The Zn binding to the clay surface increased slowly with increasing Zn concentration. Zn binding on the siloxane surface became more important when the binding sites on the ALHO were nearly all occupied. Zn bound to the ALHO could not be removed by exchange with high concentrations of cations that do not bind specifically to the ALHO surface. If CALHO is present in natural soils, Zn binding to the ALHO will strongly influence Zn availability.

This chapter is submitted for publication in *Environmental Science and Technology*. R.P.T. Janssen, M.G.M. Bruggenwert and W.H. van Riemsdijk. Ion binding of Zn by montmorillonite Al hydroxide polymer systems.

Introduction

Metal ion binding in natural systems is of great complexity. In most natural porous systems clay and Al hydroxide will be present simultaneously. It is well documented that Al hydroxide polymers (denoted as ALHO) can attach to the clay surface reducing the cation exchange capacity (CEC) and affecting the ion binding properties (Chapter 2, Shen and Rich, 1962; Carstea, 1968; Sawhney, 1968; Keren *et al.*, 1977). The binding of Zn ions to clay/ALHO systems (denoted as CALHO) is subject of this study. The system studied may also have practical relevance for treatment of metal ion containing waste streams.

When metal ions like Zn are present in a CALHO system, they can bind to two different sites i.e. the siloxane surface of the clay and the ALHO surface. Figure 1 is a schematic picture of a clay platelet with ALHO and it shows the two different binding sites for Zn. On the siloxane surface heavy metal ions e.g. Zn^{2+} ions compete with the Na^+ ions and with any Al^{3+} ions present (Chapter 2). In this chapter, Zn ions bound in this way are denoted as Zn-CEC. The selectivity coefficient for exchange between Zn and Na ions is affected by the presence of the ALHO. It is found that the selectivity for metal ion binding is increased as a result of the presence of ALHO (Chapter 2; Keren, 1979).

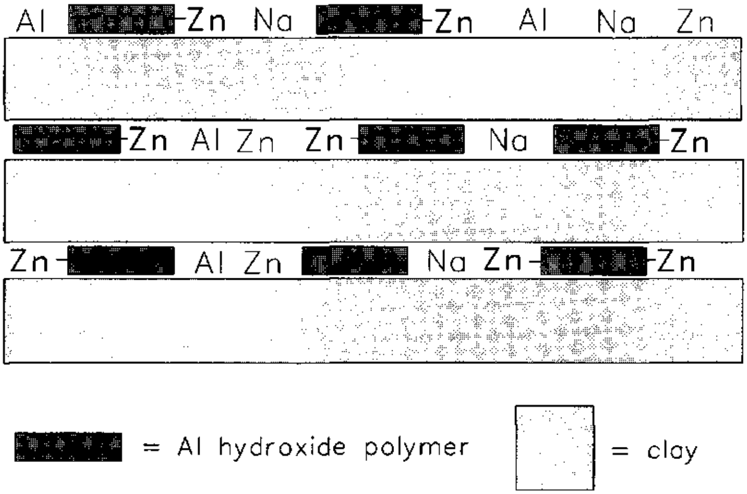

Figure 1 Schematic presentation of Zn^{2+}, Al^{3+} and Na^+ sorption on a CALHO. Al^{3+} sorption on the clay surface becomes important for pH values < 5.5.

On the ALHO, Zn ions bind with reactive surface groups. Zn ions bound in this way are denoted as Zn-ALHO. The binding of heavy metal ions on the ALHO is accompanied with a change in the charge of the ALHO (Kinniburgh *et al.*, 1975 and 1976; Micera *et al.*, 1986), decreasing the CEC of the clay. It is assumed that Na ions bind only via the exchange mechanism (Sprycha, 1989). The Zn bound to the polymers can not be removed easily by cation exchange because of the strong interaction with the reactive groups of the ALHO (Keizer and Bruggenwert, 1991).

Only a few studies dealt with metal ion binding to ALHO interlayer components, despite their wide geographic distribution and importance in many soils (Barnhisel and Bertsch, 1989). Harsh and Doner (1984) showed that Cu binding on a synthetic hydroxy-Al/montmorillonite complex was pH-dependent and that specific sites for Cu did exist. Janssen *et al.* (1991) showed that Zn in clay/Al hydroxide polymer systems, mainly adsorbed onto ALHO. According to Keizer and Bruggenwert (1991) the affinity of ALHO for heavy metal ions when the ALHO is bound to a clay surface is much greater than of free ALHO. One reason for this could be that the clay stabilizes the small ALHO particles leading to a very large reactive surface area, an explanation also suggested by Harsh and Doner (1984). Another factor is that the reactive surface of amorphous $Al(OH)_3$ has a very high pzc (9.4 according to Kinniburgh *et al.*, 1975) leading to a repulsive electrostatic interaction for metal ion binding for pH values that are relevant in natural systems. For ALHO that is bound to the negatively charged clay surface, interaction between the two electric fields will take place which may positively influence metal ion binding. The concentration of metal ions in the vicinity of the ALHO is also increased considerably compared to the concentration in the bulk solution because of ion exchange.

As shown above Zn bound on the clay surface and Zn specifically bound to the ALHO are chemically quite different. This different type of binding will express itself in a distinction in the factors governing the binding behaviour. It is to be expected that the bio-availability of the different types of Zn surface species may be quite different. For a better understanding of metal ion binding it is therefore necessary to be able to discriminate between the two different forms of ion binding. In this chapter, Zn binding is studied for clays loaded with four different amounts of ALHO at two pH values (pH 5.0 and 6.6) at a total salt concentration of $0.01M$ monovalent anions. The methodology developed in Chapter 2, is used that allows for the discrimination of the total Zn bound into Zn-ALHO and Zn-CEC.

Experimental

Preparation of the stock clay suspension

Montmorillonite clay from Clay Spur, Wyoming obtained from Ward's Natural Science Establishment, was used for all experiments. The montmorillonite was suspended in deionized water and passed through a 63 µm sieve. The suspension was saturated with Na by four washings with 1*M* NaCl. Subsequently the clay suspension was washed several times with deionized water to remove the excess salt. A 2 µm fraction was obtained by gravity sedimentation at constant temperature. The clay suspension was centrifuged at 2300 g for 20 minutes; the clear supernatant was decanted. The total electrolyte concentration in the centrifuged clay suspension was determined by measuring the Na concentration by flame emission spectrophotometry (Eppendorf Elex 6361) and was found to be 0.097*M*. The clay suspension contained 2.77 % clay. The CEC of the pure clay was measured by measuring the amount of Na desorbed from the clay by 0.0033*M* $La(NO_3)_3$ and was found to be 0.95 eq/kg clay.

Zn sorption to clay and CALHO

Various pure clay and CALHO systems were prepared as follows. A certain amount of the stock clay suspension was pipetted to 100 mL centrifuge tubes (the suspensions would finally contain 2.35 g clay/L). By adding this amount of clay each suspension contained 0.010*M* Na in solution. Deionized water was added to adjust the volume to 25 mL, which is half of the final volume. Then 0.100*M* $AlCl_3$ solution was added to the suspensions at the rate of 0.00, 0.30, 0.80, 1.20 and 2.00 mol Al/kg clay. Deionized water was added to adjust the volume to 35 mL. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.100*M* NaOH or 0.100*M* HCl was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 5.0 or 6.6 was reached. The suspensions were shaken for seven days. The pH of the suspensions were measured regularly and if necessary adjusted until a pH of 5.0 or 6.6 was reached again. Then 0.010*M* $ZnCl_2$ was added untill the suspensions finally contained 0.10, 0.30, 0.60 or 1.00 m*M* Zn. The suspensions were titrated with 0.100*M* NaOH until a pH of 5.0 or 6.6 was reached. The final volume of 50 mL was obtained by adding deionized water using a balance. The suspensions were shaken for seven days and the pH of the suspensions were measured regularly and if necessary adjusted to a pH 5.0 or 6.6. The samples were centrifuged at 2300g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solutions. The Na, Al and Zn concentrations in the supernatant solutions were determined. The total amounts of bound Zn ($Q_{Zn,t}$) were calculated based upon the measured concentrations in the supernatant and total amounts present in the system. The ionic strength of the systems varied somewhat, it increased as the loading of the clay with ALHO increased; this is because of the different amounts of $AlCl_3$ that had to be added. The ionic strength varied from 0.009 to 0.021 at pH 5.0 and 6.6.

Extraction with $La(NO_3)_3$

To the clay residue in the centrifuge tubes, 50 mL 0.0033*M* $La(NO_3)_3$ was added. The suspensions were shaken for one hour. The extraction time is long enough to achieve equilibrium since a rapid attainment of equilibrium is reached in ion exchange processes (Inskeep and Baham, 1983; Garcia-Miragaya and Page, 1976). Then the suspensions were centrifuged at 2300 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear extract solutions. The Al, Na and Zn concentrations in the extract were determined. The efficiency to exchange mono-, bi and trivalent ions by La^{3+} can easily be estimated since the selectivity coefficients for La exchange are known (Bruggenwert and Kamphorst, 1979). From simple ion exchange calculations it followed that the amount of La^{3+} (0.17 mmol/50 mL) is enough to remove essentially all Na^+ and Zn^{2+} ions attached to the clay surface in exchangeable form (total surface charge per centrifuge tube: 0.11 meq). In most cases the excess of La^{3+} over Al^{3+} in the extract is such that essentially all exchangeable Al^{3+} will be replaced by La^{3+}. However for the pH 5.0 experiments not all exchangeable Al^{3+} will be extracted and a correction is necessary (as explained in the section results and discussion). The unbuffered salt solution $La(NO_3)_3$ is not capable to remove the ALHO that is strongly bound to the clay surface (Chapter 2).

X-ray diffraction patterns

X-ray diffraction of the aged CALHO systems indicated that the ALHO was present as an interlayer between the clay platelets (Chapter 2).

Analysis

Na, Al and Zn were analysed by ICP-AES (Spectro Analytical Instruments) in the supernatant and La extract.

Chemical speciation calculations

Chemical speciation in the equilibrium solution was calculated using the program ECOSAT (Keizer and Van Riemsdijk, 1994). The adapted Davies equation was used to calculate the activity coefficients. The ECOSAT program used: the equilibrium constants for hydrolysis products of Na, Al and Zn (Lindsay, 1979); Na, Al and Zn chloride complexes (Lindsay, 1979); the solubility product of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965).

Results and Discussion

The total Zn binding ($Q_{Zn,t}$) per unit amount of clay at different loadings with Al hydroxide polymers (denoted as ALHO) measured at pH 6.6 and a total salt concentration of 0.01*M* monovalent anions, as a function of the Zn concentration in the equilibrium solution is given in Figure 2. The total Zn binding per unit clay increased the greater the coverage of the clay with ALHO over the whole concentration range studied. This leads immediately to the conclusion that binding of Zn to the polymers is an important process that more than compensates for the decrease of the cation exchange capacity (CEC) due to the presence of polymers. The decrease of the CEC as a function of the loading with ALHO is given in Chapter 2, and amounts to 0.25 mole charge units per mole Al at pH 6.6. The CEC at the highest Al loading studied is reduced with 55%. An interesting aspect is that the effect of the ALHO on the Zn binding is especially large for very low Zn concentrations in solution (Figure 2).

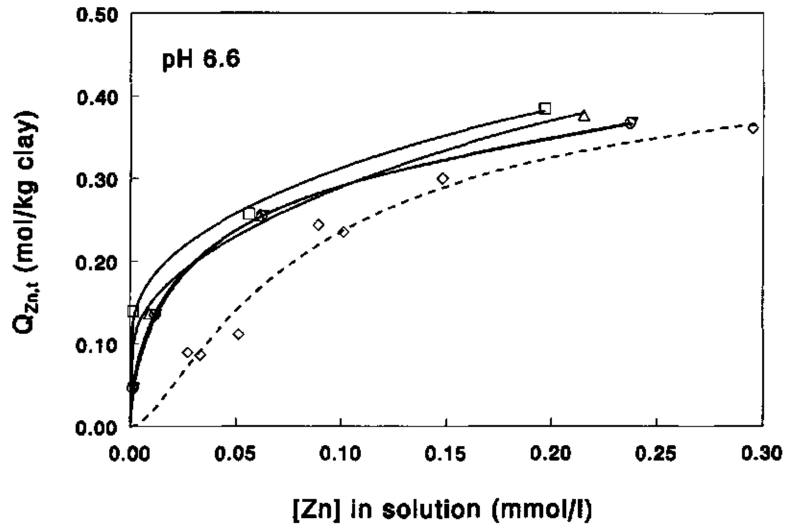

Figure 2 Total Zn binding ($Q_{Zn,t}$) by CALHO and the pure clay vs. [Zn] in the equilibrium solution at pH 6.6. The loadings of the clay with Al in mol/kg clay are: ◇ = pure clay (dotted line); ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00. The lines are smooth curves drawn through the data points.

Figure 3 gives the measured total Zn binding ($Q_{Zn,t}$) for the pure clay and four loadings of the clay with ALHO at pH 5.0 and a total salt concentration of 0.01*M* monovalent anions as a function of the Zn concentration in the equilibrium solution. Comparison of the Zn binding isotherm for the pure clay

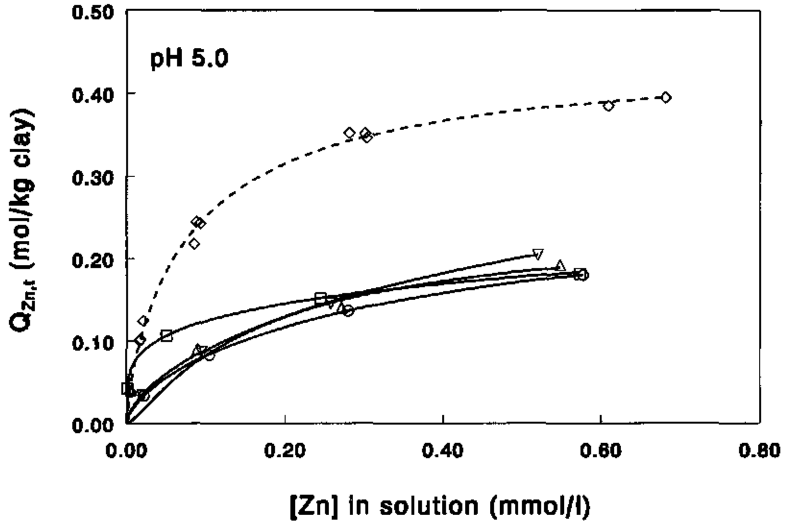

Figure 3 Total Zn binding ($Q_{Zn,t}$) by CALHO and the pure clay vs. [Zn] in the equilibrium solution at pH 5.0. The loadings of the clay with Al in mol/kg clay are: ◇ = pure clay (dotted line); ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00. The lines are smooth curves drawn through the data points.

at pH 6.6 (Figure 2) with the same at pH 5.0 (Figure 3) shows that there is a small effect of pH on the Zn binding in the absence of ALHO. The somewhat enhanced binding at pH 6.6 may be caused by some Zn binding to the edge faces of the clay platelets. The striking difference between pH 5.0 (Figure 3) and pH 6.6 (Figure 2) for the clay/ALHO systems (denoted as CALHO) is that Zn binding at pH 6.6 is enhanced by the presence of ALHO whereas it is reduced at pH 5.0. Zn binding to ALHO is nevertheless also of significance at pH 5.0. In the absence of Zn binding to the ALHO a decrease in extent of binding is expected with increasing amount of ALHO because of the decrease of the CEC. By chance, all CALHO systems examined bound about the same amount of total Zn, independent of the coverage of the clay with ALHO.

Several phenomena affect the Zn binding at pH 5.0 in the presence of ALHO. The reduction in the Zn binding at pH 5.0 compared to Zn binding at pH 6.6 is caused by three combined effects. The positive charge of the ALHO polymers at pH 5.0 is larger than at pH 6.6 leading to a larger reduction of the CEC at the same loading with ALHO (Chapter 2). The local proton concentration near the surface of the ALHO is higher at pH 5.0, leading to a stronger competition between protons and Zn ions for binding sites at the ALHO. This leads to a reduction of the Zn binding to the CALHO with a lowering of the pH. Another very important factor is that Al^{3+} ions are present at negligible quantities as exchangeable ions at pH 6.6, whereas they can form a significant fraction of the exchangeable ions present at the clay surface at pH 5.0 (Chapter 2). Al^{3+} therefore competes with Zn^{2+} and Na^+ ions for exchange sites, leading also to reduction in Zn binding at pH 5.0 compared to pH 6.6.

The total Zn binding is the amount of Zn that compensates for part of the remaining CEC plus the amount that is bound to the ALHO. Since the two processes are chemically different it is important to be able to discriminate the total observed binding into the two different parts. It is therefore necessary to be able to "speciate" the Zn in the system among Zn in solution, Zn that forms part of the exchangeable ions on the clay surface (Zn-CEC) and Zn that is specifically bound to the ALHO (Zn-ALHO). A procedure has been developed in Chapter 2, that allows for the speciation of Zn in these systems. Here we will describe the main features of this methodology. The reader is referred to this chapter for further details. The essence of the method is that the amount of Zn-CEC that is present is calculated on the basis of an ion exchange equation. The only exchangeable ions present in significant amounts for the CALHO system at pH 6.6 were Zn^{2+} and Na^+ ions. The following exchange equation is used at pH 6.6:

$$\frac{M_{Zn}}{M_{Na}^{2}} = K_{V(Zn/Na)} \times \frac{(Zn^{2+})}{(Na^{+})^{2}} \qquad (1)$$

where $K_{V(Zn/Na)}$ is the Vanselow selectivity coefficient (Vanselow, 1932) for exchange of Na ions for Zn ions, M_{Na} and M_{Zn} indicate the molar fractions of the cations Na^+ and Zn^{2+} bound to the exchange sites with respect to the total amount of exchangeable cations (Q_t in mol/kg clay) and the brackets indicate the activity of the ions in solution. The activities of Zn^{2+} and Na^+ followed from measurement of the concentrations in solution. The average value of the Vanselow selectivity coefficient for Zn/Na exchange on CALHO was determined to be 2.0 (Chapter 2). They found that the selectivity coefficient was independent of the ALHO loading and nearly independent of the exchanger composition for the experimental conditions. The molar fractions M_{Na} and M_{Zn} could be derived from the ion exchange equation using $K_{V(Zn/Na)}$, (Na^+) and (Zn^{2+}) as input and realizing that M_{Na} + M_{Zn} equals one. The amount of exchangeable Na^+ ions present on the clay (expressed in mol/kg clay) was derived from the measured concentrations in the La extract. The Q_t and the Zn-CEC can now be calculated (Q_t and Zn-CEC are both expressed in mol/kg clay). Note that the actual value of Q_t depends on the exchanger composition, on how much ALHO is bound to the clay and also on how much Zn is bound to the ALHO via formation of surface complexes. The Zn-ALHO (in mol/kg clay) was found by subtracting the Zn-CEC from the total Zn binding measured ($Q_{Zn,t}$ in mol/kg clay).

The procedure that is followed to interpret the experiments at pH 5.0 is essentially the same. However, it is slightly more complicated since also Al^{3+} ions are of relevance as exchangeable ions at this pH and form part of the total amount of exchangeable ions. Ion exchange at pH 5.0 is a ternary process and effectively a binary process at pH 6.6. For the ternary exchange reaction the ion exchange equation (1) can be rewritten as:

$$\frac{1-M_{Al}-M_{Na}}{M_{Na}^{2}}=K_{V(Zn/Na)}\times\frac{(Zn^{2+})}{(Na^{+})^{2}} \qquad (2)$$

The ternary ion exchange equation (2) can not be solved directly to obtain the values of the molar fractions. Both M_{Al} and M_{Na} are unknown since Q_t changes with the exchanger composition. The mole fraction of an exchangeable ion can be expressed as:

$$M_i=\frac{q_i}{\Sigma q_i}=\frac{q_i}{Q_t} \qquad (3)$$

where q_i is the amount adsorbed in exchangeable form of ion i expressed in mol/kg clay. Combining equations (2) and (3) results in:

$$\frac{1-\frac{q_{Al}}{Q_t}-\frac{q_{Na}}{Q_t}}{\frac{q_{Na}^{2}}{Q_t^{2}}}=K_{V(Zn/Na)}\times\frac{(Zn^{2+})}{(Na^{+})^{2}} \qquad (4)$$

The amount of Zn ions adsorbed in exchangeable form equals:

$$q_{Zn}(=Zn-CEC)=Q_t-q_{Al}-q_{Na} \qquad (5)$$

q_{Zn} is in this chapter denoted as Zn-CEC. The activities of Zn^{2+} and Na^{+} were derived from the measurement of the concentrations in solution. The values of

q_{Al} and q_{Na} were derived from the La extraction procedure. In the La extract at pH 5.0, Al ions as well as Na ions were detected. This showed that both Na^+ and Al^{3+} were present in exchangeable form. The La extraction for the experiments at pH 5.0 showed that in the presence of ALHO, Al^{3+} always occupied an important fraction of the exchange sites. The treatment with La^{3+} does not lead to a release of Al if present as ALHO (Chapter 2). The CEC remained high for the system with the lowest amount of Al added, because the majority of the Al added was for these conditions present as exchangeable Al^{3+}. For higher Al loadings only a relatively small fraction of the total Al was present in exchangeable form. The amount of Al extracted with La underestimated the amount of exchangeable Al^{3+} (Chapter 2). The amount of exchangeable Al^{3+} could be derived by considering the exchange reaction between La^{3+} and Al^{3+} and using a selectivity coefficient of one for this exchange reaction (Bruggenwert and Kamphorst, 1979). The corrected value was never more than 30% higher than the amount that was directly measured via the extraction procedure. The value of Q_t (in mol/kg clay) could be derived from equation (4) if K_V is known, since q_{Al}, q_{Na} (both expressed in mol/kg clay), (Na^+) and (Zn^{2+}) were experimentally accessible. The value of Zn-CEC (in mol/kg clay) then followed from equation (5). Finally Zn-ALHO (in mol/kg clay) was found by subtracting the Zn-CEC from the total Zn binding measured ($Q_{Zn,t}$ in mol/kg clay). The CEC of the clay in eq/kg clay followed from:

$$CEC=\Sigma z_i * q_i \qquad (6)$$

The results of the calculated speciation of Zn for the CALHO systems at pH 6.6 are given in the Figures 4a to 4d. They show that four different binding curves for the binding of Zn to ALHO are obtained. The Zn binding to the ALHO increased with increasing loading of the clay with ALHO. This increase of Zn-ALHO with increasing loading with ALHO was expected, since the ALHO surface area available will increase with increasing amounts of ALHO being present. The possibilities for binding to the exchange sites on the other hand decrease because the CEC is reduced with increasing loading with ALHO. For the lowest loading of the clay with ALHO small negative values for Zn-ALHO were calculated. Apparently the amount of Zn-CEC calculated is for these conditions slightly overestimated. The results show clearly that the preference of Zn for the ALHO is especially great for very low Zn concentrations where the binding curves for Zn-ALHO are very steep. The maximum amount of Zn-ALHO is reached already for low Zn concentrations. The Zn-CEC increases slowly with increasing Zn concentration. The available binding sites on the ALHO have apparently a high affinity for Zn ions. Zn binding on the siloxane surface becomes relatively more important when the

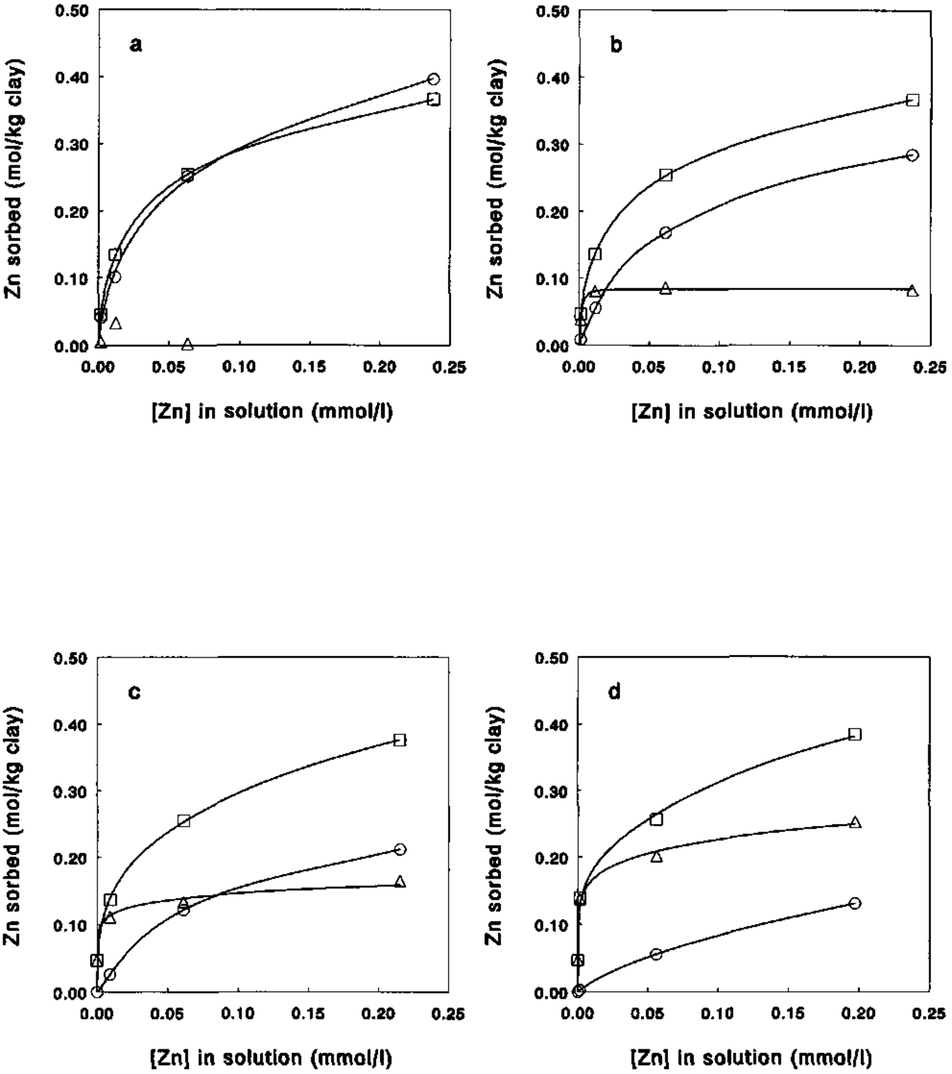

Figure 4 The calculated speciation of the total Zn binding ($Q_{Zn,t}$) (□) of CALHO between Zn-CEC (○) and Zn-ALHO (△) for four Al:clay ratios at **pH 6.6**. The loadings of the clay in mol Al/kg clay are: *a.* 0.30 *b.* 0.80 *c.* 1.20 *d.* 2.00. The lines drawn are smooth curves through the data points.

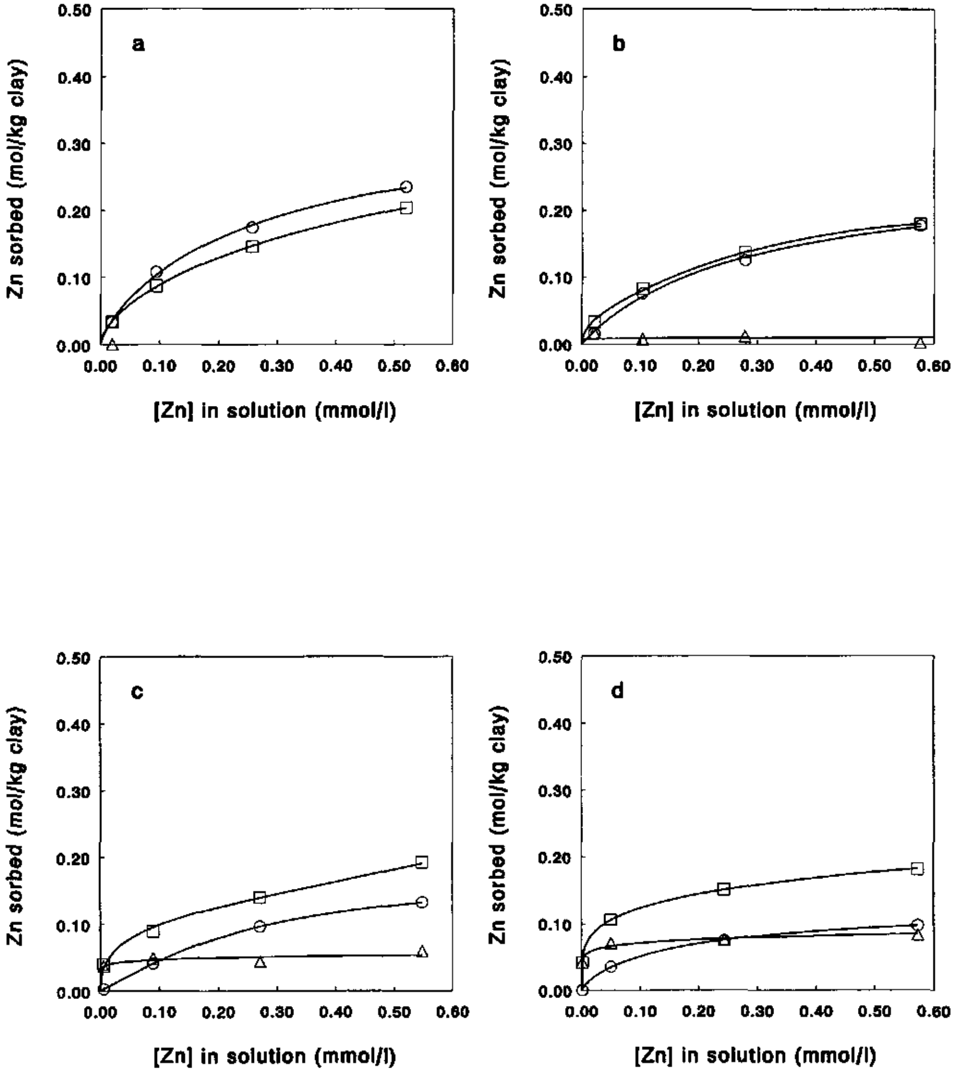

Figure 5 The calculated speciation of the total Zn binding ($Q_{Zn,t}$) (□) of CALHO between Zn-CEC (○) and Zn-ALHO (△) for four Al:clay ratios at **pH 5.0**. The loadings of the clay in mol Al/kg clay are: *a.* 0.30 *b.* 0.80 *c.* 1.20 *d.* 2.00. The lines drawn are smooth curves through the data points.

Zn binding to the ALHO reaches a plateau.

The results of the Zn speciation at pH 5.0 for four loadings of the clay with ALHO are presented in the Figure 5a to 5d. The calculated binding to the exchange sites at the lowest loading with ALHO (Figure 5a) is slightly higher than the total Zn binding, indicating again a slight overestimation of the calculated Zn-CEC. For the system with the second lowest loading of the clay with ALHO (Figure 5b) hardly any Zn is bound to the ALHO; almost all the bound Zn is present at the exchange sites. In this system very little ALHO is formed. In the two systems with a higher loading of ALHO, ALHO formation is more pronounced and Zn binding to the ALHO becomes significant. Zn binding to the ALHO increases with increasing loading of the clay with ALHO, as is to be expected. The same trend can be seen for pH 6.6, but Zn binding on the ALHO at pH 5.0 never reaches the level of Zn-ALHO at pH 6.6. The steep rise of the Zn binding curve to ALHO suggests that the affinity of the ALHO surface sites for Zn is also high at pH 5.0.

After we have been able to discriminate the total observed Zn binding into the two different parts (Zn-ALHO and Zn-CEC) the question arises how strong

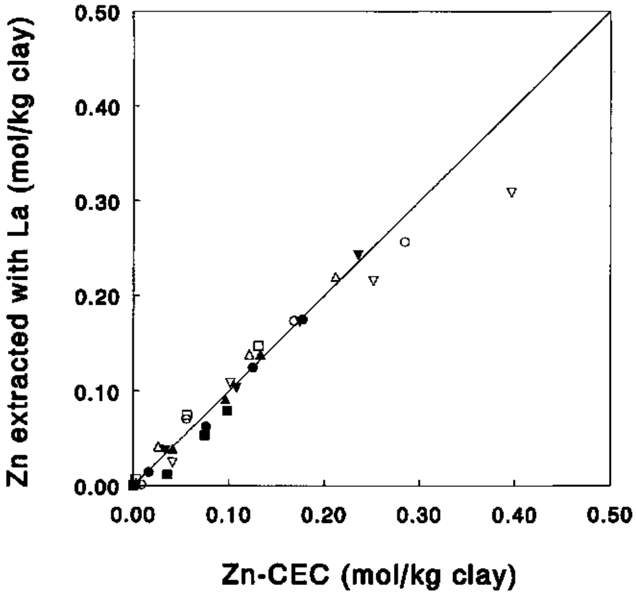

Figure 6 The amount of Zn extracted from CALHO systems with La$(NO_3)_3$ vs. the calculated amount of Zn sorbed on the clay surface (Zn-CEC) at pH 5.0 and 6.6. The loadings in mol Al/kg clay are: ▽/▼ = 0.30 ; ○/● = 0.80 ; △/▲ = 1.20; □/■ = 2.00. Closed symbols indicate the experiments at pH 5.0, open symbols the experiments at pH 6.6.

both types of bound Zn are attached to the CALHO. The calculated Zn-CEC values as found in the speciation procedure at pH 5.0 and 6.6 are plotted against the amount of Zn ions extracted with an excess of La^{3+} (Figure 6). It was expected that all Zn-CEC would be exchanged by the high amount of La^{3+} since the amount of La^{3+} added was enough to extract all bound Zn^{2+} from the siloxane surface (for more details see experimental section: extraction with $La(NO_3)_3$). However, the extent to which Zn bound to ALHO would be released is difficult to predict. Figure 6 indicates that the La procedure does not extract any Zn that is bound to the ALHO but only the amount of Zn bound to the siloxane surface. For three data points in the figure the amount of Zn extracted with La is smaller than the amount of Zn-CEC. This is most likely due to the fact that the speciation procedure leads to a small overestimation of Zn-CEC at low amounts of ALHO fixed (see also Figures 5a and 6a). However for the other data points it clearly shows that Zn bound to the ALHO cannot be removed by exchange with high concentrations of cations that do not have a high affinity for binding to the ALHO. Zn binding to the ALHO can strongly influence Zn availability when CALHO is present in natural soils. Despite the earlier assumption that the La extraction procedure cannot be used directly to determine the Zn-CEC since part of the Zn may be released from the Zn-ALHO, Figure 6 shows that La only extracts exchangeable Zn. It can be concluded that the La extraction procedure is in this case another tool (besides the ion exchange equation) to "speciate" the bound Zn in CALHO systems without knowing the actual selectivity coefficient.

Figure 7 shows the amount of Zn extracted with La^{3+} plotted against the total amount of Zn bound ($Q_{Zn,t}$). The fraction of Zn extracted with La decreased with increasing Al:clay ratio. This shows again that the amount of Zn bound to the ALHO increases with increasing Al:clay ratio.

The question arises if there is a relationship between the amount of Zn-ALHO and the amount of ALHO. Therefore we expressed the Zn-ALHO values as found in the speciation procedure per unit amount of ALHO and plotted as a function of the fraction of the Q_t that is compensated for by Zn (M_{Zn}) for all loadings of the clay with ALHO at pH 6.6 and 5.0 (Figure 8). One binding curve is obtained for the results at pH 6.6. This indicates that the Zn bound to the ALHO is independent of the amount of ALHO fixed when expressed per mole ALHO. This can be explained due to the fact that the nature of the ALHO is independent of the degree of loading of the clay with ALHO at pH 6.6 (Chapter 2). It was calculated that the average ALHO could be described by $Al(OH)_{2.75}{}^{0.25+}$ for the range of Al loadings studied at pH 6.6. Specific bound Zn ions on reactive sites on the surface of the ALHO has to overcome a repulsive positive electric field emanating from the ALHO particles which is for all Al loadings the same. Changing the amount of ALHO does not change the repulsive

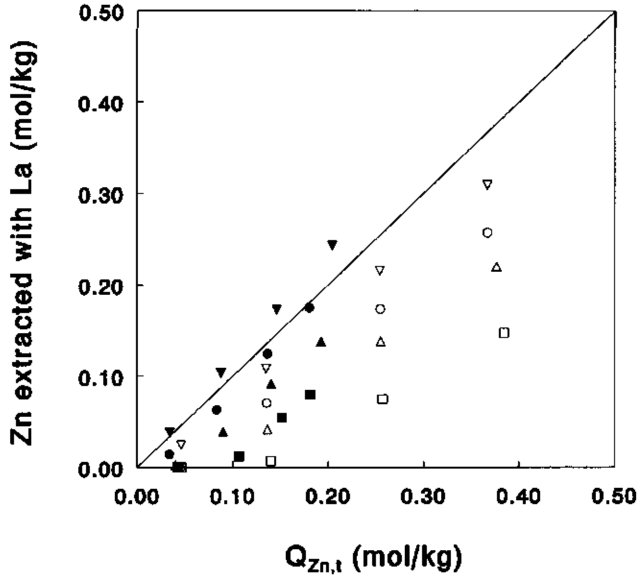

Figure 7 The amount of Zn extracted from CALHO systems with $La(NO_3)_3$ vs. the total Zn sorption ($Q_{Zn,t}$). The symbols refer to four loadings of the clay with Al. The loadings in mol Al/kg clay are: ▽/▼ = 0.30 ; ○/● = 0.80 ; △/▲ = 1.20 ; □/■ = 2.00. Closed symbols indicate the experiments at pH 5.0, open symbols the experiments at pH 6.6.

electric field emanating from the ALHO particles and thus the amount of Zn bound to the ALHO when expressed per unit amount of ALHO is the same. The plateau of the curve shows a maximum binding of 0.12 mole Zn-ALHO per mole ALHO. For the lowest loading of the clay with ALHO some small negative values were calculated for Zn-ALHO (Figure 4a) and only two points are indicated.

For pH 5.0 several binding curves are obtained (Figure 8). Zn bound to the ALHO is still dependent on the amount of ALHO fixed even when expressed per mole ALHO. The plateaus of the curves show that 0.01 to 0.05 mole Zn-ALHO per mole ALHO is bound which is considerably lower than the amount of 0.12 observed at pH 6.6. No curve was obtained for the lowest loading of the clay with ALHO since no Zn-ALHO was calculated (see Figure 5a). That several binding curves are obtained can be explained due to the fact that the nature of the ALHO is dependent on the degree of loading of the clay with ALHO at pH 5.0 (Chapter 2). It was shown that the average charge per Al ion increases with decreasing Al loading. The plateaus of the curves in Figure

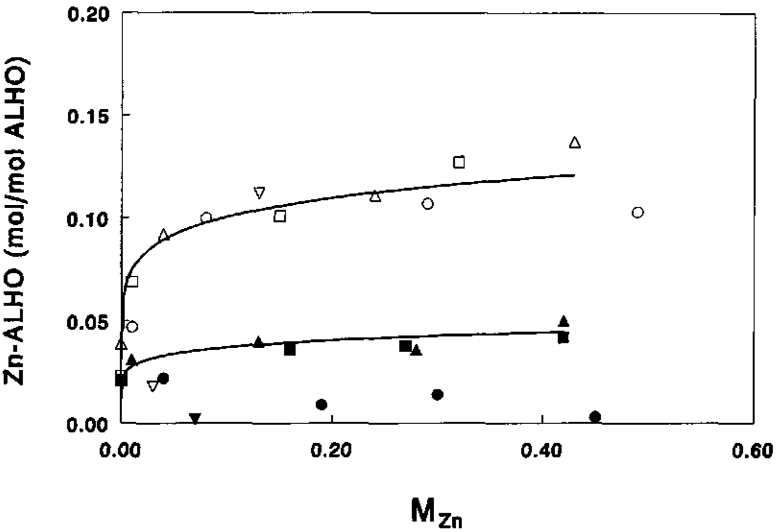

Figure 8 Zn binding by ALHO (Zn-ALHO) per mole ALHO at pH 5.0 and 6.6. The lines drawn are smooth curves through the data points. The loadings in mol Al/kg clay are: ▽/▼ = 0.30 ; ○/● = 0.80 ; △/▲ = 1.20 ; □/■ = 2.00. Closed symbols indicate the experiments at pH 5.0, open symbols the experiments at pH 6.6.

8 decrease with decreasing Al loading since the average charge per Al ion increases. Changing the amount of ALHO changes the repulsive electric field emanating from the ALHO particles and thus the amount of Zn bound to the ALHO when expressed per unit amount of ALHO changes. The plateaus of the curves are always lower than the curve for pH 6.6 since the average charge of the ALHO at pH 5.0 is always higher than the constant average charge at pH 6.6 (Chapter 2). Figure 8 shows like the Figures 4 and 5 that the preference of Zn for the ALHO is very great for both pH values and that the maximum amount of Zn-ALHO is already reached for very low M_{Zn}.

Acknowledgement

This work was partly funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

CHAPTER 4

Ion binding of Pb by montmorillonite Al hydroxide polymer systems

Abstract

The binding of Pb to Na montmorillonite/Al hydroxide polymer systems containing 0.30, 0.80, 1.20 and 2.00 mol Al/kg clay was investigated in a chloride/nitrate background medium at pH 5.0, 6.0 and 6.6 and a total salt concentration of 0.01*M* monovalent anions. Three adsorption processes can be distinguished in such systems. Pb ions can bind via an ion exchange mechanism to the siloxane surface and by binding to surface sites of Al hydroxide polymers (ALHO) present on the clay surface. Moreover, at increasing Pb concentrations and pH, Pb hydroxide polymers can be formed which bind irreversible to the clay surface, reducing the CEC in a manner similar to the binding of the ALHO polymers. At pH 6.6 the presence of ALHO on clay led to more Pb binding than in a pure clay system. The greater adsorption of the clay/ALHO (CALHO) system was the result of Pb binding to ALHO and formation of Pb hydroxide polymers. It is shown that in CALHO systems at pH 6.0 no Pb hydroxide polymers were formed. Total Pb binding to CALHO was less than that binding to the pure clay. Using a speciation model, the contribution of Pb over the different phases was calculated. The results of the calculated speciation showed that the minority of adsorbed Pb was bound to the siloxane surface. The remaining part was adsorbed to ALHO. This amount adsorbed increased with increasing amount of ALHO fixed, when expressed per mole Al. The plateaus of the binding curves ranged between 0.05 to 0.35 mole Pb bound to the ALHO per mole ALHO. ALHO showed a very high affinity for Pb ions, whereas Pb binding to the siloxane surface increased slowly with increasing Pb concentration. Pb bound to ALHO could be desorbed by adding high concentrations of cations. When the same system was investigated at pH 5.0 a strong reduction of the Pb binding occured because Al^{3+} ions competed with Pb^{2+} for exchangeable sites, and because hardly any binding to ALHO took place under these conditions.

Introduction

Metal ions can bind to hydroxy-interlayered phyllosilicates by becoming part of the charge compensation of the siloxane surface and by binding to the Al hydroxide polymers (denoted as ALHO) present on the clay surface. The ALHO bound to a clay has two effects on metal ion binding, it reduces the metal binding in the double layer because the CEC decreases and it creates new binding sites on the surface of the ALHO. On the siloxane surface metal ions compete with other electrolyte ions like Na^+ ions and Al^{3+} ions (Chapter 2). It is assumed that Na ions bind only via the exchange mechanism (Sprycha, 1989).

In Chapter 3 the Zn binding to clay/ALHO systems (denoted as CALHO) was studied. Zn bound to the clay surface and Zn bound to the ALHO were discriminated for, by using the speciation method for bound Zn ions to CALHO systems as described in Chapter 2. The preference of Zn for the ALHO is especially great for very low Zn concentrations where the binding curve for Zn-ALHO is very steep. They concluded that the available binding sites on the ALHO are highly favourable for Zn and that Zn bound in this way could not be removed by a high concentration of cations. Zn binding to the siloxane surface becomes important when the binding sites on the ALHO are nearly all occupied. Zn binding behaviour on ALHO is influenced by pH and amount of ALHO. Due to the pH dependecy of the binding to the ALHO less Zn is bound to the ALHO at lower pH and less Zn is bound via ion exchange due to competition with Al^{3+}.

Only few other studies have been done on the binding properties of such a system for heavy metals. Harsh and Doner (1984) showed that Cu binding to a synthetic hydroxy-Al/montmorillonite complex was pH-dependent and that specific sites for Cu did exist. According to Keizer and Bruggenwert (1991) the metal binding affinity of ALHO bound to a clay surface is much greater than the same for pure ALHO. Harsh and Doner (1984) suggest a mechanism for this observation, whereby the ALHO in the interlayer have much greater available surface area than gibbsite or alumina. Another mechanism can be explained by the repulsive positive electric field emanating from the ALHO particles adsorbed on clay which the specifically bound heavy metal ions have to overcome. This positive electric field is markedly reduced once the ALHO is located on a negative charged clay surface. According to Keizer and Bruggenwert (1991), ALHO has less affinity for Pb than for Zn. Pb binding to the ALHO is also more pH dependent than Zn binding.

The presence of the ALHO may lead, depending on the conditions, to a strong increase or a decrease in the capacity for metal ion binding compared to the pure clay (Chapter 3). In order to get a better insight in metal ion behaviour in natural systems it is of interest to have a better understanding of these systems. Increased understanding may also lead to the development of water treatment technologies for removal of heavy metals from certain waste streams based upon the use of CALHO systems.

As shown in Chapter 3, Zn bound to the clay surface and Zn specifically bound to the ALHO are chemically quite different. It is expected that the distribution of metal ions over clay surface and ALHO strongly influences the bio-availability. For a better understanding of metal ion binding it is therefore necessary to be able to discriminate between the two different forms of ion binding. Since heavy metal ions have ion specific adsorption characteristics (Keizer and Bruggenwert, 1991), in the present study Pb is studied. In soils a wide range of Al:clay ratios occur. Questions arises concerning the effect of this ratio on the Pb behaviour. So Pb binding is studied to clays loaded with four amounts of ALHO at three pH values (pH 5.0, 6.0 and 6.6) at a total salt concentration of $0.01M$ monovalent anions. The methodology developed in Chapter 2 is used that allows for the discrimination of Pb bound onto the ALHO (Pb-ALHO) and the clay surface (Pb-CEC). Another possibility for Pb binding to the clay is the formation of Pb hydroxide polymers on the clay surface.

Experimental

Preparation of the stock clay suspension

Montmorillonite clay from Clay Spur, Wyoming obtained from Ward's Natural Science Establishment, was used for all experiments. The montmorillonite was suspended in deionized water and passed through a 63 μm sieve. The suspension was saturated with Na by four washings with $1M$ NaCl. Subsequently the clay suspension was washed several times with deionized water to remove the excess salt. A 2 μm fraction was obtained by gravity sedimentation at constant temperature. The clay suspension was centrifuged at 2300 g for 20 minutes; the clear supernatant was decanted. The total electrolyte concentration in the centrifuged clay suspension was determined by measuring the Na concentration by flame emission spectrophotometry (Eppendorf Elex 6361) and was found to be $0.097M$. The clay suspension contained 2.77 % clay. The CEC of the pure clay was measured by measuring the amount of Na desorbed from the clay by $0.0033M$ $La(NO_3)_3$ and was found to be 0.95 eq/kg clay.

Pb sorption to clay and CALHO

Various pure clay and CALHO systems were prepared as follows. A certain amount of the stock clay suspension was pipetted to 100 mL centrifuge tubes (the suspensions would finally contain 2.35, 1.00 and 0.50 g clay/L for the experiments at pH 5.0, pH 6.0 and pH 6.6 respectively). Deionized water was added to adjust the volume to 25 mL, which is half of the final volume. Then

0.100M $AlCl_3$ solution was added to the suspensions at the rate of 0.00, 0.30, 0.80, 1.20 and 2.00 mol Al/kg clay for the experiments at pH 5.0 and 6.6, and 0.00, 0.25, 0.67, 1.00 and 1.67 mol Al/kg clay for the experiments at pH 6.0. Subsequently 0.100M $NaNO_3$ was added until each suspension contained 0.010M Na in solution. Deionized water was added to adjust the volume to 35 mL. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.100M NaOH or 0.100M HCl was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 5.0, 6.0 or 6.6 was reached. The suspensions were shaken for seven days. The pH of the suspensions were measured regularly and if necessary adjusted until a pH of 5.0, 6.0 or 6.6 was reached again. Then 0.010M $Pb(NO_3)_2$ was added untill the suspensions finally contained 0.00, 0.10, 0.30, 0.60 or 1.00 mM Pb at pH 5.0 and 6.6 and 0.00, 0.05, 0.10, 0.15 or 0.20 mM Pb at pH 6.0. The suspensions were titrated with 0.100M NaOH until a pH of 5.0, 6.0 or 6.6 was reached. The final volume of 50 mL was obtained by adding deionized water using a balance. The suspensions were again shaken for seven days and the pH of the suspensions were measured regularly and if necessary adjusted to a pH 5.0, 6.0 or 6.6. The samples were centrifuged at 2300g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solutions. The Na, Al and Pb concentrations in the supernatant solutions were determined. The total amounts of bound Pb ($Q_{Pb,t}$) were calculated based upon the measured concentrations in the supernatant and total amounts present in the system. The ionic strength of the systems varied somewhat, it increased as the loading of the clay with ALHO increased; this is because of the different amounts of $AlCl_3$ that had to be added. The ionic strength varied from 0.009 to 0.024 at pH 5.0, from 0.011 to 0.016 at pH 6.0 and from 0.009 to 0.015 at pH 6.6.

Extraction with $La(NO_3)_3$

To the clay residues in the centrifuge tubes 50, 25 or 40 mL 0.0033M $La(NO_3)_3$ was added for the experiments at pH 5.0, 6.0 and 6.6 respectively. The suspensions were shaken for one hour. The extraction time is long enough to achieve equilibrium since a rapid attainment of equilibrium is reached in ion exchange processes (Inskeep and Baham, 1983; Garcia-Miragaya and Page, 1976). Then the suspensions were centrifuged at 2300 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear extract solutions. The Al, Na and Pb concentrations in the extract were determined. The efficiency to exchange mono-, bi and trivalent ions by La^{3+} can easily be estimated since the selectivity coefficients for La exchange are known (Bruggenwert and Kamphorst, 1979). From simple ion exchange calculations it followed that the amount of La^{3+} (0.17 mmol/50 mL, 0.085 mmol/25mL or 0.14 mmol/40mL) is enough to remove essentially all Na^+ and Pb^{2+} ions attached to the clay surface in exchangeable form (total surface charge per centrifuge tube: 0.11, 0.048 or 0.024 meq respectively). In most cases the excess of La^{3+} over Al^{3+} in the extract is such that essentially all exchangeable Al^{3+} will be replaced by La^{3+}. However for the pH 5.0 experiments not all exchangeable Al^{3+} will be extracted and a correction is necessary (as explained in the section results and discussion). The unbuffered salt solution $La(NO_3)_3$ is not capable to remove the ALHO that is strongly bound to the clay surface (Chapter 2).

Analysis

Na, Al and Pb were analysed by ICP-AES (Spectro Analytical Instruments) in the supernatant and La extract.

X-ray diffraction patterns

X-ray diffraction of the aged CALHO systems indicated that the ALHO was present as an interlayer between the clay platelets (Chapter 2).

Chemical speciation calculations

Chemical speciation in the equilibrium solution was calculated using the program ECOSAT (Keizer and Van Riemsdijk, 1994). The adapted Davies equation was used to calculate the activity coefficients. The ECOSAT program used: the equilibrium constants for hydrolysis products of Na, Al and Pb (Lindsay, 1979); Na, Al, Pb chloride and nitrate complexes (Lindsay, 1979); the solubility product of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965).

Results and discussion

The results will be discussed starting with the experiments at the highest pH. First Pb binding at pH 6.6 in the absence of Al hydroxide polymers will be discussed, followed by experiments that include Al hydroxide polymers. Finally the experiments at pH 6.0 and 5.0 are discussed.

Pb binding to clay at pH 6.6

When no Al hydroxide polymers are present one may expect that only a simple ion exchange process is involved. However a large part of the bound Pb was not exchangeable with La and this irreversible fraction increased with increasing loading of the clay with Pb. The sum of the Na and Pb in the La extract was smaller than the cation exchange capacity (CEC) of the clay. This observation may be explained by assuming that positively charged polymeric Pb species were irreversibly bound to the clay in a manner similar to the formation of the CALHO system. The calculated ion activity product (IAP) for $Pb(OH)_2(s)$ ranged from -log IAP= 20.0 for the lowest Pb activity (7.06 μM) to 18.6 for the highest Pb activity (0.159 mM). In literature values for the solubilty product of $Pb(OH)_2$ range from -log IAP= 16.09 to 19.96 (Sillén and Martell, 1964). The measured IAP's were within the range as determined for pure $Pb(OH)_2$. The Pb concentrations added were much higher than the equilibrium concentrations and formation of Pb hydroxide polymers in this system are therefore very likely. Since the experiments were not done under nitrogen atmosphere also formation of Pb carbonate is in principle possible. However, formation of such Pb carbonate particles is not expected to result in a reduction of the CEC of the clay. Under the conditions, bound Pb can be part of the CEC (Pb-CEC) or it may be bound as positively charged Pb polymers to the clay (Pb fixed). One way to discriminate between these forms is the use of the La extraction procedure as discussed above. A disadvantage of this procedure is that the La may extract also small polymeric Pb species. Another procedure to determine the Pb-CEC and the Pb fixed is to use an ion exchange model. Ion exchange between Pb and Na on montmorillonite can be described by the following ion exchange equation:

$$\frac{M_{Pb}}{M_{Na}^{\,2}} = K_{V(Pb/Na)} \times \frac{(Pb^{2+})}{(Na^{+})^2} \qquad (1)$$

where $K_{V(Pb/Na)}$ is the Vanselow selectivity coefficient (Vanselow, 1932) for exchange of Pb ions for Na ions, M_{Pb} and M_{Na} indicate the molar fractions of the cations Pb^{2+} and Na^+ respectively bound to the exchange sites with respect to the total amount of cations bound (Q_t in mol/kg clay) and the brackets indicate the activity of the ions in solution. The activities of Pb^{2+} and Na^+ followed from measurement of the concentrations in solution. The average value of the Vanselow selectivity coefficient for Pb/Na exchange on pure clay was determined to be 1.6 (Chapter 2). It was found that the selectivity coefficient was nearly independent of the pH and the exchanger composition for the experimental conditions. The molar fractions M_{Pb} and M_{Na} could be derived from the ion exchange equation using $K_{V(Pb/Na)}$, (Na^+) and (Pb^{2+}) as input and realizing that $M_{Pb} + M_{Na}$ equals one. The amount of exchangeable Na^+ ions present on the clay was derived from the measured concentrations in the La extract. The Pb-CEC (expressed in mol/kg clay) and the total CEC (expressed in eq/kg clay) present can now be calculated. Pb fixed was found by subtracting the Pb-CEC and the amount Pb in the equilibrium solution from the total Pb binding measured. That the La indeed extracted small polymeric Pb species was shown by the comparison of the calculated Pb-CEC and the Pb extracted with La. La extracted always more Pb than the amount of Pb-CEC calculated, but less than the total amount of Pb adsorbed.

The thus determined CEC is shown as a function of the amount of Pb in the system that is present as Pb fixed to the clay (Figure 1). The figure shows

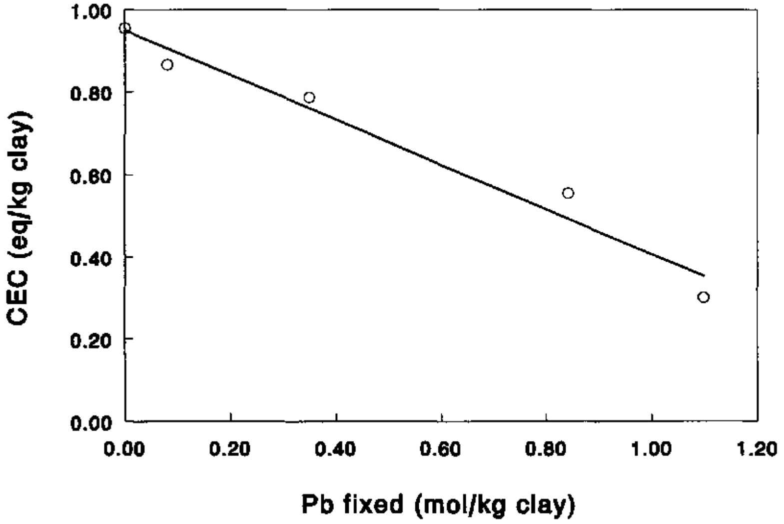

Figure 1 Relation between the CEC and the amount of Pb fixed to the clay as Pb hydroxide polymers at pH 6.6.

that the CEC reduces strongly with increasing Pb fixed to the clay. If the polymeric Pb precipitate was not bound to the clay surface, the calculation procedure should have lead to a CEC that is approximately constant. It is therefore highly likely that the polymeric Pb is bound to the clay surface.

From the slope of the curve the charge of the Pb polymers can be calculated. A straight line can be drawn through the calculated points in the figure. The intersection of the y-axis (0.95 eq/kg clay) agrees with the CEC of the pure clay. The figure suggests that the reduction of the CEC is linearly dependent on the amount of Pb fixed per unit amount of clay. This means that the nature of the Pb polymers is independent of the degree of loading of the clay with Pb polymers in the range of loadings studied. Calculated from the slope of the line in Figure 1 the charge of the Pb polymers is 0.54+. Pb polymers with the average formula $Pb(OH)_{1.46}^{0.54+}$ may be formed if a $K_{V(Pb/Na)}$ of 1.6 is assumed. Calculations showed that the major Pb species in solution is Pb^{2+}, other species present are Pb_2OH^{3+}, $Pb_4OH_4^{4+}$, $Pb_3OH_4^{2+}$, $Pb_6OH_8^{4+}$, $PbCl^+$ and $PbOH^+$. Ion exchange calculations showed that Pb^{2+} was the only exchangeable Pb species at the sorption phase which had to be taken into account. This conclusion is based upon ion exchange calculations using a Donnan approach assuming a concentration of 2.5*M* in the Donnan phase (Bolt, 1979). Probably larger polymers account for the Pb fixed fraction.

Condensation of clay platelets due to polymers could cause a slight change in ion exchange coefficient, compared to fully dispersed systems (Chapter 2). So the $K_{V(Pb/Na)}$ in systems containing Pb polymers could differ from the $K_{V(Pb/Na)}$ found in systems with only exchangeable Pb ions. This influences the calculated amount of Pb fixed and the calculated CEC. However this is not likely since the intersection of the y-axis (0.95 eq/kg clay) agrees with the CEC of the pure clay.

Pb binding to CALHO

In contrast with the previous system clay and Pb, in this section results will be presented and discussed concerning systems where also $AlCl_3$ was added. In these systems Al hydroxide polymers (denoted as ALHO) will occur. If the pH is higher than approximately 5.5 the main part of the added Al occur as ALHO, monomeric Al ions represent a negligible fraction of the exchangeable ions.

In the next three sections the results of the clay and ALHO systems (denoted as CALHO) and Pb will be presented and discussed for pH 6.6, pH 6.0 and pH 5.0 respectively.

Pb binding at pH 6.6

The experiments at pH 6.6 were done in the same concentration range as the experiments in the absence of ALHO, in order to test if the presence of the ALHO influences the Pb binding under these conditions.

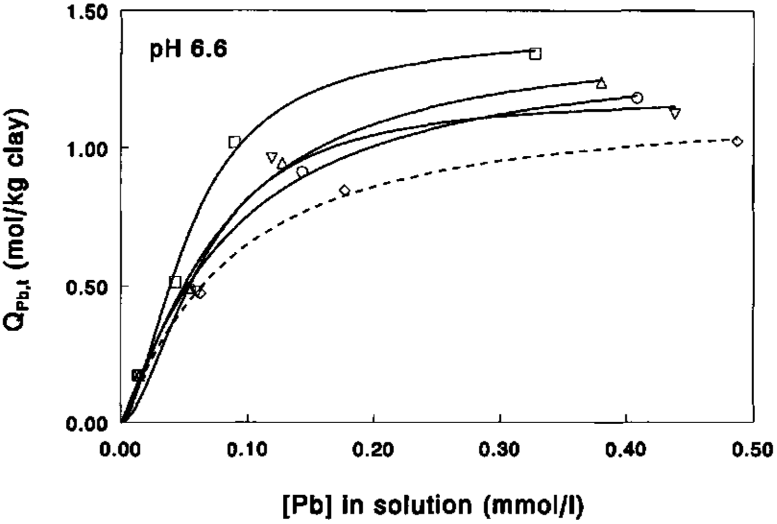

Figure 2 Total Pb binding ($Q_{Pb,t}$) by CALHO and the pure clay vs. [Pb] in the equilibrium solution at pH 6.6. The loadings of the clay with Al in mol/kg clay are: ◇ = pure clay (dotted line); ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00. The lines are smooth curves drawn through the data points.

Figure 2 gives the measured total Pb binding ($Q_{Pb,t}$ expressed in mol/kg clay) for the pure clay and four loadings of clay with ALHO and a total salt concentration of 0.01*M* monovalent anions as a function of the Pb concentration in the equilibrium solution. The total Pb binding per unit clay increased the greater the coverage of the clay with ALHO over the whole concentration range studied. The presence of the ALHO on the clay leads to more Pb binding than in the pure clay system. The maximum total amount of Pb bound is very high (1.35 mol/kg clay). The total Pb binding is the amount of Pb that compensates for part of the remaining CEC plus the amount that is bound to the ALHO plus the amount of Pb present as Pb polymers. Since the three processes are chemically different it is important to be able to discriminate the total observed binding. It is therefore necessary to be able to "speciate" the Pb in the system among Pb in solution, Pb that forms part of the exchangeable ions on the clay surface (Pb-CEC), Pb that is specifically bound to the ALHO (Pb-ALHO) and Pb present as Pb polymers. A procedure has been developed in Chapter 2, that allows for the speciation of Pb in these systems. The reader is referred to this chapter for further details. The essence of the method is that the amount of Pb-CEC that is present is calculated on the basis of the ion exchange equation as presented in equation (1). In this equation we used for the Vanselow selectivity coefficient for Pb/Na exchange in a pure clay system a value of 1.6. In Chapter 2 it was found that the selectivity coefficient for exchange between Pb and Na ions was increased as a result of the presence of ALHO. The average value of the Vanselow selectivity coefficient for Pb/Na exchange on CALHO was found to be 2.6, independent of the ALHO loading and nearly independent of the exchanger composition for the experimental conditions. The amount of Pb-CEC that was present in CALHO systems is calculated using equation (1) and 2.6 as the value for the Vanselow selectivity coefficient. Pb fixed is the amount of Pb bound to the ALHO plus the amount of Pb present as Pb polymers. To obtain the Pb fixed we subtracted the Pb-CEC from the total Pb binding measured. A further distinction of Pb fixed in Pb-ALHO and Pb polymers was with the present data set hardly possible. The calculated ion activity product (IAP) for $Pb(OH)_2(s)$ in CALHO ranged from -log IAP= 20.0 to 18.6 like for the IAP for

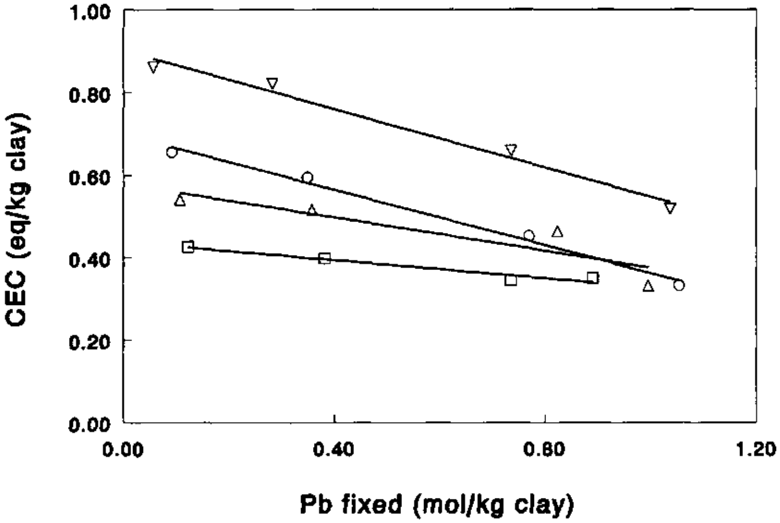

Figure 3 Relation between the CEC and the amount of Pb fixed to the clay as Pb hydroxide polymers for CALHO systems at pH 6.6. The loadings in mol Al/kg clay are: ▿ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00.

$Pb(OH)_2(s)$ in the pure clay systems.

A way to characterize Pb fixed is to calculate the average positive charge of the Pb fixed. This can be calculated from the slopes of the lines in Figure 3. The average charge per Pb ion present as Pb fixed decreased with increasing amounts of ALHO being present and equals 0.35+, 0.34+, 0.20+ and 0.11+. A gradual change of the relative importance of the ALHO on the strong binding of Pb can be seen. The lowest loading of the clay with ALHO shows a behaviour that is almost the same as in the absence of ALHO. The clay with the highest loading of ALHO clearly has a much smaller decrease of the CEC with increased metal binding.

Pb binding at pH 6.0

At higher concentrations of Pb studied at pH 6.6, Pb binding to the CALHO system was very pronounced and most of the binding was in non-exchangeable form. Discrimination between binding to the ALHO and binding as Pb hydroxide polymers was not possible. The experiments at pH 6.0 were so designed that the concentrations of Pb added were low enough that the systems were always undersaturated with respect to Pb hydroxide. Formation and binding

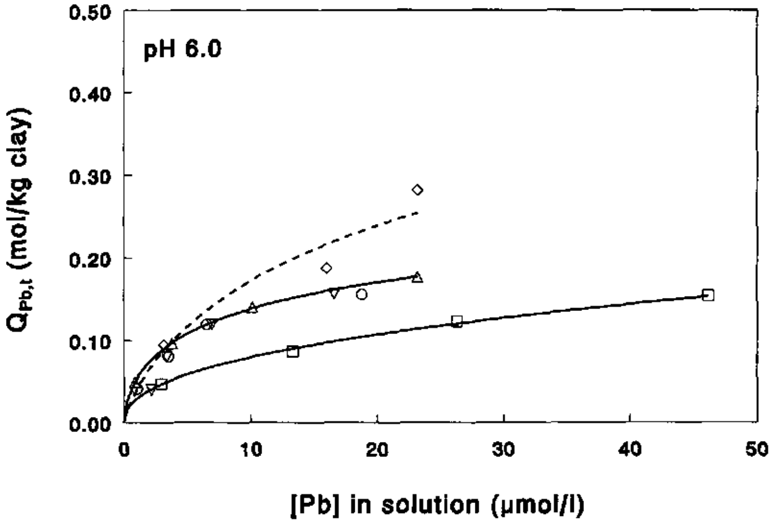

Figure 4 Total Pb binding ($Q_{Pb,t}$) by CALHO and the pure clay vs. [Pb] in the equilibrium solution at pH 6.0. The loadings of the clay with Al in mol/kg clay are: ◇ = pure clay (dotted line); ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00. The lines are smooth curves drawn through the data points.

of Pb hydroxide polymers was therefore not likely in these systems. That these species were not formed in CALHO systems is also shown by the comparison of the Pb extracted with La and the total amount of Pb present in the systems. La extracted always the same amount of Pb than the total amount of Pb present (see also Figure 6). For the pure clay systems La extracted less Pb than the total amount of Pb present. In these systems Pb hydroxide polymers may be formed, despite an IAP much smaller than the solubility product of $Pb(OH)_2$.

In Figure 4 the total Pb binding ($Q_{Pb,t}$ expressed in mol/kg clay) is given as a function of the concentration Pb in the equilibrium solution for the pure clay and four loadings of clay with ALHO and a total salt concentration of 0.01*M* monovalent anions. At this pH the adsorption capacity of Pb on CALHO systems have led to a lower binding of Pb than the pure montmorillonite for the higher concentrations of dissolved Pb. This is probably due to the formation of Pb hydroxide polymers in the pure clay systems. Pb binding to the ALHO is nevertheless also of significance at pH 6.0. In the absence of binding to the ALHO a decrease in extent of binding was expected with increasing amount of ALHO because of the decrease of the CEC. By chance, all CALHO systems we examined bound about the same amount of Pb, except for the highest coverage of the clay with ALHO.

Using ion exchange equation (1) and 2.6 as the value for the Vanselow selectivity coefficient for Pb/Na exchange in CALHO systems, we could estimate which part of the Pb bound is due to Pb-CEC. To obtain the Pb-ALHO we subtracted the Pb-CEC from the total Pb binding measured. The results of the Pb speciation at pH 6.0 for four loadings of the clay with ALHO are presented in the Figures 5a to 5d. They show that Pb binding to the ALHO increases with increasing loading of the clay with ALHO, except the clay with the highest coverage of ALHO. We obtained four different binding curves for the binding of Pb to ALHO. This is largely because of the different amounts of ALHO present. All loadings with ALHO clearly show that the preference of Pb for the ALHO is especially great for very low Pb concentrations where the binding curve for Pb-ALHO is very steep. Relatively high amounts of Pb-ALHO are reached already for low Pb concentrations. The available binding sites on the ALHO have apparently a high affinity for Pb ions. Subsequently Pb-ALHO more slowly increases with increasing Pb concentration. Also the Pb-CEC increases with increasing Pb concentration but never reaches the level of Pb-ALHO under these experimental conditions except for the lowest Al loading. Similar results were found for Zn in Chapter 3. However Zn-ALHO binding reached a plateau already for low Zn concentrations. Whereas Pb-ALHO binding still slowly increases with increasing Pb concentration and seems not to have reached a plateau yet.

After we have been able to discriminate the total observed Pb binding into

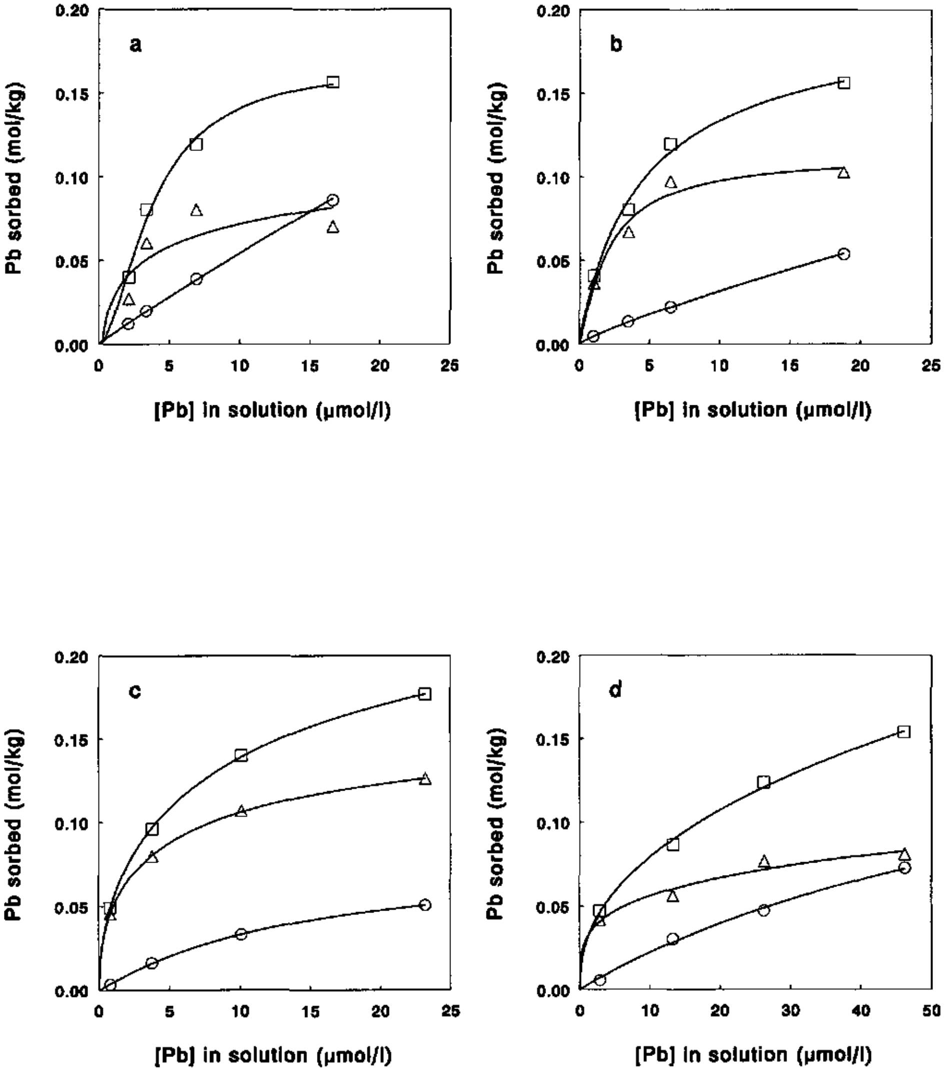

Figure 5 The calculated speciation of the total Pb binding ($Q_{Pb,t}$) (□) of CALHO between Pb-CEC (○) and Pb-ALHO (△) for four Al:clay ratios at pH 6.0. The loadings of the clay in mol Al/kg clay are: *a.* 0.30 *b.* 0.80 *c.* 1.20 mol *d.* 2.00. The lines drawn are smooth curves through the data points.

the two different parts (Pb-ALHO and Pb-CEC) the question arises how both fractions are affected by adding a high concentration of polyvalent cations like La^{3+}. It was expected that all Pb-CEC would be exchanged by the high amount of La^{3+} since the amount of La^{3+} added was enough to extract all bound Pb^{2+} from the siloxane surface (for more details see experimental section: extraction with $La(NO_3)_3$). Whether the Pb bound to the ALHO would be affected by adding La^{3+} is difficult to predict. Figure 6 indicates that the La procedure extracts a high amount of Pb that is bound to the ALHO. When the amount of Pb extracted with La^{3+} is plotted against the total amount of Pb bound ($Q_{Pb,t}$), this shows that all Pb-ALHO is extracted independent the Al:clay ratio and that indeed no irreversibly bound Pb hydroxide polymers were present under the experimental conditions. Pb bound to the ALHO can easily be removed by exchange with high concentrations of La ions.

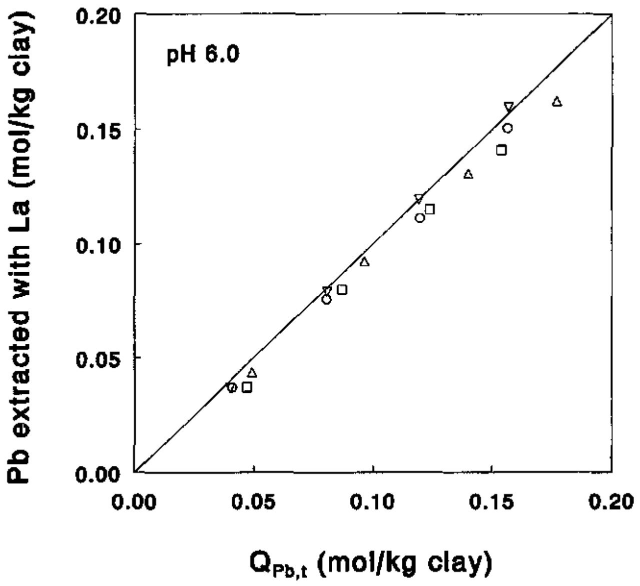

Figure 6 The amount of Pb extracted from CALHO systems with $La(NO_3)_3$ vs. the total Pb sorption ($Q_{Pb,t}$) at pH 6.0. The symbols refer to four loadings of the clay with Al. The loadings in mol Al/kg clay are: ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20; □ = 2.00.

This is in strong contrast with Zn ions bound to ALHO as studied in Chapter 3. It was shown that Zn ions bound to the ALHO could not be desorbed by a high concentration of La ions. This difference in sorption property to the ALHO is most likely due to the differences in the properties of the Zn and Pb ions. Keizer and Bruggenwert (1991) suggested that the relatively large ionic radius of Pb compared to Zn plays a role. Incorporation of certain favourable ions (e.g. Zn) into the ALHO might occur (Keizer and Bruggenwert, 1991; Kinniburgh *et al.*, 1976). This would involve an irreversible step and as a consequence Zn-ALHO can not be desorbed by a high concentration of cations. In contrast with Zn, Pb-ALHO is probably not incorporated into the ALHO and is reversibly bound.

When the Pb-ALHO is expressed per unit amount of ALHO and plotted as a function of the molar fraction (M_{Pb}) of the Q_t that is compensated for by Pb (Figure 7), the results do not coincide into one binding curve. Similar experiments for Zn at pH 6.6 (Chapter 3) did show a relation between Zn-ALHO (mol/mol) and M_{Zn}. The reason why such relation was not found in this case is not clear. Such a relation was also expected for Pb since the nature of the ALHO is independent of the amount of ALHO present (Chapter 2).

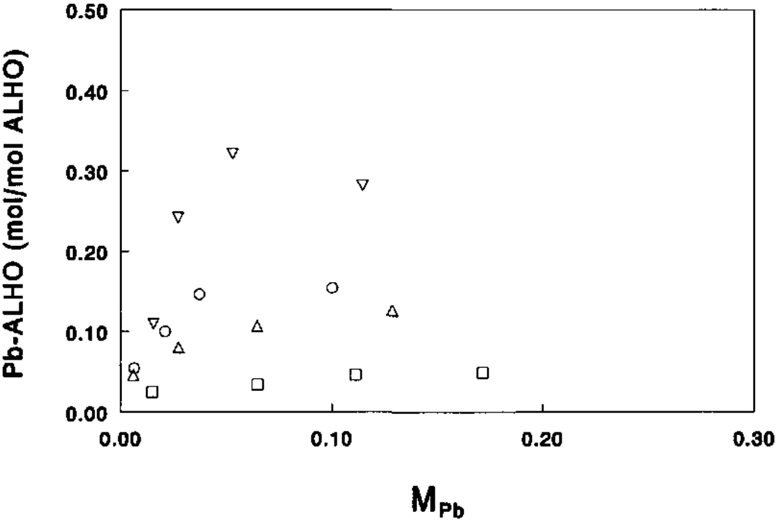

Figure 7 Pb binding by ALHO (Pb-ALHO) per mole ALHO at pH 6.0. The lines drawn are smooth curves through the data points. The loadings in mol Al/kg clay are: ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00.

Pb binding at pH 5.0

As was shown earlier in Chapters 2 and 3, several phenomena will affect the heavy metal ion binding at pH 5.0. This will have its consequences on the

Pb binding at pH 5.0.

Figure 8 gives the total measured Pb binding ($Q_{Pb,t}$ expressed in mol/kg) as a function of the concentration Pb in the equilibrium solution for the pure clay and for the same loadings of clay with ALHO as at pH 6.6 and a total salt concentration of 0.01*M* monovalent anions. It shows that with increasing loading of the clay with ALHO, the total Pb binding decreases. The highest total Pb binding is reached in the pure clay system. This can only be explained when a very small part or maybe no Pb was bound to the ALHO. Pb-ALHO (if present) does not compensate for the decrease of the CEC due to the presence of ALHO.

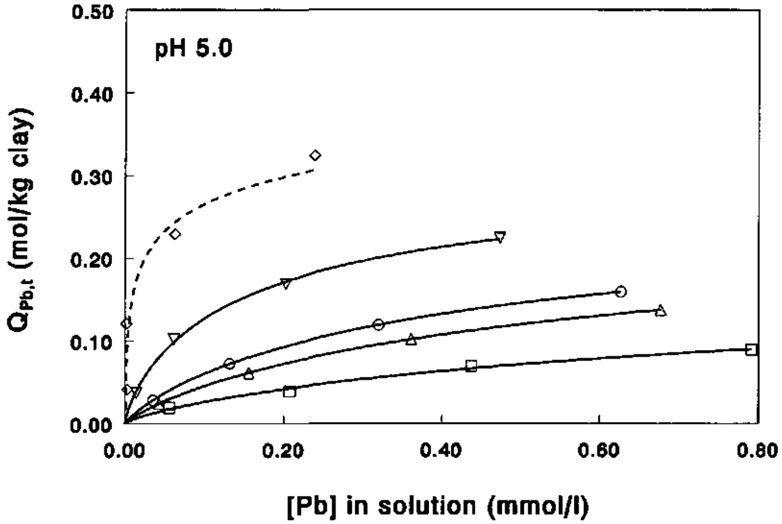

Figure 8 Total Pb binding ($Q_{Pb,t}$) by CALHO and the pure clay vs. [Pb] in the equilibrium solution at pH 5.0. The loadings of the clay with Al in mol/kg clay are: ◇ = pure clay (dotted line); ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00. The lines are smooth curves drawn through the data points.

In order to elucidate Pb adsorption behaviour, we "speciated" the Pb binding at pH 5.0 according the same procedure that was used to analyse the adsorption behaviour at pH 6.0. Unfortunately at pH 5.0 it is more complicated to ascertain the proportions of Pb binding to ALHO and CEC since also Al^{3+} ions are of relevance as exchangeable ions at this pH and form part of the total amount of exchangeable ions. Ion exchange at pH 5.0 is a ternary process and effectively a binary process at pH 6.0 and 6.6. For the ternary exchange reaction the ion exchange equation (1) can be rewritten as:

$$\frac{1-M_{Al}-M_{Na}}{M_{Na}^2}=K_{V(Pb/Na)}\times\frac{(Pb^{2+})}{(Na^+)^2} \qquad (2)$$

The ternary ion exchange equation (2) can not be solved directly to obtain the values of the molar fractions. Both M_{Al} and M_{Na} are unknown since Q_t changes with the exchanger composition. The mole fraction of an exchangeable ion can be expressed as:

$$M_i=\frac{q_i}{\Sigma q_i}=\frac{q_i}{Q_t} \qquad (3)$$

where q_i is the amount adsorbed in exchangeable form of ion i expressed in mol/kg. Combining equations (2) and (3) results in:

$$\frac{1-\frac{q_{Al}}{Q_t}-\frac{q_{Na}}{Q_t}}{\frac{q_{Na}^2}{Q_t^2}}=K_{V(Pb/Na)}\times\frac{(Pb^{2+})}{(Na^+)^2} \qquad (4)$$

The amount of Pb ions adsorbed in exchangeable form equals:

$$q_{Pb}(=Pb\text{-}CEC)=Q_t-q_{Al}-q_{Na} \qquad (5)$$

q_{Pb} is in this chapter denoted as Pb-CEC. The activities of Pb^{2+} and Na^+ were derived from the measurement of the concentrations in solution. The values of q_{Al} and q_{Na} were derived from the La extraction procedure. In the La extract of the systems, Al ions as well as Na ions were detected. This shows that both Na^+ and Al^{3+} were present in exchangeable form. The La extraction for the experiments at pH 5.0 showed that in the presence of ALHO, Al^{3+} always occupied an important fraction of the exchange sites. The treatment with La^{3+} does not lead to a release of Al if present as ALHO (Chapters 2 and 3). The CEC remained high for the system with the lowest amount of Al added, because the majority of the Al added is present as exchangeable Al^{3+} under these conditions. For higher Al loadings only a relatively small fraction of the total Al was present in exchangeable form. The amount of Al extracted with La underestimated the amount of exchangeable Al^{3+} (Chapter 2). The amount of exchangeable Al^{3+} could be derived by considering the exchange reaction between La^{3+} and Al^{3+} and using a selectivity coefficient of one for this exchange reaction (Bruggenwert and Kamphorst, 1979). The calculated value was never more than 30% higher than the amount that was directly measured via the extraction procedure. The value of Q_t (in mol/kg clay) could be derived from equation (4) if K_V is known, since q_{Al}, q_{Na} (both expressed in mol/kg clay), (Na^+) and (Pb^{2+}) were experimentally accessible. The value of Pb-CEC (in mol/kg clay) then followed from equation (5). Finally Pb-ALHO (in mol/kg clay) was found by subtracting the Pb-CEC from the total Pb binding measured ($Q_{Pb,t}$ in mol/kg clay).

The Pb speciation at pH 5.0 was calculated for four loadings of the clay with ALHO. The results show that at all loadings of the clay with ALHO almost no Pb is bound to the ALHO; almost all bound Pb is present at the exchange sites (Figure 9). In this figure the calculated Pb-CEC values as found in the speciation procedure are plotted against the amount of Pb ions extracted with an excess of La^{3+}. These calculations confirm the results of Keizer and Bruggenwert (1991). They measured the Pb binding to a CALHO system with an Al:clay ratio of 2 mol Al/kg clay at pH 5.0 and observed almost no Pb binding to the ALHO.

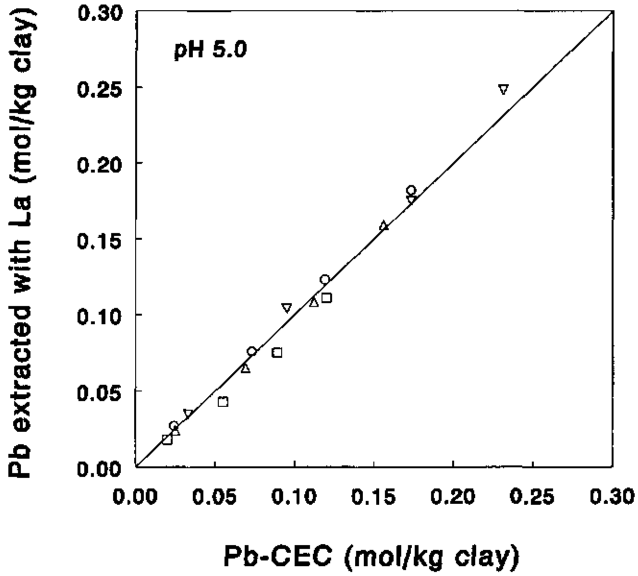

Figure 9 The amount of Pb extracted from CALHO systems with $La(NO_3)_3$ vs. the calculated amount of Pb sorbed on the clay surface (Pb-CEC) at pH 5.0. The loadings in mol Al/kg clay are: ▽ = 0.30 ; ○ = 0.80 ; △ = 1.20 ; □ = 2.00.

Acknowledgement

This work was partly funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

CHAPTER 5

Interactions between citrate and montmorillonite Al hydroxide polymer systems

Abstract

Organic acids with a low molecular weight like citric acid are common in the natural environment (Stevenson and Fitch, 1986) and form complexes with Al ions and may thus influence the adsorption properties and formation of the clay/Al hydroxide polymer system (CALHO). The effect of citrate depends on the pH, Al:clay ratio and Al:citrate ratio. The study reported in this chapter focused on the influence of citrate on the formation and stability of CALHO systems at different Al:clay and Al:citrate ratios and pH values and at a total salt concentration of 0.01*M* monovalent anions. It was found that the amount of citrate sorbed to the aged CALHO was independent of the Al fixed to the clay as Al hydroxide polymers (ALHO). It is concluded that the added citrate does not sorb to the ALHO but only to the edge faces of the clay, probably because of the strong repulsion encountered by the citrate molecules when they approach the negatively charged clay platelets and/or because the conformation of the citrate molecules prevents them from entering the layer between two clay platelets. The influence of citrate on aged CALHO systems with citrate:Al ratios of 1:5 and 1:1 at pH 6.0 was studied. It was found that as the citrate:Al ratio increased, more of the ALHO of the aged CALHO systems dissolved. From the change in the cation exchange capacity (CEC) of the clay, it can be concluded that the nature of the remaining ALHO is independent of the amount of Al dissolved. It was found that citrate influences the formation of CALHO systems as measured at pH 6.6. The degree of influence depended on the citrate:Al ratio. When this ratio was low (1:5), ALHO formed and all citrate was incorporated in the ALHO, probably leading to a co-precipitate. The amount of citrate incorporated was linearly dependent on the amount of ALHO present. Co-precipitation of ALHO and citrate probably leads to the formation of a separate phase, which is only weakly bound to the clay particles. At a high citrate:Al ratio (1:1), soluble Al citrate complexes become dominant and only a small part of the added Al is present as ALHO.

This chapter is submitted for publication in *European Journal of Soil Science.*
R.P.T. Janssen, M.G.M. Bruggenwert and W.H. van Riemsdijk.
Interactions between citrate and montmorrillonite Al hydroxide polymer systems.

Introduction

Al interlayered clay minerals have a wide geographic distribution and are of relevance in many soils (Barnhisel and Bertsch, 1989). They play an important role in the adsorption behaviour and capacity of metal binding in soils. Studies concerning the interaction between clay and Al hydroxide polymers (denoted as ALHO) have shown that the CEC of the clay is reduced (Chapter 2), whereas heavy metal adsorption is enhanced because of adsorption to the ALHO (Keizer and Bruggenwert, 1991; Chapters 3 and 4). Low molecular weight organic acids like citric acid which are commonly present in natural environment (Stevenson and Fitch, 1986) form complexes with Al ions and may thus influence the adsorption properties (Chapter 6) and the formation of the clay/ALHO complex (denoted as CALHO). The extent of this influence on CALHO is dependent on the pH, Al:clay ratio and Al:citrate ratio.

Adsorption processes of low molecular weight organic acids onto variable charge mineral surfaces and their model description, are subject of several studies (Bowden *et al.*, 1980; Kummert and Stumm, 1980; Zhang *et al.*, 1985). Anions such as citrate can sorb on variable charge mineral surfaces. The extent of the adsorption is dependent on several factors like the pzc of the variable charge mineral and the pH. Citrate may bind in a system containing CALHO to two separate variable charge mineral surfaces: the edge faces of the clay and to the ALHO. Cambier and Sposito (1991) studied the adsorption of citric acid onto aged Al interlayered clay at one Al:clay ratio, different pH values and different Al:citrate ratios. They suggest that citrate binds to ALHO interlayers for pH values between 4 and 5.5. For higher pH values they suggest that the ALHO desorbs from the clay mineral and that a new citrate containing phase is formed under these conditions. Up till now the relation between citrate sorption on ALHO interlayered clay as a function of the Al:clay ratio has not been studied. Such a study could shed more light on the interaction processes occuring in such systems.

At higher citrate:Al ratios Al citrate complexes are formed and become dominant in the equilibrium solution (Goh and Huang, 1984 and 1986; Violante and Jackson, 1981). A quantitative description of the speciation of the Al citrate in the equilibrium solution has been studied by several authors (Pattnaik and Pani, 1961; Kwong and Huang, 1979; Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984; Gregor and Powell, 1986). An interesting question is whether the results of these studies can also be applied to CALHO systems. However the relation between the composition of the solid ALHO phase and the composition of the equilibrium solution has so far not been studied.

Citrate can be incorporated in the ALHO interlayer during its formation (Goh and Huang, 1984 and 1986). Several studies show that low molecular weight organic acids like citric and tannic acid, can perturb the formation of Al interlayered clay minerals as a consequence of the formation of soluble Al organic acid complexes (Buondonno *et al.*, 1989; Goh and Huang, 1984 and 1986; Violante and Jackson, 1981). It may be expected that the citrate incorporation in the ALHO interlayers is related to the amount of ALHO interlayers present. However until now this relation has not been studied.

In this study we measured the binding of citrate to aged CALHO systems with various Al:clay and Al:citrate ratios, and pH in order to determine the contribution of the two possible "sites" on the sorption of citrate and to ascertain the relation between citrate binding and the amount of ALHO. The study intends also to give more insight in the competition between the possible sorption on one hand and possible dissolution induced by formation of soluble Al citrate complexes on the other hand. In order to describe the composition of the equilibrium solution quantitatively, several sets of the Al citrate complexation constants mentioned in the literature (Pattnaik and Pani, 1961; Kwong and Huang, 1979; Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984; Gregor and Powell, 1986) are tested. The nature of the partly dissolved ALHO is also subject of study.

Another topic of this study is the influence of citrate on the formation of CALHO systems. The composition of the final equilibrium solution and the composition of the ALHO present depends in these systems also on the ratios of Al:clay and Al:citrate. Systems with varying Al:clay and Al:citrate ratios have been studied. In order to describe the systems quantitatively an attempt has been made to calculate the speciation of these systems in the equilibrium solution by using Al citrate complex forming constants taken from literature.

Experimental

Preparation of the stock clay suspension

Montmorillonite clay from Clay Spur, Wyoming obtained from Ward's Natural Science Establishment, was used for all experiments. The montmorillonite was suspended in deionized water and passed through a 63 μm sieve. The suspension was then saturated with Na by four washings with 1*M* NaCl. Subsequently the clay suspension was washed several times with deionized water to remove the excess salt. A 2 μm fraction was obtained by gravity sedimentation at constant temperature. The clay suspension was centrifuged at 2300 g for 20 minutes; the clear supernatant was decanted. The electrolyte concentration of the concentrated clay suspension was further lowered by dialyzing the clay suspension. After dialysis the total electrolyte concentration in the solution of the clay suspension was determined by measuring the Na concentration and was found to be

0.0115*M*. The clay suspension contained 2.63% clay. The CEC of the clay was measured by measuring the amount of Na desorbed from the clay by 0.0033*M* $La(NO_3)_3$ and was found to be 0.95 eq/kg clay.

Sorption of citrate on the pure clay

A certain amount of the stock clay suspension was pipetted to 50 mL bottles (the suspensions would finally contain 17.53 g clay/L). Then 0.100*M* NaCl was added until each suspension contained 0.010*M* Na in solution. Subsequently a certain amount of a solution containing 0.010*M* citric acid was added. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.100*M* NaOH or 0.100*M* HCl was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 5.0, 6.0 or 6.6 was reached. The final volume of 30 mL was obtained by adding deionized water using a balance. The clay suspensions were shaken for five to six hours (Cambier and Sposito, 1991) and the pH of the suspensions were measured and if necessary adjusted to a pH 5.0, 6.0 or 6.6. Under constant stirring, 25 mL of each clay suspension was pipetted into a centrifuge tube and centrifuged at 40,000 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solutions and stored overnight at 5°C. The Na, Si and citrate concentrations in the supernatant solutions were determined. Citrate was determined the next day to avoid lowering of the citrate concentration by microbiological degradation. Sorbed citrate was calculated based upon the measured concentrations in the supernatant and total amounts present in the system.

Sorption of citrate on aged CALHO

Various CALHO systems were prepared as follows. A certain amount of clay suspension was pipetted to 100 mL bottles (the suspensions would finally contain 9.56 g clay/L). Subsequently 25 mL deionized water was added. Then 0.100*M* $AlCl_3$ solution was added to the suspensions at the rate of 0.25, 0.67, 1.00 and 1.67 mol/kg clay. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.300*M* NaOH was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 5.0, 6.0 or 6.6 was reached. The suspensions were shaken for seven days. The pH of the suspensions were measured regularly and if necessary adjusted until a pH of 5.0, 6.0 or 6.6 was reached again. In order to obtain a salt level of approximately 0.01*M*, the CALHO suspensions were subject in this seven days period of the following procedure. The bottles were filled up to the rim with deionized water (ca.100 ml) and stand overnight. The next day the above clear solution was removed to have left a CALHO suspension with a total salt level of approximately 0.01*M*. The bottles were filled up again to the rim with deionized water if the salt level was still higher than 0.01*M*. Finally an 0.01*M* NaCl solution was added to the CALHO suspensions to obtain a total salt level of nearly 0.01*M*. The next day the above clear solution was removed. The final Na solution concentrations were determined and ranged from 0.008 to 0.013*M*. Subsequently after seven days a certain amount of a solution containing 0.010*M* citric acid was added to the CALHO suspensions and titrated with 0.300*M* NaOH until a pH of 5.0, 6.0 or 6.6 was reached. The final volume of 55 mL was obtained by adding deionized water using a balance. The CALHO suspensions were shaken for five to six hours (Cambier and Sposito, 1991) and the pH of the suspensions were measured and if necessary adjusted to a pH 5.0, 6.0 or 6.6. Under constant stirring, 30 mL of each CALHO suspension was pipetted into a centrifuge tube and centrifuged at 40,000 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear supernatant solutions and stored overnight at 5°C. The Al, Na, Si and citrate concentrations in the supernatant solutions were determined. Citrate was determined the next day to avoid lowering of the citrate concentration by microbiological degradation. Sorbed citrate and Al were calculated based upon the measured concentrations in the supernatant and total amounts present in the system.

Degradation of aged CALHO by citrate

The systems were the same way as for the citrate sorption experiments on CALHO, except that the suspensions finally contained 1.00 g clay/L, the citrate:Al ratios were higher and the experiments were carried out at pH 6.0 only. Further on it was not necessary to decrease the salt level to 0.01*M*, since the clay content was low. Instead 0.100*M* NaCl was added directly after the addition of the $AlCl_3$ solution, until each suspension contained 0.010*M* Na in solution. The $AlCl_3$ solution was added at the same rate to the clay suspensions as in the preceding section and the CALHO suspensions were also allowed to age seven days before citric acid was added.

Formation of CALHO in the presence of citrate

The systems were the same way as for the degradation of CALHO by citrate experiments, except that the 0.01*M* citric acid solution was added directly after the addition of the stock clay suspension and the CALHO systems were allowed to age for 5 to 6 hours only. Before the CALHO systems were pipetted into a centrifuge tube, 0.300*M* NaOH was slowly added to the suspensions until a pH of 6.0 was reached. The $AlCl_3$ solution was added at the same rate to the clay suspensions and the citrate:Al ratios were the same as in the preceding section.

Extraction with $La(NO_3)_3$

To the CALHO residues in the centrifuge tubes (for the CALHO experiments with a clay content of 1.00 g/L), 30 ml 0.0033*M* $La(NO_3)_3$ was added. The

CALHO suspensions were shaken for two hours. The extraction time is long enough to achieve equilibrium since a rapid attainment of equilibrium is reached in ion exchange processes (Inskeep and Baham, 1983; Garcia-Miragaya and Page, 1976). Then the suspensions were centrifuged at 40,000 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear extract solutions. The Al, Si and Na concentrations in the extract were determined. The concentration of La^{3+} (0.10 mmol/30 mL) is high enough to remove essentially all exchangeable mono- and divalent ions attached to the clay surface (total surface charge per centrifuge tube: 0.024 meq). This follows from simple ion exchange calculations. The efficiency to exchange monovalent Na^+ can easily be estimated since the selectivity coefficient for La^{3+}/Na^+ exchange is known (Bruggenwert and Kamphorst, 1979). It also replaces positively charged exchangeable Al citrate complexes from the clay surface if present. The amount of exchangeable Al^{3+} on the clay surface is negligible since the Al ion concentration in solution at pH 6.0 is extremely low (Chapter 2; Bruggenwert *et al.*, 1987; Turner and Brydon, 1965). The unbuffered salt solution $La(NO_3)_3$ is not capable to remove the ALHO that is strongly bound to the clay surface (Chapter 2).

X-ray diffraction patterns

X-ray diffraction of the aged CALHO systems indicated that the ALHO was present as an interlayer between the clay platelets (Chapter 2).

Analysis

Na, Al and Si were analyzed by ICP-AES (Spectro Analytical Instruments) in the supernatant and La extract. Only very little Si was determined in the supernatant and La extract, meaning that (almost) no clay was decanted. Citrate was determined in the supernatant by the enzymatic reaction of citrate with citrate lyase (Anonymous, 1989). The amount of oxidized NADH originating from the enzymatic reaction is stoichiometric with the amount of citrate. NADH is determined by means of the spectrophotometric determination at 340 nm (Hitachi 100-20). To avoid the complexation of citrate with Al which disturbs the enzymatic reaction, 0.2 mL 0.2*M* NaF was added to the (plastic) cuvet (volume solution 3 mL). Citrate concentrations for the experiments of citrate sorption to pure clay, were determined in the supernatant based upon total organic carbon (TOC) analysis with a Skalar SK 12 organic carbon analyser.

Results and Discussion

Citrate sorption on pure Na clay

Under neutral and slightly acid conditions, citrate ions are negatively charged and it is assumed that citrate does not sorb to the siloxane surface of the clay but only to the edge faces of the clay platelet. Since these surfaces have a variable charge, it is expected that the citrate sorption is pH-dependent. We therefore measured the citrate sorption at three pH values after a five hours' reaction time. The chosen reaction time is assumed to be sufficient to achieve equilibrium (Cambier and Sposito, 1991). Preliminary experiments showed that after five hours' reaction, no degradation of citrate by microbes had taken place, but after one week an appreciable part had degraded.

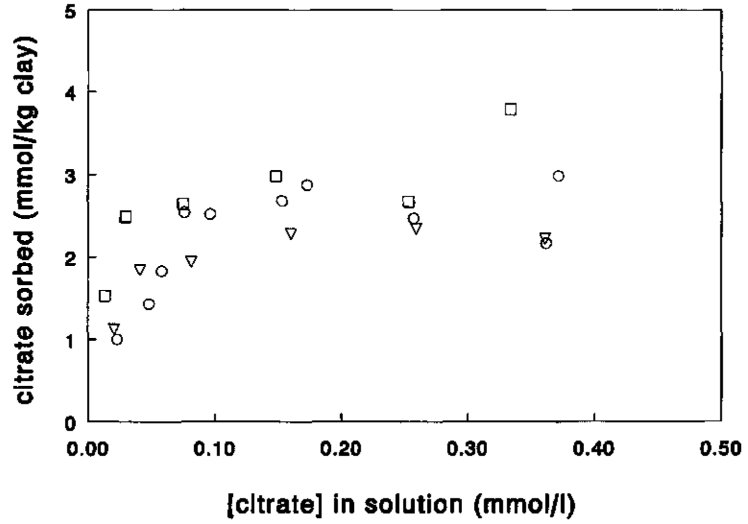

Figure 1 Citrate sorbed to the pure clay vs. [citrate] in the equilibrium solution at pH 5.0 (□), 6.0 (○) and 6.6 (▿).

Figure 1 shows the measured citrate sorption curve on the pure clay at pH 5.0, 6.0 and 6.6. Citrate sorbed to the edge faces of the clay is slightly pH-dependent. Sorption is greatest at pH 5.0 and least at pH 6.6. This can be explained by the higher positive charge of the edge face of the clay at pH 5.0, as a consequence of which more citrate will be sorbed. The plateaus of the curves show that the citrate sorption ranges from 2.5 to 3.5 mmol/kg clay.

The specific surface area of the edge faces of the clay can be estimated from the dimensions of the clay particles. It can be shown that the edge face area (A_e) is equal to:

$$A_e = \frac{4}{\rho R} \qquad (1)$$

where ρ is the density and R the diameter of the clay particle. An assumption must be made about ρ and R. Estimates of the areal dimensions of the particles are difficult to obtain because these particles are so irregular, but diameters from 0.02 to 2.0 μm have been reported (Worrall, 1968). An average diameter of 0.2 μm for the clay particle is acceptable. The density of montmorillonite is about 2650 kg/m^3. We calculated the specific surface area of the edge faces of the clay to be approximately 8 m^2/g. This leads to estimates of maximum citrate sorption on the edge faces ranging from 0.3 $\mu mol/m^2$ at pH 6.6 to 0.4 $\mu mol/m^2$ at pH 5.0. This is somewhat lower than values found for citrate sorption on goethite (Bowden *et al.*, 1980) and on hematite (Zhang *et al.*, 1985; Kallay and Matijević, 1985). For the pH range from 5 to 7 Bowden *et al.* (1980) measured a maximum amount of 1.3 to 0.9 $\mu mol/m^2$ citrate bound to goethite. For the same pH range Zhang *et al.* (1985) and Kallay and Matijević (1985) measured a maximum amount of 1.6 to 0.8 $\mu mol/m^2$ citrate bound to hematite.

Influence of citrate on aged CALHO

Citrate sorption to CALHO

Figure 2 shows the measured citrate sorption to clay/Al hydroxide polymer systems (denoted as CALHO) as a function of the amount of Al in the system that is present as Al hydroxide polymers (denoted as ALHO) fixed to the clay. The citrate sorption was measured for two added initial citric acid concentrations (C_i) and three pH values (C_i= 0.1 m*M* (= 10.5 mmol/kg clay) at pH 5.0, 6.0 and 6.6 and C_i= 0.2 m*M* (= 21.0 mmol/kg clay) at pH 6.0) after 5 hours' reaction time. The 5 hours for equilibration was chosen on the basis of the results of Cambier and Sposito (1991) and of preliminary experiments. The citrate sorption was also measured in two samples after 22 hours of equilibration. It was found that the citrate sorption had increased slightly (probably due to some degradation of citrate), indicating that the systems were in equilibrium.

For all measured pH values the citrate sorption in the systems in which Al is fixed to the clay was greater than that in systems with pure clay (Figure 2). The average measured citrate concentrations in the equilibrium solution for

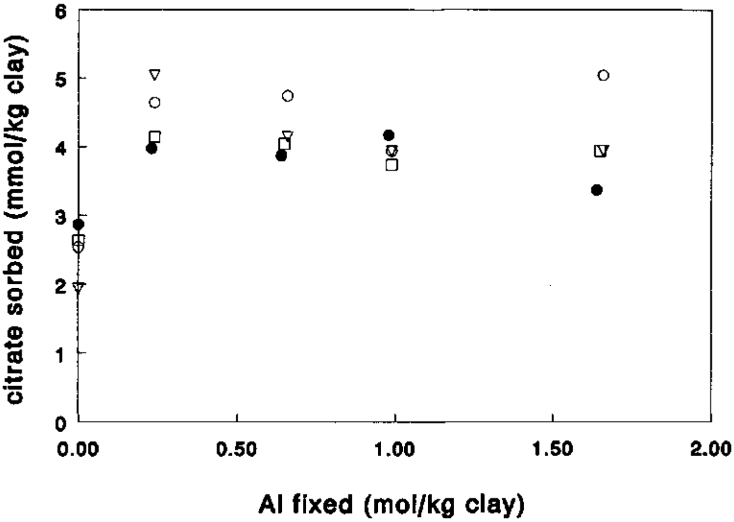

Figure 2 Relation between the amount of citrate sorbed to aged CALHO and the pure clay vs. the amount of Al fixed to the clay as ALHO at C_i= 0.1 mmol/L and three pH values (pH 5.0 = □, 6.0 = ○, 6.6 = ▽), and at C_i= 0.2 mmol/L (pH 6.0 = •).

the CALHO systems in the range of fixed Al studied were 0.06 m*M* for C_i= 0.1 m*M* and and 0.16 m*M* for C_i= 0.2 m*M*. The citrate sorption did not increase with increasing amounts of Al fixed to the clay. The only possible explanation for this observation is that citrate does not bind to the ALHO but that the binding is limited to the edge faces of the clay. This is in strong contrast with the binding mechanism suggested by Cambier and Sposito (1991). They suggest that citrate binds to ALHO interlayers for pH values between 4 and 5.5. We found that the citrate sorption for C_i= 0.1 m*M* citric acid added to the CALHO systems at pH 6.0 was approximately constant over the whole range of fixed Al measured. We expected that as the concentration of added citric acid increased, the citrate sorption to the ALHO would also increase. However, the experiments measured at pH 6.0 with C_i= 0.2 m*M* show a slightly diminished binding. We infer that the small differences in amounts of sorbed citrate between C_i= 0.1 and 0.2 m*M* are probably due to experimental error and that no significant change in citrate sorption occurred.

The reason that citrate does not bind to the ALHO may be the strong repulsion encountered by the citrate molecules when they approach the negatively charged clay platelets, or the structural conformation of the citrate molecules which may prevent them from entering between two clay platelets, or both. This explanation is in line with the observation that most of the ALHO is present in the interlayers (Chapter 2).

Some of the added Al may have reacted with edge sites of the clay particles which may have enhanced the reactivity of the edge phases towards binding of citrate. An alternative explanation is that a small addition of Al is sufficient to disturb the edge to face structure of the Na montmorillonite platelets, which then become aligned in parallel by sorption of ALHO; consequently the edge faces of the clay platelets are free to sorb citrate whereas initially they were partly "sorbed" to other platelets.

Contrary to the pure clay systems, no marked pH dependence was observed for CALHO (Figure 2). The reason for this is unclear. Perhaps the pzc of the clay edge face was changed by the fixation of Al. The observed amounts of sorbed citrate (ranging from 3.7 to 5.0 mmol/kg clay) agree with the sorption data presented by Cambier and Sposito (1991). However, contrary to our findings, they did observe some pH dependence for citrate binding.

Description of the composition of the equilibrium solution

Citric acid in two Al:citric acid ratios (5:1 and 1:1) was added to a series of the same aged CALHO systems as used for the adsorption experiments at pH 6.0. At high citrate:Al ratios the ALHO may be degraded and soluble Al citrate complexes become dominant in the equilibrium solution. The experiments were designed so that soluble Al citrate complexes would occur in the equilibrium solution.

The amount of Al fixed to the clay was calculated by subtracting the measured amount of Al in solution and the amount of Al bound in the diffuse double layer of the clay from the total amount of Al added. The amount of Al bound by an exchange mechanism was ascertained by measuring the Al ions released from the clay upon addition of a high concentration of lanthanum (La^{3+}) as a competitor. No Al was detected in the La extract, indicating that no exchangeable Al citrate complexes or Al ions were present on the clay.

Table 1 shows the results of these experiments. Since the solubility product for ALHO on clay is low (10^{-33} according to Bruggenwert *et al.*, 1987; Turner and Brydon, 1965) all added Al will be fixed to the clay for CALHO systems in the absence of citrate at pH 6.0. Comparing the amounts of Al added and the amounts of Al fixed shows that an important part of the ALHO has been dissolved, especially at the Al:citrate ratio of 1:1. We decided to study whether our experimental results could be described by a model using equilibrium constants from the literature. These calculations can elucidate the behaviour of a CALHO system in the presence of ions that form strong complexes with Al^{3+}.

Table 1 Citrate sorption to aged CALHO systems.

Measurements and calculations related to different CALHO/citrate systems at pH 6.0 (clay content 1 g/L).

Al concentrations in the supernatant solutions are calculated according to the stability constants of:

Öh & Sj = Öhman and Sjöberg (1983)
Mo & Ma = Motekaitis and Martell (1984)
Gr & Po = Gregor and Powell (1986)

total amounts initial present					**supernatant analyses**		**supernatant concentrations calculated according to:**		
Al (m*M*)	citrate (m*M*)	Al:citrate ratio	Al fixed (mol/kg)	CEC (mol/kg)	[citrate] (m*M*)	[Al] (m*M*)	[Al] (m*M*) Öh & Sj	[Al] (m*M*) Mo & Ma	[Al] (m*M*) Gr & Po
0.251	0.050	5:1	0.181	0.79	0.045	0.070	0.043	0.047	0.029
0.667	0.133	5:1	0.496	0.72	0.128	0.170	0.125	0.130	0.075
1.000	0.200	5:1	0.755	0.66	0.197	0.245	0.192	0.198	0.112
1.667	0.334	5:1	1.261	0.50	0.336	0.406	0.329	0.337	0.188
0.251	0.251	1:1	0.109	0.82	0.252	0.142	0.246	0.251	0.141
0.667	0.667	1:1	0.190	0.80	0.671	0.475	0.661	0.666	0.358
1.000	1.000	1:1	0.232	0.79	0.995	0.768	0.983	0.994	0.524
1.667	1.667	1:1	0.316	0.76	1.654	1.351	1.638	1.651	0.858

Various studies of the formation constants of Al(III) citrate complexes were found in the literature: Pattnaik and Pani (1961), Kwong and Huang (1979), Öhman and Sjöberg (1983), Motekaitis and Martell (1984), Gregor and Powell (1986). Since Pattnaik and Pani (1961) and Kwong and Huang (1979) neglected hydrolysis of the Al^{3+} ion and the formation of ALHO, their studies have limited relevance for describing our systems. On the other hand, the equilibrium constants of Öhman and Sjöberg (1983), Motekaitis and Martell (1984) and Gregor and Powell (1986) are, in principle, all applicable. Unfortunately, there is little agreement between the various authors. To test the validity of the complexation models for our experimental data, we performed calculations according to all three models.

The total Al concentrations measured in the equilibrium solution were compared with the calculated Al concentrations. The calculations used the measured citrate and Na concentrations in the equilibrium solution, the equilibrium constants for Al citrate complexes and the citric acid dissociation constants according to Öhman and Sjöberg (1983), or Motekaitis and Martell (1984) or Gregor and Powell (1986). In addition, we used the constant of the Na citrate complex (Martell and Smith, 1977), a constant IAP of 10^{-33} for ALHO on clay (Turner and Brydon, 1965; Bruggenwert *et al.*, 1987), the constants for Al hydrolysis products and Al chloride complexes (Lindsay, 1979). We used the ECOSAT program (Keizer and Van Riemsdijk, 1994) for all speciation calculations. The calculations show that the measured Al concentration in solution is predicted reasonably well when the equilibrium constants as given by Öhman and Sjöberg (1983) and Motekaitis and Martell (1984) are used in combination with a constant solubility product for the ALHO. Using the equilibrium constants given by Gregor and Powell (1986) leads to underestimates over the whole range (see Figure 3 and Table 1).

We found that the relation between the solid ALHO phase and the composition of the equilibrium solution for aged CALHO systems could be described by known Al citrate complex constants from the literature. These results do not support the suggestion by Cambier and Sposito (1991) that a new external solid ALHO phase is formed. However, they can be explained by postulating that some of the ALHO dissolved in the interlayer because of complexing of Al^{3+} and citrate.

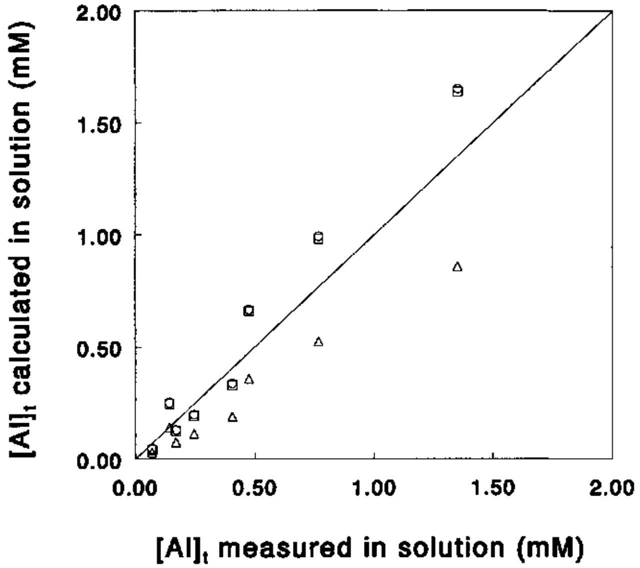

Figure 3 Relation between the total concentration of Al measured in solution and the concentration of Al calculated in aged CALHO systems, according to the Al citrate complexes and citric acid dissociation constants of Öhman and Sjöberg (1983)(□); Motekaitis and Martell (1984)(○); Gregor and Powell (1986)(△).

Nature of the ALHO

In Chapter 2 the decrease of the CEC in CALHO systems as a function of the loading of the clay with ALHO at pH 6.6 was studied. It was found that the ALHO reduced the CEC by 0.24 eq per mole Al, independent of the ALHO loading. Therefore it was concluded that the nature of the ALHO formed was independent of the degree of loading of the clay with ALHO. This raises the question whether the partial dissolution of the ALHO by the complexation of Al from the ALHO with citrate influences the nature of the remaining ALHO. To find an answer, we studied the CEC of the CALHO systems with two Al:citrate ratios (1:1 and 5:1) and four Al:clay ratios at pH 6.0. We also studied the CEC of CALHO systems in the absence of citrate for four Al:clay ratios at pH 6.0. The initial four Al:clay ratios were: 0.25, 0.67, 1.00 and 1.67 mol/kg clay. The CEC of the clay was ascertained by measuring the release of ions from the clay upon addition of a high concentration of La^{3+} as a competitor. Only Na ions were detected as exchangeable ions. It may be assumed that the released Na ions originate from the negative clay surface only, and not from the positive ALHO surface (Sprycha, 1989). Under these conditions the CEC of the clay can be derived from the measured release of Na^+ ions (see Table 1 and Figure 4).

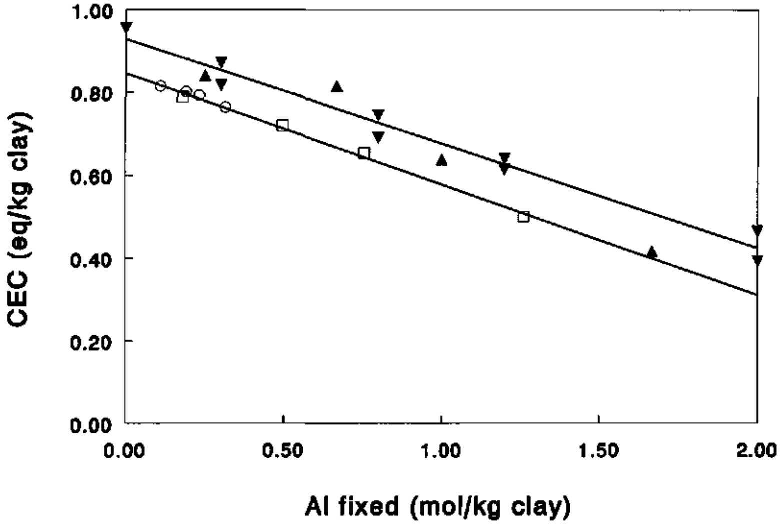

Figure 4 Relation between the amount of Al fixed to the clay as ALHO and the reduction of the CEC for aged CALHO systems in the absence and presence of citrate at pH 6.0. Open symbols indicate addition of citric acid (Al:citrate ratio 1:1 indicated by ○ and 5:1 by □); closed symbols indicate no addition of citric acid (▲ at pH 6.0 and ▼ at pH 6.6).

The CEC of the CALHO systems in the presence and absence of citric acid measured in this way at pH 6.0 as a function of the amount of Al fixed to the clay is shown in Figure 4. The same figure shows the results for the CEC of CALHO systems at pH 6.6 obtained in earlier experiments (Chapter 2). The figure shows that the CEC of the clay is inversely related to the amount of ALHO. This strongly suggests that all the ALHO present has been sorbed to the clay. The ALHO would have had no effect on the CEC if it had been present as a separate phase. This finding also contradicts the contention that a new external solid ALHO phase is formed when citrate is added to a CALHO system (Cambier and Sposito, 1991). In CALHO systems with or without added citric acid, we found the reduction of the CEC at pH 6.0 and pH 6.6 was linearly dependent on the amount of ALHO per unit amount of clay. A comparable reduction of the CEC was observed in the CALHO systems in the absence of citrate at pH 6.0 and 6.6.

The average charge of the ALHO, expressed per Al atom, can be derived from the slope of the curves. It is a positive charge of 0.25+ per Al atom in the presence of citrate and 0.27+ in the absence of citrate, suggesting average OH/Al mole ratios for the ALHO component of 2.75 and 2.73, respectively. Since the slopes of the CEC reduction of the CALHO systems in the presence or absence of citrate are nearly identical, it is very probable that the nature of the ALHO in CALHO systems has not changed as a result of partial dissolution by adding citrate. The intersection of the y-axis of the CALHO systems in the absence of citrate (0.95 eq/kg clay) agrees with the CEC of the pure clay. However, it is unclear why the curve for the CALHO systems in the presence of citrate is shifted slightly downwards.

Figure 4 also shows what proportion of the ALHO in CALHO systems in the presence of citrate has been dissolved by the Al complexing with citrate. The initial four Al:clay ratios for the CALHO systems at pH 6.0 in the presence and absence of citrate were the same. In the figure, the data points for the CALHO systems in the presence of citrate have shifted to the left. This shift is equal to the amount of ALHO dissolved as a result of the complexation with citrate and now present as Al citrate complexes in the equilibrium solution. This follows from Table 1 too.

Influence of citrate on the formation of CALHO

Description of the composition of the equilibrium solution

In addition to the sorption and influence of citrate on the ALHO of aged CALHO systems, we studied the influence of citrate on the formation of CALHO systems. These systems were made by adding clay, $AlCl_3$ and citric acid simultaneously and then titrating to a constant pH 6.6. The Al:clay and Al:citrate ratios used were the same as for the experiments with aged CALHO and citrate. At these high citrate:Al ratios it may be expected that soluble Al citrate complexes in the equilibrium solution are dominant and that CALHO formation is greatly perturbed. We focused on the influence of citric acid on the formation of the CALHO at Al:citrate ratios of 5:1 and 1:1 at pH 6.6.

The amount of ALHO formed was calculated by subtracting the measured amount of Al in solution and the amount of Al bound in the diffuse double layer of the clay from the total amount of Al added. No Al was detected in the La extract, indicating that no positively charged Al citrate complexes or Al ions were present as exchangeable ions. As expected, some of the added Al was present as soluble Al citrate complexes; however a fair part was apparently associated with the ALHO, especially at the Al:citrate 5:1 ratio. The results are shown in Table 2.

Table 2 CALHO formed in the presence of citrate.

Measurements and calculations related to different CALHO/citrate systems at pH 6.6 (clay content 1 g/L).

Al concentrations in the supernatant solutions are calculated according to the stability constants of:

Öh & Sj = Öhman and Sjöberg (1983)
Mo & Ma = Motekaitis and Martell (1984)
Gr & Po = Gregor and Powell (1986)

total amounts initial present					**supernatant analyses**		**supernatant concentrations calculated according to:**		
Al (mM)	citrate (mM)	Al:citrate ratio	ALHO (mol/kg)	CEC (mol/kg)	[citrate] (mM)	[Al] (mM)	[Al] (mM) Öh & Sj	[Al] (mM) Mo & Ma	[Al] (mM) Gr & Po
0.250	0.065	5:1	0.135	0.55	0.053	0.116	0.030	0.053	0.009
0.634	0.148	5:1	0.496	0.93	0.074	0.137	0.047	0.074	0.014
0.961	0.205	5:1	0.879	0.82	0.054	0.080	0.031	0.054	0.009
1.641	0.345	5:1	1.478	1.03	0.096	0.162	0.065	0.095	0.019
0.270	0.270	1:1	0.091	0.81	0.276	0.179	0.228	0.270	0.075
0.707	0.723	1:1	0.103	0.79	0.731	0.604	0.656	0.707	0.242
1.011	1.035	1:1	0.107	0.73	1.031	0.904	0.944	1.006	0.362
1.604	1.683	1:1	0.081	0.72	1.666	1.523	1.551	1.604	0.616

As in the case of the aged CALHO systems, we were interested to see if the experimental results could be described by a model based upon equilibrium constants found in the literature. Therefore we compared the measured total Al concentrations in the equilibrium solution with the calculated Al concentrations. The calculations used the same input and stability constants as used for the equilibrium solution description of the aged CALHO systems. They showed that using equilibrium constants given by Öhman and Sjöberg (1983) and Motekaitis and Martell (1984) in combination with a constant solubility product for the ALHO, the measured Al concentration in solution is predicted reasonably. Using the equilibrium constants as given by Gregor and Powell (1986) gave underestimates over the whole range (see Figure 5 and Table 2).

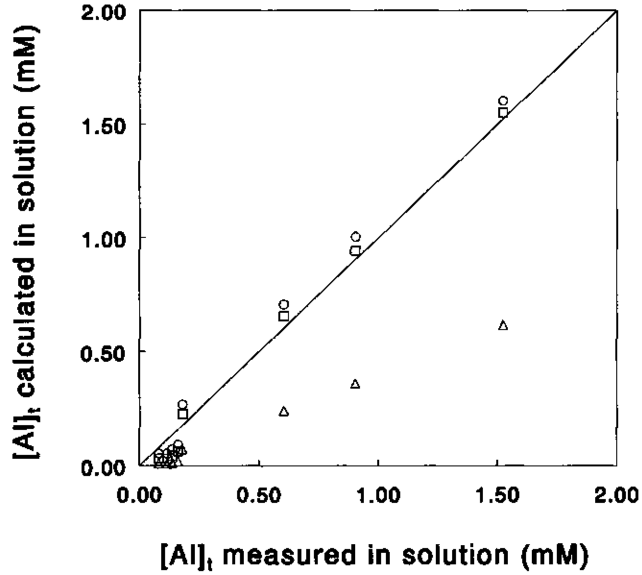

Figure 5 Relation between the total concentration of Al measured in solution and the concentration of Al calculated Al in CALHO systems formed in the presence of citrate, according to the Al citrate complexes and citric acid dissociation constants of Öhman and Sjöberg (1983)(□); Motekaitis and Martell (1984)(○); Gregor and Powell (1986)(△).

Independent of how the CALHO systems were prepared, the amount of Al in the equilibrium solution was predicted fairly well by taking as input the measured citrate and Na concentrations in the equilibrium solution, the constants of Al citrate complexes and the citric acid dissociation constants according to Öhman and Sjöberg (1983), or Motekaitis and Martell (1984), the constant of the Na citrate complex (Martell and Smith, 1977), a constant IAP of 10^{-33} for ALHO on clay (Turner and Brydon, 1965; Bruggenwert *et al.*, 1987), and the constants for Al hydrolysis products and for Al chloride complexes (Lindsay, 1979).

Citrate sorption to CALHO and nature of the ALHO

At the relatively high Al:citrate ratio of 5:1, most of the added Al was present as ALHO, but at the low Al:citrate ratio of 1:1, only a small part of the added Al was present as ALHO (see Table 2). Contrary to the aged CALHO systems, the citrate sorption of the systems appeared to be largely dependent on the amount of ALHO. Since most of the added Al in the systems with a Al:citrate ratio of 5:1 was present as ALHO, we inferred that citrate sorption was present, whereas at an Al:citrate ratio of 1:1 citrate sorption was nearly absent.

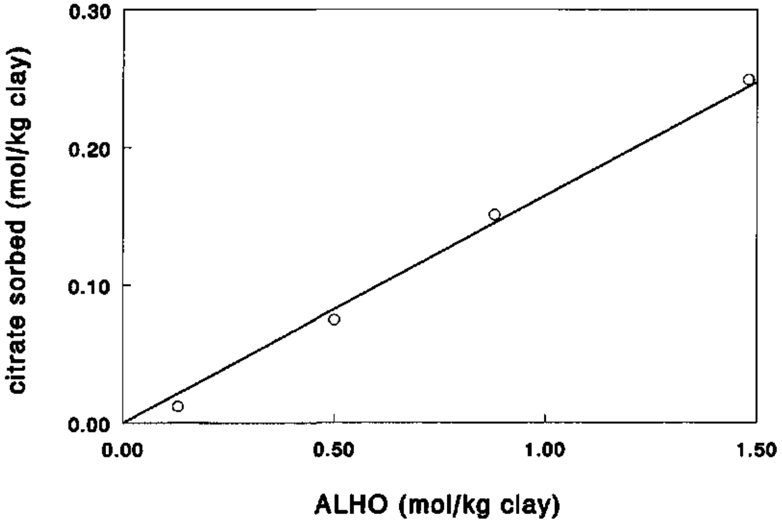

Figure 6 Relation between the amount of citrate sorbed to ALHO during the formation of the CALHO vs. the amount of ALHO present at pH 6.6.

Figure 6 shows the amount of citrate sorbed to the CALHO systems with a Al:citrate ratio of 5:1 as a function of the amount of ALHO. Large amounts of citrate were sorbed, peaking at the highest Al:clay ratio. This maximum amount of about 0.25 mol/kg clay is about 100 times more than the citrate sorption on the aged system with the same Al:clay ratio and pH! Under these experimental conditions all the added citrate was sorbed to the CALHO. The figure also shows that the amount of sorbed citrate is linearly dependent on the amount of ALHO present. This suggests that the sorbed citrate was incorporated in the ALHO (see also Goh and Huang, 1984 and 1986). It is not unlikely that a co-precipitate formed between ALHO and citrate. To ascertain whether these particles were present attached to the clay surface, or present as a separate phase, we studied this aspect by measuring the CEC of these systems. We ascertained the CEC of the clay by the amount of Na released from the clay surface as a result of the addition of La^{3+}. The CEC for the CALHO with an Al:citrate ratio of 5:1 seemed to increase, whereas for the CALHO with an Al:citrate ratio of 1:1 it decreased slightly as ALHO increased (Table 2). We found no clear relation between the CEC and the amount of ALHO present as co-precipitate. This is in stark contrast with the linear relation found between the CEC and fixed Al for the aged CALHO/citrate systems (Figure 4). According to Goh and Huang (1984 and 1986) the perturbation of the crystallization of Al hydroxides by the presence of citrate leads to structural distortion of the ALHO. It seems probable that in our experiment the CEC of the CALHO decreased in general only slightly in the presence of citrate because of the formation of a co-precipitate. From this we inferred that the charge of the co-precipitate is only slightly positive if it is attached to the clay. It seems likely that the binding between the clay surface and the co-precipitate is weak, and the clay and the co-precipitate can be considered as separate phases.

Conclusions

- Citrate is bound to pure clay by adsorption to the edge faces.
- Citrate does not bind to the ALHO present in the interlayer of aged CALHO systems.
- More citrate is adsorbed to the edge faces of a CALHO than in a pure clay system.
- Adding citrate to aged CALHO leads to partial dissolution of the ALHO, but does not change the nature of the remaining ALHO or the strong binding between clay particles and ALHO.
- Co-precipitation of ALHO and citrate probably leads to the formation of a separate phase that is only weakly bound to the clay particles.
- Relatively large amounts of citrate can be incorporated in the co-precipitate - up to 100 times more than the binding of citrate to aged CALHO systems.
- The equilibrium solution composition of aged CALHO/citrate systems and co-precipitated CALHO/citrate systems is in accordance with simple chemical speciation calculations.

Acknowledgements

The authors would like to thank Mr. E.M. Wittich for analytical assistance. This work was partly funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

CHAPTER 6

Zn binding by montmorillonite Al hydroxide polymer systems in the presence of citrate

Abstract

The availability of metal ions in natural systems is influenced by sorption processes. Metal ions can be sorbed to the solid phase via different processes such as ion exchange, specific adsorption to various reactive surfaces and incorporation into other solids through co-precipitation. The binding of Zn, via the formation of a clay/Al hydroxide polymer system (CALHO) in the presence or absence of citrate is studied. Citrate forms dissolved Al citrate and Zn citrate complexes. The distribution of Zn over the various species is calculated with a speciation model using constants for dissolved complexes in combination with an ion-exchange equation. The constants for the various Al citrate complexes and citric acid dissociation products of Motekaitis and Martell (1984) led to a reasonably good interpretation of the results. When the molar fractions of Zn bound to the exchange sites is smaller than 0.5, only slightly less Zn was sorbed to the Al hydroxide polymers (ALHO) in the presence of citrate when compared with Zn sorption to ALHO in the absence of citrate. For molar fractions of Zn bound to the exchange sites larger than 0.5, binding of Zn to the ALHO increased strongly in the presence of citrate. This suggests the formation of a co-precipitate or solid solution between ALHO, Zn hydroxide and citrate. The CALHO systems are suitable for use in treatment processes of waste water streams containing Zn, even in the presence of low molecular weight organic acids like citric acid.

This chapter is accepted for publication in *Environmental Geochemistry and Health.* R.P.T. Janssen, M.G.M. Bruggenwert and W.H. van Riemsdijk.
Zn binding by montmorillonite Al hydroxide polymer systems in the presence of citrate.

Introduction

At low Zn levels biota may grow sub-optimumally due to Zn deficiency, whereas at high levels Zn may become toxic. The bio-availability of Zn is dependent on the distribution of the metal amongst free Zn ions, dissolved Zn complexes, or Zn bound to various reactive surfaces of the solid phase of soil or sediment. To interpret bio-availability of Zn, it is necessary to know more about the distribution of Zn over various possible species.

Clay/Al hydroxide polymer systems (CALHO) have a wide geographic distribution and are of relevance in many soils (Barnhisel and Bertsch, 1989). They play an important role in the sorption behaviour and capacity of metal ion binding (Harsh and Doner, 1984; Keizer and Bruggenwert, 1991). Another aspect of CALHO is that they flocculate well and have a relatively high hydraulic conductivity when used as column materials, which makes them potentially suitable for treating metal ion containing waste water streams. Studies concerning the interaction between clay and Al hydroxide polymers (ALHO) have shown that the cation exchange capacity (CEC) of the clay is reduced whereas heavy metal sorption is enhanced because of sorption to ALHO (Keizer and Bruggenwert, 1991). Low molecular weight organic acids like citric acid are commonly present in the natural environment (Stevenson and Fitch, 1986) and can be produced as root exudates by various plant species. Citric acid forms strong complexes with Al ions and may thus influence the properties and formation of the CALHO system. Moreover citrate may be incorporated in the ALHO during its formation (Chapter 5).

The influence of low molecular weight organic acids on the formation of CALHO systems is the subject of several studies (Buondonno *et al.*, 1989; Goh and Huang, 1984 and 1986; Violante and Jackson, 1981; Chapter 5). These studies show that low molecular weight organic acids such as citric and tannic acids can perturb the formation of CALHO systems. Several authors (Pattnaik and Pani, 1961; Kwong and Huang, 1979; Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984; Gregor and Powell, 1986) describe the speciation of Al/citric acid systems in solution. Unfortunately there is little agreement between them.

Janssen *et al.* (1991) and Chapter 3 showed that the presence of CALHO led to increased Zn ion sorption at pH 6.6, as the result of Zn ion binding to the ALHO.

Few detailed studies have been carried out on systems in which metal ions, Al ions, clay and citrate were all present (Chairidchai and Ritchie, 1990 and 1992). In the present work the Zn binding by CALHO systems formed in the presence of citrate is studied under controlled conditions. The Al:clay ratio and the concentrations citric acid and Zn have been varied and the influence on Zn speciation has been studied. Because of the complexity of these systems numerous interactions can occur and it is difficult to predict which interactions are dominant. The objective of this study is to gain more insights into the binding processes of this system. The results will be compared with those obtained for Zn binding to CALHO systems, where the Zn was added after the ALHO was formed and no citrate was present. It will be tested in how far one can estimate the behaviour of this complex system using information derived from simpler systems.

Experimental

Preparation of the stock clay suspension

Montmorillonite clay from Clay Spur, Wyoming obtained from Ward's Natural Science Establishment, was used for all experiments. The montmorillonite was suspended in deionized water and passed through a 63 µm sieve. The suspension was saturated with Na by four washings with 1*M* NaCl. Subsequently the clay suspension was washed several times with deionized water to remove the excess salt. A 2 µm fraction was obtained by gravity sedimentation at constant temperature. The clay suspension was centrifuged at 2300 g for 20 minutes; the clear supernatant was decanted. The total electrolyte concentration in the centrifuged clay suspension was determined by measuring the Na concentration by flame emission spectrophotometry (Eppendorf Elex 6361) and was found to be 0.097*M*. The clay suspension contained 2.77% clay. The CEC of the pure clay was measured by measuring the amount of Na desorbed from the clay by 0.0033*M* $La(NO_3)_3$ and was found to be 0.95 eq/kg clay.

Zn sorption to CALHO/citrate

Various systems were prepared as follows. A certain amount of the stock clay suspension was pipetted to 500 mL bottles (the suspensions would finally contain 0.500 g clay/L). Subsequently a solution containing 0.010*M* citric acid was added to the suspension until a concentration of 0.1 or 1.0 m*M* at the final volume was obtained. Deionized water was added to adjust the volume to 200 mL, which is half of the final volume. Then 0.010*M* $AlCl_3$ solution was added to the suspensions at the rate of 0.77, 1.16 and 1.93 mol/kg clay. Then 0.010*M* $ZnCl_2$ was added until the suspensions finally contained 1.0 or 0.1 m*M* Zn. Subsequently 0.100*M* NaCl was added until each suspension contained 0.010*M* Na in solution. Deionized water was added to adjust the volume to 350 mL. Using a Radiometer ABU 80 autoburette and stirring constantly, 0.100*M* NaOH was slowly added (about 0.02 mmol/min) to the suspensions until a pH of 6.0 was reached. The final volume of 400 mL was obtained by adding deionized water using a balance. The suspensions were shaken constantly for the duration of the experiment (21 days). At t= 1, 2, 3, 7, 14 and 21 days the pH of the suspensions were measured and at the same time under constant stirring 25 mL of each suspension was pipetted into a centrifuge tube and centrifuged at 2300 g for 20 minutes. One drop of concentrated nitric acid was added to the supernatant of the subsample and stored overnight at 5°C. The Al, Zn, Na and citrate concentrations in the supernatant were determined. Citrate was determined the next day after taking the subsample to avoid lowering of the citrate concentration by microbiological degradation. Sorbed citrate, Zn and Al were calculated based on the measured concentrations in the supernatant and total amounts present in the system. In comparable preliminary experiments no Si was present in the supernatant, suggesting that no clay was decanted.

Extraction with $La(NO_3)_3$

To the clay residue in the centrifuge tubes, 20 mL 0.0033*M* $La(NO_3)_3$ was added. The suspensions were shaken for one hour. The extraction time is long enough to achieve equilibrium because equilibrium is rapidly attained in ion-exchange processes (Inskeep and Baham, 1983; Garcia-Miragaya and Page, 1976). Then the suspensions were centrifuged at 2300 g for 20 minutes. After decantation one drop of concentrated nitric acid was added to the clear extract solutions. The Al, Zn and Na concentrations in the extract were determined. The efficiency to exchange mono- and bivalent ions by La^{3+} can easily be estimated since the selectivity coefficients for La exchange are known (Bruggenwert and Kamphorst, 1979). From simple ion exchange calculations it followed that the amount of La^{3+} (0.066 mmol/20 mL) is enough to remove essentially all Na^+ and Zn^{2+} ions attached to the clay surface in exchangeable form (total surface charge per centrifuge tube: 0.012 meq). La^{3+} also replaces the positively charged exchangeable Al citrate complexes from the clay surface if present. The amount of exchangeable Al^{3+} on the clay surface is negligible since the concentration in solution at pH 6.0 is extremely low (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965). The unbuffered salt solution $La(NO_3)_3$ is not capable to remove the ALHO that is strongly bound to the clay surface (Chapter 2).

Analysis

Na concentrations in the supernatant and La extract were determined by flame emission spectrophotometry (Eppendorf Elex 6361). Zn concentrations in the supernatant were determined by atomic absorption spectrophotometry (Instrumentation Laboratory S11). Al concentrations in the supernatant and La extract were determined by spectrophotometry. Al ions form a red-coloured complex with the colour reagent Eriochrome Cyanine R. (Hill, 1966). The absorbance of the complex was measured in a continuous-flow analysis system (Skalar) at 595 nm. Citrate was determined in the supernatant by the enzymatic reaction of citrate with citrate lyase (Anonymous, 1989). The amount of oxidized NADH originating from the enzymatic reaction is stoichiometric with the amount of citrate. NADH is determined by means of the spectrophotometric determination at 340 nm (Hitachi 100-20). To avoid the complexation of citrate with Al which disturbs the enzymatic reaction, 0.2 mL 0.2*M* NaF was added to the (plastic) cuvet (volume solution 3 mL).

Results and Discussion

As described in the experimental section, all systems were made by adding clay, citric acid, $AlCl_3$ and $ZnCl_2$ at the same time. Subsequently, the systems were titrated to pH 6.0, and Al hydroxide polymers (denoted as ALHO) were formed. On the other hand, no $Zn(OH)_2$ precipitate was formed, since the log IAP calculated in the equilibrium solution was always lower than the log K_{so} for $Zn(OH)_2$ (-15.5 according to Smith and Martell, 1981). After about 20 hours (t= 1), Na, Al and Zn concentrations attained equilibrium in the supernatant solution. However, citrate concentrations in the supernatant solution decreased slowly until t= 21 days, probably due to microbiological degradation. Other experiments showed that a reaction time of 20 hr was enough to achieve equilibrium before any degradation of citrate by microbes (Cambier and Sposito, 1991). All data in this chapter are based on a reaction time of 20 hr (t= 1).

Results will be presented showing the effects of two different concentrations of citrate on Zn sorption by clay/Al hydroxide systems (denoted as CALHO) with three Al:clay ratios at an initial pH of 6.0. The pH of the clay suspensions were measured the next day, and varied from 6.01 to 6.43 (Table 1). In the ionic- exchange calculations we always used the actual pH. The ionic strength increased as the loading of the clay with Al hydroxide polymers formed in the presence of citrate (denoted as ALHOC) increased, because of the different amounts of $AlCl_3$ that had to be added. The ionic strength (I) varied from 0.012 to 0.019 (Table 1).

According to Stevenson and Fitch (1986), approximate concentrations of individual simple organic acids in the soil solution vary from 1 m*M* to 4 m*M*. We used an initial citrate concentration within this range (1.0 m*M*) and a lower concentration (0.1 m*M*) to ensure that some ALHOC formed at the Al:clay ratio chosen. Table 1 shows the total amounts of Al, citrate and Zn present, the concentrations in the supernatant solution and the amounts sorbed after a reaction time of 20 hr. The initial amounts of citrate added were 0.199 mol (= 0.1 m*M*) and 1.99 mol (= 1.0 m*M*) per kg of clay. About 5-10% of the citrate was sorbed by the CALHO systems, probably present as a co-precipitate of citrate and ALHO which is weakly bound to the clay surface (Chapter 5)(a

CALHO/citrate system is denoted as CALHOC). At an initial concentration of 0.1 m*M* citrate added, the citrate:Al molar ratio in the co-precipitate ranges from 0.01 to 0.04, whereas at 1.0 m*M* citrate a ratio of 0.5 was found. Since no Al was determined in the La extract, no exchangeable Al citrate complexes were sorbed to the clay surface.

Chapter 2 showed that when clay and Al are added at the same time and titrated to pH 6.6, all added Al is present as ALHO. When besides clay and ALHO also citrate is present, the amount of ALHOC formed is influenced and Al citrate complexes become important in solution (Goh and Huang, 1984 and 1986; Violante and Jackson, 1981; Chapter 5). This follows also from Table 1. The initial added amounts of Al were 0.77, 1.16 and 1.93 mol/kg clay. As can be seen from the amounts of Al sorbed in Table 1, a considerable amount of Al is present as soluble Al citrate complexes, especially at 1.0 m*M* citrate concentration.

When we compare the Zn concentrations shown in Table 1 at 0.1 and 1.0 m*M* citrate concentrations, it appears that the Zn concentration in solution is slightly increased at the higher citrate concentration, probably because soluble Zn citrate complexes were formed. Increasing the citrate concentration greatly affects the concentration of Al in solution. At 0.1 m*M* citrate in solution, the concentration of Al in solution is about 0.15 m*M*, irrespective of the Al:clay ratio. The ALHOC probably acts like a reservoir with a constant solubility product, buffering the citrate concentration. At 1.0 m*M* citrate the amount of dissolved Al increases with increasing amounts of Al added. The ALHOC reservoir is severely depleted by Al citrate complexation (Table 1).

Hence, citrate influences Zn sorption both by forming Zn citrate complexes and by inhibiting the formation of ALHOC. Zn citrate complexation reduces the activity of Zn^{2+} and thus the sorption of Zn^{2+} ions on the clay surface. Complexation of Al by citrate reduces the amount of ALHOC and thus the sorption of Zn on the ALHOC. Figure 1 shows the total Zn sorption ($Q_{Zn,t}$ in mol/kg clay) to CALHOC systems in the presence of citrate for three Al:clay ratios. The solid lines give for two Al:clay ratios the total Zn sorption for CALHO systems in the absence of citrate as found in Chapter 3. Compared to the pure CALHO systems, total Zn sorption is strongly influenced when 1.0 m*M* citrate is added. This is due to Zn and Al complexation by citrate. Total Zn sorption is only slightly influenced when 0.1 m*M* citrate is added. The binding of Zn to the ALHOC is still an important process despite the added citrate.

The total Zn sorption is the amount of Zn that compensates for part of the remaining CEC plus the amount that is bound to the ALHOC. Since the two processes are chemically different, it is important to be able to discriminate the total observed sorption between them. Therefore it is necessary to be able to "speciate" the Zn in the system among Zn and Zn citrate complexes in solution,

Table 1 Total amounts initial present, the concentrations in the supernatant solution and the amounts sorbed of Al, Zn and citrate. The data are related to different CALHOC/Zn systems (clay content 0.5 g/L).

total amounts initial present (m*M*)					**supernatant analyses** (m*M*)			**sorbed** (mol/kg clay)		
Al	citrate	Zn	I	pH	Al	citrate	Zn	ALHOC	citrate	Zn
0.4	1.0	1.0	0.016	6.43	0.276	0.935	0.889	2.22	0.130	0.203
0.4	1.0	0.1	0.016	6.23	0.276	0.923	0.100	2.22	0.154	0
0.6	1.0	1.0	0.017	6.22	0.500	0.911	0.887	1.63	0.178	0.208
0.6	1.0	0.1	0.016	6.18	0.485	0.911	0.100	1.92	0.178	0
1.0	1.0	1.0	0.019	6.07	0.776	0.935	0.905	3.86	0.130	0.172
1.0	1.0	0.1	0.017	6.24	0.791	0.899	0.090	3.57	0.202	0.018
0.4	0.1	1.0	0.014	6.01	0.135	0.093	0.796	5.05	0.013	0.389
0.4	0.1	0.1	0.012	6.02	0.191	0.091	0.041	3.92	0.018	0.116
0.6	0.1	1.0	0.015	5.98	0.128	0.089	0.789	9.05	0.023	0.402
0.6	0.1	0.1	0.012	6.12	0.206	0.095	0.039	7.50	0.010	0.120
1.0	0.1	1.0	0.016	6.06	0.131	0.081	0.762	16.70	0.039	0.457
1.0	0.1	0.1	0.013	6.06	0.181	0.090	0.027	15.71	0.020	0.144

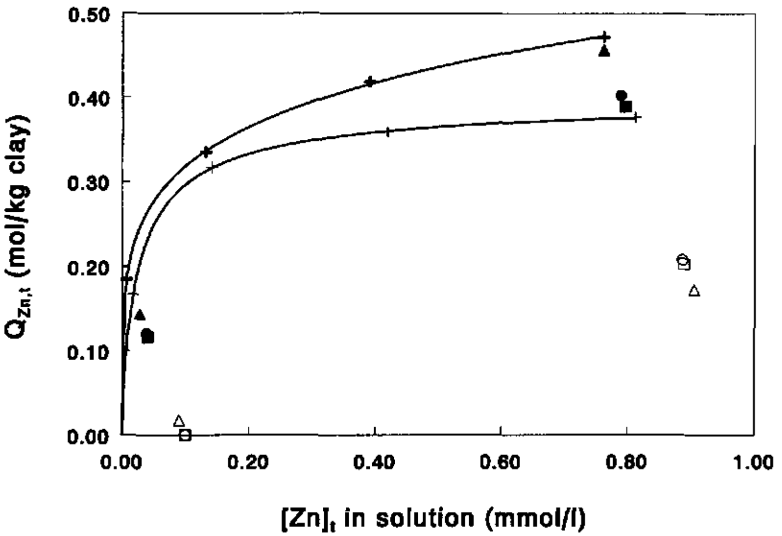

Figure 1 Total Zn binding ($Q_{Zn,t}$) by CALHO and CALHOC vs. [Zn] in the equilibrium solution. The symbols refer to different loadings of the clay with Al and to two total citric acid concentrations added. The loadings of Al in mol/kg of clay are: + = 0.80 and + = 2.00 for CALHO systems (no citrate present); □/■ = 0.77; ○/• = 1.16; △/▲ = 1.93 for CALHOC systems (citrate present). Closed symbols indicate that 0.1 m*M* citric acid was added; open symbols indicate that 1.0 m*M* citric acid was added. The lines are smooth curves drawn through the data points for the systems with no citric acid added.

Zn that forms part of the exchangeable ions on the clay surface (denoted as Zn-CEC); and Zn specifically bound to the ALHOC (denoted as Zn-ALHOC). The La extraction procedure cannot be used directly to assess the exchangeable Zn, since part of the Zn may be released from the Zn-ALHOC.

The value of Zn-CEC can be calculated using an ion exchange model. We used the following exchange model to estimate Zn-CEC:

$$\frac{M_{Zn}}{M_{Na}^{2}} = K_{V(Zn/Na)} \times \frac{(Zn^{2+})}{(Na^{+})^{2}} \qquad (1)$$

where $K_{V(Zn/Na)}$ is the Vanselow selectivity coefficient (Vanselow, 1932) for exchange of Na^+ ions for Zn^{2+} ions; M_{Na} and M_{Zn} are the molar fractions of Na^+ and Zn^{2+} bound to the exchange sites with respect to the total amount of cations bound; and the brackets indicate the activity of the ions in solution. Na^+ and Zn^{2+} activities in solution were calculated.

In equation (1) the molar fractions M_{Na} and M_{Zn} can be derived from the ion exchange equation using $K_{V(Zn/Na)}$, (Na^+) and (Zn^{2+}) as inputs and realizing that M_{Na} + M_{Zn} equals one. We determined the Zn-CEC (in mol/kg clay) by combining the amount of exchangeable Na (in mol/kg clay) measured in the La extract and the calculated M_{Na} and M_{Zn}. The Zn-ALHOC was found by subtracting the Zn-CEC from the total Zn sorption measured.

In order to be able to use equation (1), it is necessary to know $K_{V(Zn/Na)}$ and the activity of Zn^{2+} in solution. For the calculation of Zn^{2+}, the stability constants of the various citrate complexes were required. Several literature studies were found concerning the formation constants of Al(III) citrate complexes (Pattnaik and Pani, 1961; Kwong and Huang, 1979; Öhman and Sjöberg, 1983; Motekaitis and Martell, 1984; Gregor and Powell, 1986). Since Pattnaik and Pani (1961) and Kwong and Huang (1979) neglected hydrolysis of the Al^{3+} ion and the formation of ALHO, these studies are only partly relevant for describing our systems. However, the equilibrium constants of Öhman and Sjöberg (1983), Motekaitis and Martell (1984) and Gregor and Powell (1986) are in principle all applicable. Unfortunately, however, there is little agreement between the various authors. To test the validity of the complexation models for our experimental data, calculations were done according to the three models using preliminary CALHOC formation experiments influenced by citrate in the absence of Zn.

The measured total Al concentrations in the equilibrium solution were compared with the calculated Al concentrations. The calculations used the measured citrate and Na concentrations in the equilibrium solution, the equilibrium constants for Al citrate complexes and the citric acid dissociation constants according to Öhman and Sjöberg (1983), or Motekaitis and Martell (1984) or Gregor and Powell (1986). The constant of the Na citrate complex (Martell and Smith, 1977), a constant IAP of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965), and the constants for Al hydrolysis products and Al chloride complexes (Lindsay, 1979) were also used. The ECOSAT program (Keizer and Van Riemsdijk, 1994) was used for all speciation calculations. The calculations showed that the Al concentration in solution was predicted reasonably well when the equilibrium constants of Öhman and Sjöberg (1983) and Motekaitis and Martell (1984) were used in combination with a (constant) solubility product for the ALHOC. Using the equilibrium constants as given by Gregor and Powell (1986) led to values that were much too low values over the whole range (Figure 2).

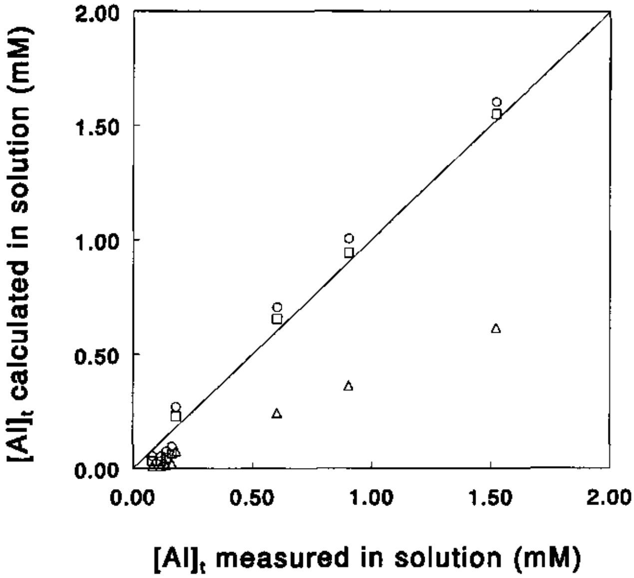

Figure 2 The relation between the total concentration of Al measured in solution and the concentration of Al calculated in CALHOC systems without Zn, according to the Al citrate complexes and citric acid dissociation constants of Öhman and Sjöberg (1983)(□); Motekaitis and Martell (1984)(○); Gregor and Powell (1986)(△).

The same calculations were done for the data of the CALHOC systems with Zn described in this chapter. Again, the concentrations of dissolved Al calculated were compared with measured concentrations of Al in solution. Apart from the input of Na and citrate concentrations and the equilibrium constants mentioned earlier, the Zn concentration and the stability constants of the Zn citrate complexes (Martell and Smith, 1977), Zn hydrolysis products and the Zn chloride complexes (Lindsay, 1979) were also input in the ECOSAT program (Keizer and Van Riemsdijk, 1994). The only Zn citrate complex for the experimental conditions was $ZnCit^-$. There is little disagreement between the various authors about the stability constant of $ZnCit^-$ (Martell and Smith, 1977). A log stability constant for $ZnCit^-$ of 6.27 at zero ionic strength was taken (Martell and Smith, 1977).

The dissolved Al concentrations calculated are shown in Figure 3. No good correlation was found for any of the three models. The equilibrium constants of Gregor and Powell (1986) led to predicted values that were too low. The equilibrium constants of Öhman and Sjöberg (1983) led to predictions that

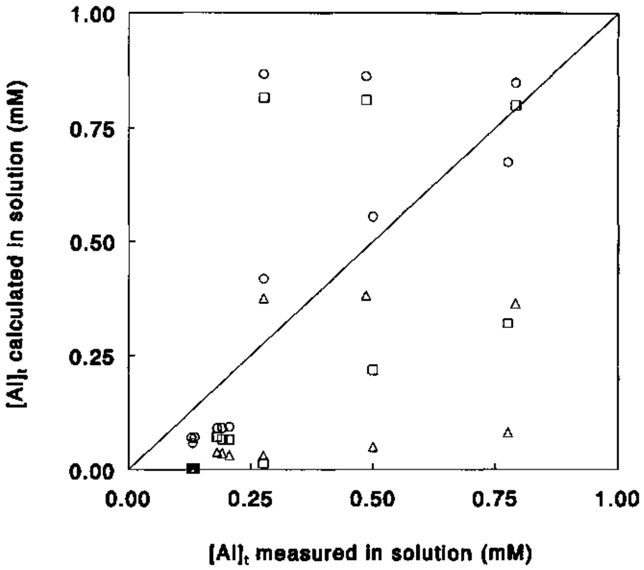

Figure 3 The relation between the total concentration of Al measured in solution and the concentration of Al calculated in CALHOC systems with Zn, according to the Zn citrate complexes of Martell and Smith (1977) and the Al citrate complexes and citric acid dissociation constants of Öhman and Sjöberg (1983)(□); Motekaitis and Martell (1984)(○); Gregor and Powell (1986)(△).

were either too low or too high. Using the equilibrium constants of Motekaitis and Martell (1984), however, led to a reasonable agreement between measurement and prediction for most data points. The wide range of Al:citrate ratios used in these experiments, the influence of Zn citrate complexation or the fact that the assumption of a constant solubility product for ALHOC is an oversimplification, make the Al concentrations in these systems difficult to predict.

Since Motekaitis and Martell (1984) gave the most reasonable predictions of the Al concentration in solution, Zn speciation in solution was calculated by using these complex-forming constants of Al citrate and the citric acid dissociation constants. Still two options are open to calculate the Zn speciation. A constant IAP of 10^{-33} for ALHO on clay (Bruggenwert *et al.*, 1987; Turner and Brydon, 1965) or the measured total concentration Al in solution can be input in the calculation. The latter method is the most direct and reliable.

Finally in order to be able to use equation (1), it is necessary to know $K_{V(Zn/Na)}$. Since ALHO can influence the selectivity coefficient of cation exchange reactions (Barnhisel and Bertsch, 1989; Zelazny and Jardine, 1989), we have to study this more carefully. Kozak and Huang (1971) observed no difference between the selectivity coefficient for K/Ca in a pure Na montmorillonite system and in a Na montmorillonite/ALHO system. On the other hand in Chapter 2 we observed an increase in the selectivity coefficient for Ca/Na exchange when ALHO was present. Using the K_V for Zn/Na exchange as found in CALHO systems ($K_{V(Zn/Na)}$= 2.0; Chapter 2), resulted in values of Zn-CEC that were larger than what was extracted with La^{3+}, which indicated that this estimate is somewhat too high. This is probably due to the weak binding between clay and ALHOC and/or the presence of citrate. According to Goh and Huang (1984 and 1986) the perturbation of the crystallization of Al hydroxides by the presence of citrate is leads to structural distortion of the ALHOC. Using the K_V found in pure clay systems ($K_{V(Zn/Na)}$= 1.2; Chapter 2), resulted in values of Zn-CEC that corresponded very well with the amount extracted with La^{3+}. This indicated that the selectivity coefficient was not affected by the presence of the ALHOC. We therefore used a value of 1.2 for $K_{V(Zn/Na)}$ for ion exchange calculations of the CALHOC systems.

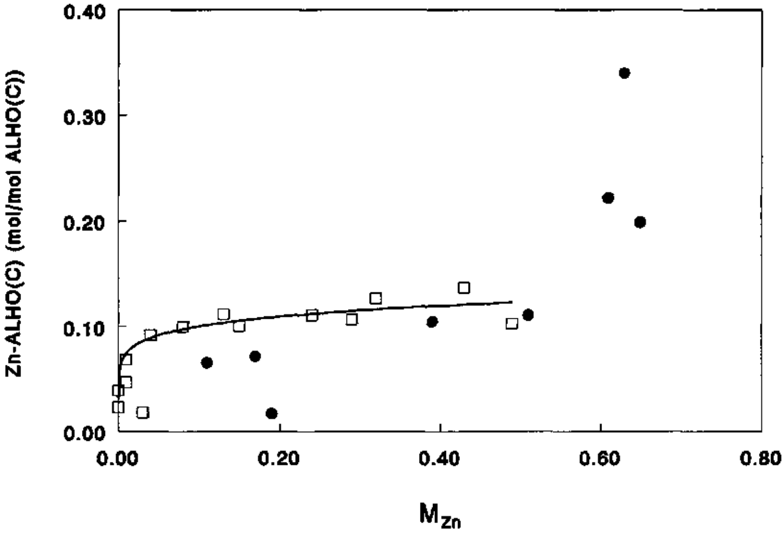

Figure 4 Zn binding by ALHO(C) (Zn-ALHO(C)) per unit ALHO(C). The symbols refer to: □ = no addition of citric acid; • = addition of citric acid. The results are calculated by inputting total dissolved Al in the speciation calculations. The line drawn is a smooth curve through the data points for systems with no citric acid added.

Thereafter, Zn-CEC and Zn-ALHOC were calculated by using equation (1). In Figure 4 the Zn-ALHOC (as mol per mol of ALHOC) calculated using total dissolved Al as input in the speciation calculations, is plotted against the molar fraction of Zn^{2+} (M_{Zn}). Occasionally, no Zn-ALHOC was calculated because in some systems only a small amount of ALHOC was formed.

In Chapter 3 Zn sorption to aged CALHO systems was studied, which were made by being left for one week before adding Zn, at pH 5.0 and 6.6. At pH 6.6 a strongly non-linear isotherm was found between Zn-ALHO (in mol per mol of ALHO) and M_{Zn}. The plateau of the curve shows an adsorption maximum of 0.12 mol Zn-ALHO per mol of ALHO. This is shown in Figure 4 by a solid line through the data points.It can be concluded from Figure 4 that for $M_{Zn}<0.5$, Zn-ALHOC formation in CALHOC systems in the presence of citrate is only slightly reduced and is still an important process compared to Zn-ALHO in aged CALHO systems in the absence of citrate.

For CALHOC where $M_{Zn}>0.5$, a very high molar ratio of bound Zn to ALHOC was observed, which suggested that a solid solution or co-precipitate between ALHOC and Zn hydroxide may have been formed (Farley *et al.*, 1985).

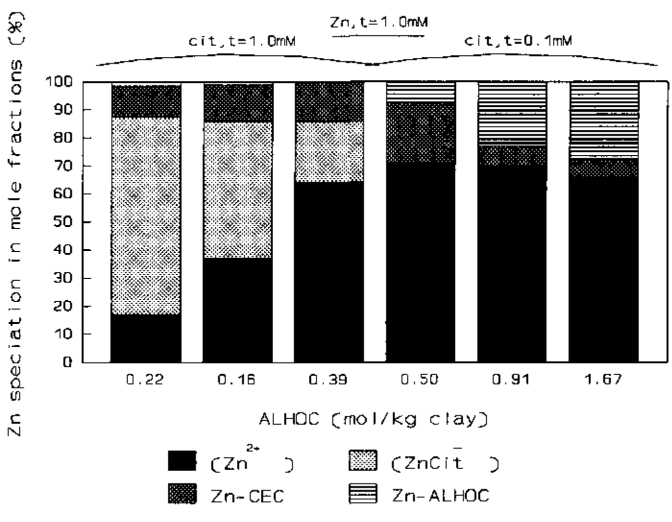

Figure 5a The speciation of Zn among Zn^{2+} and Zn citrate complexes in solution, Zn sorbed on the clay surface (Zn-CEC) and Zn sorbed to ALHOC (Zn-ALHOC) as mole fractions of the total Zn present (Zn,t). Zn,t= 1.0 m*M*. Total citric acid added (cit,t) for column 1 to 3: 1.0 m*M* and for column 4 to 6: 0.1 m*M*. On the x-axis the amount of ALHOC formed is shown (clay content 0.5 g/L).

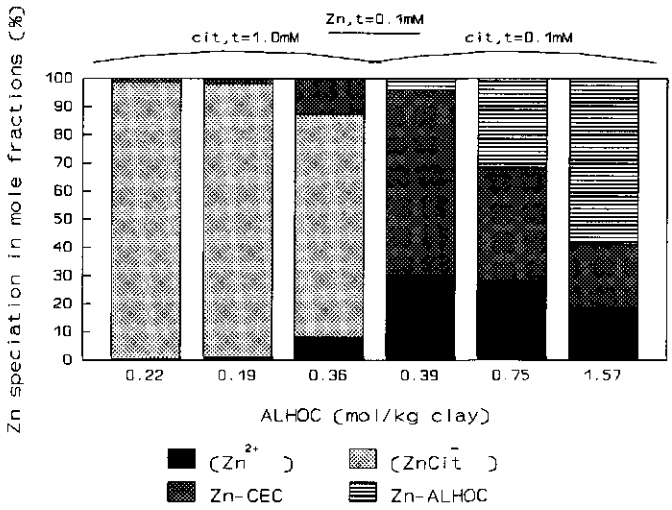

Figure 5b The speciation of Zn among Zn^{2+} and Zn citrate complexes in solution, Zn sorbed on the clay surface (Zn-CEC) and Zn sorbed to ALHOC (Zn-ALHOC) as mole fractions of the total Zn present (Zn,t). Zn,t= 0.1 m*M*. Total citric acid added (cit,t) for column 1 to 3: 1.0 m*M* and for column 4 to 6: 0.1 m*M*. On the x-axis the amount of ALHOC formed is shown (clay content 0.5 g/L).

A precipitate of Zn hydroxide is not very likely because the concentrations of Zn added always led to undersaturation with respect to Zn hydroxide.

The main effects of citrate under these conditions were the amount of ALHOC formed and the complexation in solution, which could be accounted for via the solution complexation in combination with the ion exchange model.

In Figures 5a and 5b the speciation of Zn among Zn^{2+} and Zn citrate complexes in solution, Zn-CEC and Zn-ALHOC as mole fractions (in %) of the total Zn present in the systems is shown. Zn speciation is calculated according to Motekaitis and Martell (1984) using the measured total dissolved Al concentration as input in the model calculation in combination with the ion-exchange model. Other Zn species did not account for the total Zn concentration in the systems. The results are given for various amounts of ALHOC formed expressed in mol/kg clay. As shown earlier, the amount of ALHOC formed depended on the concentration of citrate present and the total amount of Al added. With increasing concentration of citrate, less ALHOC was formed for the same amount of Al added. Zn also slightly influences the amount of ALHOC.

At higher Zn concentrations, more ALHOC was formed, because Zn competes with Al for citrate.

At high citrate concentrations most of the Zn occurred as Zn citrate complexes and Zn^{2+}. Only a small amount of Zn was present as Zn-CEC and Zn-ALHOC. When the citrate concentration was lowered, the $ZnCit^-$ part was strongly reduced and the fractions Zn^{2+}, Zn-CEC and Zn-ALHOC became more important. Zn was predominantly bound to the ALHOC at low Zn and citrate concentrations. As expected, Zn sorption to the ALHOC increased with increasing loading of the clay with ALHOC. Zn-ALHOC predominated over Zn-CEC when about 1 mol Al per kg of clay was formed.

Overall it can be concluded that the binding of Zn to ALHOC was important when 0.1 m*M* citrate was added to CALHOC systems (Al:citrate molar ratio ranged from 10:1 to 4:1). In the presence of 1.0 m*M* citrate (Al:citrate molar ratio ranged from 1:1 to 1:2.5), Al- and Zn citrate complexes in solution became important and Zn-ALHOC was almost absent.

Acknowledgements

The authors would like to thank Mr. E.M. Wittich for analytical assistance. This work was partly funded by the Netherlands Integrated Soil Research Programme under contractnumber PCBB 8964.

References

Anonymous. 1989. *Methods of biochemical analysis and food analysis using single reagents.* Boehringer Mannheim GmbH, Mannheim.

Argersinger, W.J., Davidson, A.W. and Bonner, O.D. 1950. Thermodynamics and ion exchange phenomena. *Kans. Acad. Sci. Trans.*, **53,** 404-410.

Banin, A. 1968. Ion exchange isotherms of montmorillonite and structural factors affecting them. *Isr. J. Chem.*, **6,** 27-36.

Barnhisel, R.I. and Bertsch, P.M. 1989. Chlorites and hydroxy-interlayered vermiculite and smectite. In: J.B. Dixon and S.B. Weed (eds.), *Minerals in soil environments,* 2nd ed., pp.729-788. Soil Sci. Soc. Am., Madison, WI.

Bar On, P., Shainberg, I. and Michaeli, I. 1970. Electrophoretic mobility of montmorillonite particles saturated with Na/Ca ions. *J. Colloid Interface Sci.*, **3,** 471-472.

Blackmore, A.V. and Miller, R.D. 1961. Tactoid size and osmotic swelling in calcium montmorillonite. *Soil Sci. Soc. Am. Proc.*, **25,** 169-173.

Bolt, G.H. 1955. Ion adsorption by clays. *Soil Sci.*, **79,** 267-276.

Bolt, G.H. 1979. The ionic distribution in the diffuse double layer. In: G.H. Bolt (ed.), *Soil chemistry B. Physico-chemical models,* pp.1-25. Elsevier Scientific Publishing Company, Amsterdam.

Bowden, J.W., Nagarajah, S., Barrow, N.J., Posner, A.M. and Quirk, J.P. 1980. Describing the adsorption of phosphate, citrate and selenite on a variable-charge mineral surface. *Aust. J. Soil Res.*, **18,** 49-60.

Bruggenwert, M.G.M. 1972. Adsorption of Al-ions to the clay mineral montmorillonite. Ph.D. thesis, Wageningen Agricultural University (in Dutch).

Bruggenwert, M.G.M. and Kamphorst, A. 1979. Survey of experimental information on cation exchange in soil systems. In: G.H. Bolt (ed.), *Soil chemistry B. Physico-chemical models,* pp.141-203. Elsevier Scientific Publishing Company, Amsterdam.

Bruggenwert, M.G.M., Keizer, P. and Koorevaar, P. 1987. Adsorption of aluminum ions by montmorillonite: influence on aluminum speciation. *Neth. J. Agric. S.*, **35,** 259-269.

Buondonno, A., Felleca, D. and Violante, A. 1989. Properties of organo-mineral complexes formed by different addition sequences of hydroxy-Al, montmorillonite, and tannic acid. *Clays Clay Miner.*, **37,** 235-242.

Cambier, P. and Sposito, G. 1991. Interactions of citric acid and synthetic hydroxy-aluminum montmorillonite. *Clays Clay Miner.*, **39,** 158-166.

Carstea, D.D. 1968. Formation of hydroxy-Al and -Fe interlayers in montmorillonite and vermiculite: influence of particle size and temperature. *Clays Clay Miner.*, **16,** 231-238.

Chairidchai, P. and Ritchie, G.S.P. 1990. Zinc adsorption by a lateritic soil in the presence of organic ligands. *Soil Sci. Soc. Am. J.*, **54,** 1242-1248.

Chairidchai, P. and Ritchie, G.S.P. 1992. The effect of pH on zinc adsorption by a lateritic soil in the presence of citrate and oxalate. *J. Soil Sci.*, **43,** 723-728.

Davies, B.E. 1990. Lead. In: B.J. Alloway (ed.), *Heavy metals in soils*, pp.177-196. Blackie Academic and Professional, Glasgow.

Dixon, J.B. and Jackson, M.L. 1962. Properties of intergradient chlorite-expansible layer silicates of soils. *Soil Sci. Soc. Am. Proc.*, **26,** 358-362.

Farley, K.J., Dzombak, D.A. and Morel, F.M.M. 1985. A surface precipitation model for the sorption of cations on metal oxides. *J. Colloid Interface Sci.*, **106,** 226-242.

Fergusson, J.E. 1990. *The heavy elements: chemistry, environmental impact and health effects.* Pergamon Press, Oxford.

Frink, C.R. 1965. Characteristics of aluminum interlayers in soil clays. *Soil Sci. Soc. Am. Proc.*, **29,** 379-382.

Gaines, G.L. and Thomas, H.C. 1953. Adsorption studies on clay minerals. II A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.*, **21,** 714-718.

Garcia-Miragaya, J. and Page, A.L. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. *Soil Sci. Soc. Am. J.*, **40,** 658-663.

Glaeser, R. and Méring, J. 1954. Isothermes d'hydratation des montmorillonites bi-ioniques (Na,Ca). *Clay Min. Bull.*, **12,** 188-193.

Goh, T.B. and Huang, P.M. 1984. Formation of hydroxy-Al-montmorillonite complexes as influenced by citric acid. *Can. J. Soil Sci.*, **64,** 411-421.

Goh, T.B. and Huang, P.M. 1986. Influence of citric and tannic acids on hydroxy-Al interlayering in montmorillonite. *Clays Clay Miner.*, **34,** 37-44.

Gregor, J.E. and Powell, H.K.J. 1986. Aluminium(III)-citrate complexes: a potentiometric and ^{13}C N.M.R. study. *Aust. J. Chem.*, **39,** 1851-1864.

Harsh, J.B. and Doner, H.E. 1984. Specific adsorption of copper on an hydroxy-aluminium-montmorillonite complex. *Soil Sci. Soc. Am. J.*, **48,** 1034-1039.

Harsh, J.B. and Doner, H.E. 1985. The nature and stability of aluminum hydroxide precipitated on Wyoming montmorillonite. *Geoderma*, **36,** 45-56.

Hiemstra, T., Van Riemsdijk, W.H. and Bruggenwert, M.G.M. 1987. Proton adsorption mechanism at the gibbsite and aluminium oxide solid/solution interface. *Neth. J. Agric. S.*, **35,** 281-293.

Hiemstra, T., De Wit, J.C.M. and Van Riemsdijk, W.H. 1989. Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: a new approach II. Application to various important (hydr)oxides. *J. Colloid Interface Sci.*, **133,** 105-117.

Hill, U.T. 1966. New direct spectrophotometric determination of aluminium in steel, spelter, and iron ores. *Anal. Chem.*, **38,** 654-656.

Inskeep, W.P. and Baham, J. 1983. Adsorption of Cd(II) and Cu(II) by Na-montmorillonite at low surface coverage. *Soil Sci. Soc. Am. J.*, **47,** 660-665.

Janssen, R.P.T., Bruggenwert, M.G.M. and Van Riemsdijk, W.H. 1991. Interaction of heavy metals in the system clay, Al-hydroxide polymers and citric acid. In: J.G. Farmer (ed.), *Proc. Int. Conf. Heavy Metals in the Environment,* Edinburgh, Sept. 1991, Vol. 1: pp.173-176. CEP Consultants, Edinburgh.

Kallay, N. and Matijević, E. 1985. Adsorption at solid/solution interfaces. 1. Interpretation of surface complexation of oxalic and citric acids with hematite. *Langmuir* **1,** 195-201.

Keizer, P. and Bruggenwert, M.G.M. 1991. Adsorption of heavy metals by clay-aluminum complexes. In: G.H. Bolt, M.F. De Boodt, M.H.B. Hayes and M.B. McBride (eds.), *Interactions at the soil colloid-soil solution interface,* pp.177-203. Kluwer Academic Publishers, Dordrecht.

Keizer, M.G. and Van Riemsdijk, W.H. 1994. *ECOSAT, a computer program for the calculation of speciation and transport in soil-water systems.* Department of Soil Science and Plant Nutrition, Wageningen Agricultural University.

Keren, R., Gast, R.G. and Barnhisel, R.I. 1977. Ion exchange reactions in nondried Chambers montmorillonite hydroxy-aluminum complexes. *Soil Sci. Soc. Am. J.*, **41,** 34-39.

Keren, R. 1979. The effect of hydroxy-aluminum precipitation on the exchange properties of montmorillonite. *Clays Clay Miner.*, **27,** 303-304.

Keren, R. 1980. Effects of titration rate, pH, and drying process on cation exchange capacity reduction and aggregate size distribution of montmorillonite hydroxy-aluminum complexes. *Soil Sci. Soc. Am. J.*, **44,** 1209-1212.

Kiekens, L. 1990. Zinc. In: B.J. Alloway (ed.), *Heavy metals in soils*, pp.261-279. Blackie Academic and Professional, Glasgow.

Kielland, J. 1935. Thermodynamics of base-exchange equilibria of some different kinds of clays. *J. Cos. Chem. Ind.*, **54,** 232-234.

Kinniburgh, D.G., Syers, J.K. and Jackson, M.L. 1975. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminium. *Soil Sci. Soc. Am. Proc.*, **39,** 464-470.

Kinniburgh, D.G., Jackson, M.L. and Syers, J.K. 1976. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. *Soil Sci. Soc. Am. J.*, **40,** 796-799.

Kozak, L.M. and Huang, P.M. 1971. Adsorption of hydroxy-Al by certain phyllosilicates and its relation to K/Ca cation exchange selectivity. *Clays Clay Miner.*, **19,** 95-102.

Kummert, R. and Stumm, W. 1980. The surface complexation of organic acids on hydrous γ-Al_2O_3. *J. Colloid Interface Sci.*, **75,** 373-385.

Kwong, K. F. Ng Kee and Huang, P.M. 1979. The relative influence of low-molecular-weight, complexing organic acids on the hydrolysis and precipitation of aluminum. *J. Soil Sci.*, **128,** 337-342.

Lindsay, W.L. 1979. *Chemical equilibria in soils.* John Wiley and Sons, New York.

Maes, A. 1973. Ion exchange of some transition metal ions in montmorillonite and synthetic faujasites. Ph.D. thesis, University of Leuven.

Martell, A.E. and Smith, R.M. 1977. *Critical stability constants. Volume 3: other organic ligands.* Plenum Press, New York.

McBride, M.B. 1980. Interpretation of the variability of selectivity coefficients for exchange between ions of unequal charge on smectites. *Clays Clay Miner.*, **28,** 255-261.

Micera, G., Gessa, C., Melis, P., Premoli, A., Dallocchio, R. and Deiana, S. 1986. Zinc(II) adsorption on aluminium hydroxide. *Colloids Surfaces* **17,** 389-394.

Motekaitis, R.J. and Martell, A.E. 1984. Complexes of aluminum(III) with hydroxy carboxylic acids. *Inorg. Chem.*, **23,** 18-23.

Norrish, J. and Quirk, J.P. 1954. Crystalline swelling of montmorillonite. *Nature,* **173,** 255-257.

Öhman, L.-O. and Sjöberg, S. 1983. Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. Part 9. A potentiometric study of mono- and poly-nuclear aluminium(III) citrates. *J. Chem. Soc. Dalton Trans.*, 2513-2517.

Parker, D.R., Zelazny, L.W., and Kinraide, T.B. 1989. Chemical speciation and plant toxicity of aqueous aluminum. In: T.E. Lewis (ed.), *Environmental chemistry and toxicology of aluminum,* 2nd printing 1990, pp.117-145. Lewis Publishers Inc., Chelsea, Michigan.

Pattnaik, R.K. and Pani, S. 1961. Studies on the citrate complex of aluminium(III). *Jour. Indian Chem. Soc.*, **38,** 379-384.

Rich, C.I. and Obenshain, S.S. 1955. Chemical and clay mineral properties of a red-yellow podzolic soil derived from muscovite schist. *Soil Sci. Soc. Am. Proc.*, **19,** 334-339.

Rich, C.I. 1968. Hydroxy interlayers in expansible layer silicates. *Clays Clay Miner.*, **16,** 15-30.

Sawhney, B.L. 1960. Aluminium interlayers in clay minerals, montmorillonite and vermiculite: laboratory synthesis. *Nature,* **187,** 261-262.

Sawhney, B.L. 1968. Aluminium interlayers in layer silicates - effect of OH/Al ratio of Al solution, time of reaction, and type of structure. *Clays Clay Miner.*, **16,** 157-163.

Schwertmann, U. 1962. Die selektieve Kationensorption der Tonfraktion einiger Böden as Sedimenten. *Z. Pflanzenernaehr. Dueng. Bodenkd.*, **97,** 9-25.

Secor, R.B. and Radke, C.J. 1985. Spillover of the diffuse double layer on montmorillonite particles. *J. Colloid Interface Sci.*, **103,** 237-244.

Shainberg, I. and Kemper, W.D. 1966. Electrostatic forces between clay and cations as calculated and inferred from electrical conductivity. *Clays Clay Miner.*, **14,** 117-132.

Shainberg, I. and Otoh, H. 1968. Size and Shape of montmorillonite particles saturated with Na/Ca ions (inferred from viscosity and optical measurements). *Isr. J. Chem.*, **6,** 251-259.

Shainberg, I., Oster, J.D. and Wood, J.D. 1980. Sodium/calcium exchange in montmorillonite and illite suspensions. *Soil Sci. Soc. Am. J.*, **44,** 960-964.

Shen, M.J., and Rich, C.I. 1962. Aluminium fixation in montmorillonite. *Soil Sci. Soc. Am. Proc.*, **26,** 33-36.

Sillén, L.G. and Martell, A.E. 1964. *Stability constants of metal-ion complexes.* Spec. Publ. No. 17, The Chemical Society, London.

Smith, R.M. and Martell, A.E. 1981. *Critical stability constants. Volume 4: inorganic complexes,* 2nd printing. Plenum Press, New York.

Sposito, G. and Mattigod, S.V. 1979. Ideal behavior in Na^+-trace metal cation exchange on Camp Berteau montmorillonite. *Clays Clay Miner.*, **27,** 125-128.

Sposito, G., Holtzclaw, K.M., Johnston, C.T. and LeVesque-Madore, C.S. 1981. Thermodynamics of sodium-copper exchange on Wyoming bentonite at 298 K. *Soil Sci. Soc. Am. J.*, **45,** 1079-1084.

Sposito, G., Holtzclaw, K.M., Charlet, L., Jouany, C. and Page, A.L. 1983a. Sodium-calcium and sodium-magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. *Soil Sci. Soc. Am. J.*, **47,** 51-56.

Sposito, G., Holtzclaw, K.M., Jouany, C. and Charlet, L. 1983b. Cation selectivity in sodium-calcium, sodium-magnesium, and calcium-magnesium exchange on wyoming bentonite at 298 K. *Soil Sci. Soc. Am. J.*, **47,** 917-921.

Sprycha, R. 1989. Electrical double layer at alumina/electrolyte interface. II. Adsorption of supporting electrolyte ions. *J. Colloid Interface Sci.*, **127,** 12-25.

Stevenson, F.J. and Fitch, A. 1986. Chemistry of complexation of metal ions with soil solution organics. In: P.M. Huang, and M. Schnitzer (eds.), *Interactions of soil minerals with natural organics and microbes,* pp.29-58. Spec. Publ. No. 17, Soil Sci. Soc. Am., Madison, WI.

Turner, R.C. and Brydon, J.E. 1965. Factors affecting the solubility of $Al(OH)_3$ precipitated in the presence of montmorillonite. *Soil Sci.*, **100,** 176-181.

Van Bladel, R., Gavria, G. and Laudelout, H. 1972. A comparison of the thermodynamic, double layer theory and empirical studies of the Na-Ca exchange equilibria in clay water systems. In: J.M. Serratosa (ed.), *Proc. Int. Clay Conf.*, Madrid, 1972, pp.385-398.

Van Bladel, R. and Gheyi, H.R. 1980. Thermodynamic study of calcium-sodium and calcium-magnesium exchange in calcareous soils. *Soil Sci. Soc. Am. J.*, **44,** 938-942.

Van Bladel, R., Halen, H. and Cloos, P. 1993. Calcium-zinc and calcium-cadmium exchange in suspensions of various types of clays. *Clay minerals*, **28,** 33-38.

Vanselow, A.P. 1932. Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. *Soil Sci.*, **33,** 95-113.

Violante, A. and Jackson, M.L. 1981. Clay influence on the crystallization of aluminum hydroxide polymorphs in the presence of citrate, sulfate or chloride. *Geoderma*, **25,** 199-214.

Waldron, H.A. 1980. Lead. In: H.A. Waldron (ed.), *Metals in the environment,* pp.155-197. Academic Press, London.

Warkentin, B.P., Bolt, G.H. and Miller, R.D. 1957. Swelling pressure of montmorillonite. *Soil Sci. Soc. Am. Proc.*, **21,** 495-497.

Wild, A. and Keay, J. 1964. Cation-exchange equilibria with vermiculite. *J. Soil Sci.*, **15,** 135-144.

Worrall, W.E. 1968. *Clays, their nature, origin and general properties.* Maclaren and Sons, London.

Zelazny, L.W. and Jardine, P.M. 1989. Surface reactions of aqueous aluminum species. In: G. Sposito (ed.), *The environmental chemistry of aluminum,* pp.147-184. CRC Press, Boca Raton, FL.

Zhang, Y., Kallay, N. and Matijević, E. 1985. Interactions of metal hydrous oxides with chelating agents. 7. Hematite-oxalic acid and -citric acid systems. *Langmuir*, **1,** 201-206.

Summary

Heavy metal ions are trace elements, usually found in low concentrations in natural, unpolluted soils. However, they are input to the environment in relatively large amounts as a result of human activity, thereby increasing the heavy metal level in soils. Heavy metal ions in soils are mainly bound to clay minerals, hydroxides of Al, Fe and Mn and organic matter present in soils. Their mobility can be increased strongly, e.g. through complexation by soluble organic acids or soil acidification by acid rain. Mobilization of heavy metal ions, facilitates their uptake by plants, human beings and animals. Therefore it is of great practical interest and importance to have a better insight into the interactions that influence the binding and related mobility of heavy metal ions in soils.

Many studies reported in the literature focus on the behaviour of heavy metal ions in terms of their interaction with clay minerals or Al hydroxide or organic matter. Heavy metal ions react to these reactive phases in different ways. They bind reversibly on clay minerals via an ion-exchange reaction. Heavy metal ions bind specifically to the reactive sites present on the Al hydroxide particles. The term "specific sorption" implies complexation (chemisorption) by singly coordinated OH groups present on the surface of the Al hydroxide particles. Heavy metal ions form complexes with so-called functional groups (mainly carboxyl and phenolic OH-groups) present on organic matter.

Clay minerals, Al hydroxide and organic matter can bind heavy metal ions; moreover they also interact with each other. These mutual interactions influence the metal binding to a significant extent. So, neither the interaction between metal ions nor the mixture of clay minerals, Al hydroxide and organic matter can be calculated from the weighted summation of the interaction of heavy metal ions with the individual components using models of binding for each separate component of the mixture. Unfortunately, little is known about this, since only a few studies have investigated heavy metal binding to multi-component systems. However, this knowledge is essential in order to predict the behaviour of heavy metal ions in natural soil systems which always consist of a mixture of soil components. In this study, the binding of the heavy metal ions Zn and Pb is investigated in model systems consisting of various combinations of the clay mineral montmorillonite (Na saturated), Al hydroxide and citric acid (as an example of a soluble low molecular organic acid).

Chapter 2 investigates the interaction between montmorillonite and Al hydroxide and its influence on the cation exchange. Al ions added to a clay suspension give rise to the binding of different Al species (Al^{3+}, $AlOH^{2+}$,

$Al_2(OH)_2^{4+}$, ... Al hydroxide polymers). The speciation of the Al in the adsorption phase is a function of pH, ionic strength, type of competitive cations and total amount of Al present. At increasing pH the speciation shifts towards the Al hydroxide polymers (in this thesis denoted as ALHO). At decreasing pH the extent of Al^{3+} bound as exchangeable cation to the clay surface increases. ALHO binds irreversibly to the siloxane surface of phyllosilicate clay minerals, forming layers of ALHO between the clay platelets and reducing the cation exchange capacity (CEC). At pH 6.6 and a total salt concentration of 0.01*M* Na in solution, the reduction of the CEC is linearly dependent on the amount of ALHO fixed (i.e. nonexchangeable). This suggests that under these conditions the nature of the ALHO is independent of the degree of loading of the clay with ALHO in the range of loadings studied. The constant average charge of the ALHO was determined to be 0.25+ per Al atom. At pH 6.6 exchangeable Al^{3+} ions are negligible.

At pH 5.0 the situation is different. The reduction of the CEC is no longer linearly dependent on the amount of ALHO fixed. The average charge per Al atom decreases with increasing loading with ALHO. This suggests that the nature of these Al species changes towards increased polymerization with increasing Al:clay ratio. As expected, at pH 5.0 the average charge per Al atom of the ALHO was always higher than the constant average charge of 0.25+ found at pH 6.6. At pH 5.0 Al^{3+} ions play a role and are present as exchangeable cations on the clay surface.

In clay/ALHO systems (in this thesis denoted as CALHO), heavy metal ions can bind to two adsorption sites. They can bind to the siloxane surface by becoming part of its charge compensation and by specific sorption to the ALHO present on the clay surface. Since these two adsorption processes are chemically different, they have a different impact on the behaviour of Zn and Pb in CALHO systems. It is important to discriminate the total observed Zn and Pb binding into the different parts. However here a problem arises. The aggregation of clay minerals changes as a result of the presence of the ALHO. This influences the exchange behaviour of the siloxane surface. The exchange behaviour cannot be measured directly in CALHO systems when Zn and Pb ions are involved. The effect of the presence of ALHO on the exchange coefficient is estimated by extrapolating the Zn/Na and Pb/Na exchange coefficient measured in pure clay systems with the effect of ALHO on the Ca/Na exchange. Based on this a speciation model is developed to determine the distribution of Zn and Pb in CALHO systems over all the phases present.

In chapter 3 this model is used to describe the speciation of Zn in a number of CALHO systems which differ in pH and Al:clay ratio. The pH has a very strong effect on the Zn binding. At pH 6.6 the total Zn binding is greater to CALHO than to the pure clay. This is the result of the Zn ions being bound to the ALHO. At pH 5.0, the total Zn binding is less to the CALHO than to the pure clay. There are three reasons for this: the affinity of ALHO for Zn ions decreases strongly with decreasing pH; moreover, the CEC of the siloxane surface decreases with pH, due to the increasing surface charge of the ALHO; and finally Al^{3+} adsorption to the clay surface becomes important and competes with Zn^{2+} for exchange sites.

The effect of the Al:clay ratio on the Zn binding is influenced by the pH. At pH 6.6 Zn binding to the ALHO, expressed per mole ALHO, is independent of the Al:clay ratio. This is because the nature of the ALHO is independent of the degree of loading of the clay with ALHO at pH 6.6. On the other hand, Zn binding to the ALHO at pH 5.0, expressed per mole ALHO, is dependent on the Al:clay ratio. This is because at pH 5.0 the nature of the ALHO depends on the degree of loading of the clay with ALHO. With increasing loading of the clay with ALHO, the average charge per Al atom decreases and the amount of Zn binding to the ALHO per mole ALHO increases.

The results of the speciation calculations show the difference in Zn ion binding to the ALHO and siloxane surfaces. The binding of Zn to the ALHO is especially great for very low Zn concentrations where the binding curves for Zn binding to the ALHO are very steep. The maximum amount of Zn bound to the ALHO is reached already at low Zn concentrations. The Zn binding to the clay surface increases slowly with increasing Zn concentration. The available binding sites on the ALHO apparently have a high affinity for Zn ions. Zn binding on the siloxane surface becomes more important when the binding sites on the ALHO are nearly all occupied.

Zn bound to the ALHO cannot be removed by exchange with high concentrations of cations that do not bind specifically to the ALHO surface. If CALHO is present in natural soils, Zn binding to the ALHO will strongly influence Zn availability.

Chapter 4 describes the binding of Pb to CALHO systems which differ in pH and Al:clay ratio. Three adsorption processes can be distinguished. Pb can be bound to the siloxane surface and the ALHO, just as found for the adsorption of Zn ions. Moreover, at increasing Pb concentrations and pH, Pb hydroxide polymers can be formed which bind irreversibly to the clay surface, reducing the CEC in a manner similar to the binding of the ALHO polymers.

At pH 6.6 the presence of the ALHO on the clay leads to more Pb binding than in a pure clay system. The greater adsorption of the CALHO system is the result of Pb binding to the ALHO and the formation of Pb polymers.

For CALHO systems at pH 6.0 it is shown that no Pb hydroxide polymers are formed. The total Pb binding to CALHO is less than that binding to the pure clay. Using the speciation model, the contribution of Pb over the different phases is calculated. The results of the calculated speciation show that the minority of the adsorbed Pb is bound to the siloxane surface. The remaining part is adsorbed to the ALHO. This amount adsorbed increases with increasing amount of ALHO fixed, when expressed per mole Al. The ALHO shows a very high affinity for Pb ions, whereas the Pb binding to the siloxane surface increases slowly with increasing Pb concentration. Pb bound to the ALHO can be desorbed by adding high concentrations of cations.

When the same system is investigated at pH 5.0 a strong reduction of the Pb binding occurs, because Al^{3+} ions compete with Pb^{2+} for exchangeable sites, and because hardly any binding to the ALHO takes place under these conditions.

Chapter 5 deals with the influence of citric acid on the formation and stability of CALHO complexes. Organic acids of low molecular weight, such as citric acid, are commonly present in the natural environment and form complexes with Al ions and may thus influence the binding properties and formation of the CALHO system. The interaction depends strongly on the conditions under which the CALHO has been formed.

When citrate is added to an aged CALHO system, citrate does not sorb to the ALHO but only to the edge faces of the clay. This is probably due to the strong repulsive force which the citrate molecules encounter when they approach the negatively charged clay platelets and/or the result of the conformation of the citrate molecules which may prevent them from entering the interlayer between two clay platelets. At increasing citrate:Al ratio an increasing fraction of the ALHO of the aged CALHO systems dissolve. The nature of the remaining ALHO is not affected by the dissolution of a part of the ALHO.

Citric acid perturbs the formation of the ALHO, when clay, Al hydroxide and citric acid are added simultaneously. This process is dependent on the citrate:Al ratio. At a low citrate:Al ratio, ALHO is formed and citrate is incorporated in the ALHO probably leading to a co-precipitate. The amount of citrate incorporated is linearly dependent on the amount of ALHO present. Co-precipitation of ALHO and citrate probably leads to the formation of a separate phase which is only weakly bound to the clay particles. Soluble Al citrate complexes become dominant as the citrate:Al ratio increases, and only a small part of the Al is present as ALHO.

The Al concentration in the equilibrium solution can be calculated using Al citrate complexation constants and citric acid dissociation products found by Motekaitis and Martell (1984) and Öhman and Sjöberg (1983).

The binding of Zn during the formation of a clay/ALHO/citrate complex is discussed in chapter 6. In such a system, citrate forms dissolved Al citrate and Zn citrate complexes. The distribution of Zn over the various species is calculated with a speciation model using constants for dissolved complexes in combination with an ion-exchange equation. Different sets of complexation constants can be found in literature. The constants for the various Al citrate complexes and citric acid dissociation products of Motekaitis and Martell (1984) lead to a reasonably good interpretation of the results.

The calculated amounts of Zn bound to the CALHO formed in the presence of citrate at a low citrate:Al ratio, are compared with Zn binding to CALHO systems in the absence of citrate. When the molar fraction of Zn bound to the exchange sites is smaller than 0.5, only slightly less Zn is sorbed to the ALHO in the presence of citrate than is sorbed to ALHO in the absence of citrate. The binding of Zn to the ALHO is still an important process, despite the presence of citrate. For molar fractions of Zn larger than 0.5, binding of Zn to the ALHO increases strongly in the presence of citrate. This suggests the formation of a co-precipitate or solid solution between ALHO, Zn hydroxide and citrate. At increasing citrate:Al ratios Zn sorption decreases strongly. This is due to Zn and Al complexation by citrate.

Samenvatting

Zware metaalionen zijn spoorelementen, die in natuurlijke niet verontreinigde bodems gewoonlijk in lage concentraties voorkomen. Echter, door menselijke activiteiten zijn ze in relatief grote hoeveelheden in het milieu terechtgekomen, hierdoor zijn de gehaltes aan zware metalen in bodems sterk verhoogd. Zware metaalionen worden in bodems hoofdzakelijk gebonden aan de in bodems voorkomende kleimineralen, Al-, Fe- en Mn-hydroxyden, en organische stof. Hun mobiliteit kan sterk worden vergroot door complexatie met opgeloste organische stof of door bodemverzuring door zure regen. Door de mobilisatie van zware metalen wordt de opname door planten, dieren en mensen vergemakkelijkt. Daarom is het van groot praktisch belang om beter inzicht te krijgen in de interacties welke de binding en de daaraan gerelateerde mobiliteit van zware metalen in bodems beïnvloedt.

Vele studies in de literatuur beschrijven het gedrag en de interacties van zware metaalionen met kleimineralen of Al-hydroxyde of organische stof. Zware metaalionen binden op verschillende manieren met deze reactieve fasen. Zij binden reversibel aan kleimineralen via een ionenomwisellingsreactie. Zware metaalionen binden specifiek met de reactieve bindingsplaatsen van de Al-hydroxyde deeltjes. Waarbij de term "specifieke binding" aangeeft dat er complexvorming optreedt met enkelvoudig gebonden OH-groepen die aanwezig zijn op het oppervlak van de Al-hydroxyde deeltjes. Zware metaalionen tenslotte, vormen complexen met de functionele groepen (hoofdzakelijk carboxyl- en fenolische OH-groepen) van organische stof.

Kleimineralen, Al-hydroxyde en organische stof kunnen zware metaalionen binden, maar ze kunnen ook met elkaar interacties aangaan. Deze onderlinge interacties beïnvloeden de metaalbinding in sterke mate. Hierdoor kunnen de interacties die optreden in een systeem bestaande uit een mengsel van zware metalen, kleimineralen, Al-hydroxyde en organische stof niet worden berekend op grond van de sommatie van de interacties van de zware metalen met de individuele bodemcomponenten. Helaas is hierover weinig bekend aangezien er slechts weinig studies zijn waarin de metaalbinding aan deze multicomponent systemen wordt onderzocht. Echter, deze kennis is essentieel om het gedrag van zware metaalionen te kunnen voorspellen aangezien natuurlijke bodemsystemen altijd uit een mengsel van bodemcomponenten bestaan. In dit onderzoek wordt de binding van de zware metalen Zn en Pb onderzocht in modelsystemen welke bestaan uit verschillende combinaties van het kleimineraal montmorilloniet (Na verzadigd), Al-hydroxyde en citroenzuur (als voorbeeld van een opgelost laagmoleculair organisch zuur).

In hoofdstuk 2 zijn de interacties tussen montmorilloniet en Al-hydroxyde, en de invloed van deze interacties op de kationenomwisseling bestudeerd. Wanneer Al ionen worden toegevoegd aan een kleisuspensie, kunnen de verschillende gevormde Al species (Al^{3+}, $AlOH^{2+}$, $Al_2(OH)_2^{4+}$, ... Al-hydroxyde polymeren) worden geadsorbeerd. De Al speciatie in de adsorptiefase is een functie van pH, ionensterkte, type van competatieve ionen en totale hoeveelheid Al. Met toenemende pH neemt de relatieve hoeveelheid Al-hydroxyde polymeren (ALHO) als aandeel van de Al species toe. Met afnemende pH neemt de hoeveelheid omwisselbaar Al^{3+} aan het kleioppervlak toe. ALHO bindt irreversibel aan het siloxaanoppervlak van phyllosilicaat kleimineralen. Het vormt lagen tussen kleiplaatjes en verlaagt de kationen omwisselingscapaciteit (CEC). Bij pH 6,6 en een totale zoutconcentratie van 0,01*M* Na in oplossing, neemt de CEC rechtevenredig af met de hoeveelheid vastgelegde ALHO (d.w.z. niet uitwisselbaar). Dit suggereert dat onder deze experimentele condities het type ALHO onafhankelijk is van de Al:klei verhouding. De constante gemiddelde lading van de ALHO is bepaald en was 0,25+ per Al atoom. Bij pH 6,6 bleek de hoeveelheid Al^{3+} verwaarloosbaar klein.

Voor pH 5,0 is de situatie anders. De afname van de CEC is niet langer meer rechtevenredig met de hoeveelheid vastgelegde ALHO. De gemiddelde lading per Al atoom neemt af met toenemende Al:klei verhouding. Dit suggereert dat bij toenemende Al:klei verhouding, ALHO wat betreft hoeveelheid, het belangrijkste Al specie is. Zoals verwacht mag worden is bij pH 5,0 de lading van de ALHO per Al atoom, altijd groter dan de constante gemiddelde lading van 0,25+ bij pH 6,6. Bij pH 5,0 zijn omwisselbare Al^{3+} ionen aanwezig aan het kleioppervlak.

In klei/ALHO (CALHO) systemen, kunnen zware metaalionen binden aan twee verschillende adsorptieplaatsen. Ze kunnen binden aan het siloxaanoppervlak van de klei of door specifieke adsorptie aan het op het kleioppervlak aanwezige ALHO. Omdat deze twee processen chemisch gezien verschillend zijn, hebben ze een verschillende invloed op het gedrag van Zn en Pb in CALHO systemen. Daarom is het belangrijk om de gemeten totale Zn en Pb adsorptie te kunnen onderscheiden in de twee verschillende delen. Helaas is dit niet zonder meer mogelijk. De ruimtelijke ordening van de kleiplaatjes verandert door de aanwezigheid van de ALHO. Hierdoor verandert ook het omwisselingsgedrag van het siloxaanoppervlak. Het omwisselingsgedrag van Zn en Pb kan niet rechtstreeks in CALHO systemen worden gemeten. Het effect van de aanwezigheid van ALHO op de Zn/Na en Pb/Na omwisselingscoëfficiënt, is geschat door extrapolatie van de gemeten Zn/Na en Pb/Na omwisselingscoëfficiënt in pure kleisystemen en het effect van ALHO op de Ca/Na omwisseling. Gebaseerd op deze metingen is een speciatiemodel ontwikkeld voor de bepaling van de verdeling van Zn en Pb in CALHO systemen over alle aanwezige fasen.

Dit model is in hoofdstuk 3 gebruikt om de speciatie van Zn in een aantal CALHO systemen welke verschillen in pH en Al:klei verhouding te beschrijven. De pH heeft een zeer groot effect op de Zn binding. De totale Zn binding bij pH 6,6 is voor CALHO systemen groter dan voor de pure klei. Dit komt doordat Zn ionen worden gebonden aan de ALHO. De totale Zn binding bij pH 5,0 is voor CALHO systemen kleiner dan voor de pure klei. Dit wordt door drie redenen veroorzaakt: de affiniteit van Zn ionen voor de ALHO neemt sterk af met dalende pH; door de toenemende lading van de ALHO bij een dalende pH daalt de CEC van het siloxaanoppervlak; en tenslotte wordt Al^{3+} adsorptie aan het kleioppervlak belangrijk en concurreert met Zn^{2+} om de omwisselingsplaatsen.

Het effect van de Al:klei verhouding op de Zn binding wordt beïnvloed door de pH. De Zn binding bij pH 6,6, uitgedrukt per mol ALHO, is onafhankelijk van de Al:klei verhouding. Dit komt doordat het type ALHO onafhankelijk is van de Al:klei verhouding bij pH 6,6. Anderszins is de Zn binding bij pH 5,0, uitgedrukt per mol ALHO, afhankelijk van de Al:klei verhouding. Dit komt omdat het type ALHO afhankelijk is van de Al:klei verhouding bij pH 5,0. Met toenemende Al:klei verhouding, daalt de lading per Al atoom en de hoeveelheid Zn gebonden aan de ALHO per mol ALHO neemt toe.

De resultaten van de speciatieberekeningen tonen de verschillen tussen de Zn binding aan de ALHO en het siloxaanoppervlak. De Zn binding aan de ALHO is juist groot bij zeer lage Zn concentraties omdat de bindingscurven voor de Zn binding aan de ALHO erg stijl zijn. De maximum hoeveelheid gebonden Zn aan de ALHO wordt reeds bereikt bij lage Zn concentraties. De Zn binding aan het kleioppervlak neemt langzaam toe met toenemende Zn concentratie. De beschikbare bindingsplaatsen aan de ALHO hebben blijkbaar een zeer hoge affiniteit voor Zn ionen. Zn binding aan het siloxaanoppervlak wordt belangrijk wanneer de bindingsplaatsen aan de ALHO vrijwel allemaal bezet zijn.

Zn ionen die zijn gebonden aan de ALHO kunnen niet worden gedesorbeerd met hoge concentraties kationen die niet specifiek binden aan het ALHO oppervlak. Wanneer CALHO aanwezig is in natuurlijke bodems, beïnvloedt dit in hoge mate de beschikbaarheid van Zn.

In hoofdstuk 4 wordt de Pb binding aan CALHO systemen beschreven, welke verschillen in pH en Al:klei verhouding. Drie sorptieprocessen kunnen worden onderscheiden. Pb kan net als Zn worden gebonden aan het siloxaanoppervlak en de ALHO. Tevens kunnen bij toenemende Pb concentraties en pH, Pb-hydroxyde polymeren worden gevormd die irreversibel binden aan het kleioppervlak. Net als bij de binding van ALHO, wordt hierdoor de CEC verlaagd.

Bij pH 6,6 leidt de aanwezigheid van ALHO op de klei tot meer Pb binding dan aan pure kleisystemen. Deze toename wordt veroorzaakt door Pb binding aan de ALHO en vorming van Pb-hydroxyde polymeren.

Adsorptie van Pb aan het siloxaanoppervlak van de pure klei bij pH 6,0, gaat gepaard met de vorming van Pb-hydroxyde polymeren; dit treedt ook op in systemen waarbij het ionenprodukt veel kleiner is dan het oplosbaarheidsprodukt van $Pb(OH)_2$. Aangetoond wordt dat voor de gemeten experimentele condities geen Pb-hydroxyde polymeren worden gevormd. De totale Pb binding is voor CALHO systemen groter dan voor de pure klei. Met behulp van het speciatiemodel is de verdeling van Pb over de verschillende fasen berekend. De speciatieberekeningen laten zien dat een ondergeschikte hoeveelheid van het geadsorbeerde Pb, gebonden is aan het siloxaanoppervlak. Het resulterende gedeelte is geadsorbeerd aan de ALHO. De hoeveelheid Pb gebonden aan de ALHO, uitgedrukt per mol ALHO, neemt toe met toenemende hoeveelheid gebonden ALHO. De beschikbare bindingsplaatsen aan de ALHO hebben een zeer hoge affiniteit voor Pb ionen, terwijl de Pb binding aan het siloxaanoppervlak langzaam toeneemt met stijgende Pb concentratie. Pb gebonden aan de ALHO kan worden gedesorbeerd door toevoeging van hoge concentraties kationen.

Wanneer hetzelfde systeem wordt bestudeerd bij pH 5,0, blijkt dat de Pb binding sterk afneemt. Dit wordt veroorzaakt door competitie van Al^{3+} met Pb^{2+} om adsorptieplaatsen aan het kleioppervlak en omdat nauwelijks enig Pb bindt aan de ALHO onder de experimentele condities.

Hoofdstuk 5 behandelt de invloed van citroenzuur op de vorming en stabiliteit van CALHO systemen. Laagmoleculaire organische zuren zoals citroenzuur, zijn een normaal bestanddeel van natuurlijke bodems. Citroenzuur vormt met Al ionen complexen en kunnen hierdoor de bindingseigenschappen en de vorming van CALHO systemen beïnvloeden. Welke interacties optreden hangt sterk af van de omstandigheden waaronder de CALHO systemen zijn gevormd.

Wanneer citraat wordt toegevoegd aan een verouderde CALHO, adsorbeert het citraat niet aan de ALHO maar alleen aan de zijkanten van de kleiplaatjes. Dit wordt waarschijnlijk veroorzaakt door de sterke afstotende kracht die de citraatmoleculen ondervinden wanneer ze de negatief geladen kleiplaatjes benaderen. Een andere verklaring zou kunnen zijn dat de ruimtelijke ordening van de citraatmoleculen verhindert dat ze tot de ALHO kunnen doordringen welke zich tussen twee kleiplaatjes bevindt. Bij een toenemende Al:klei verhouding lost een toenemend gedeelte van de ALHO van een verouderde CALHO op. Het type van de resterende ALHO wordt niet beïnvloed door het gedeeltelijk oplossen van de ALHO.

Citroenzuur verhindert de vorming van de ALHO wanneer klei, Al-hydroxyde en citroenzuur gelijktijdig worden toegevoegd. Dit proces is afhankelijk van de citraat:Al verhouding. Bij lage citraat:Al verhoudingen wordt ALHO gevormd en citraat geïncorporeerd in de ALHO, dit leidt waarschijnlijk tot de vorming van een co-precipitaat. De hoeveelheid citraat die geïncorporeerd wordt in de ALHO is rechtevenredig met de hoeveelheid gevormde ALHO. De co- precipitatie van ALHO en citraat leidt waarschijnlijk tot de vorming van een aparte fase, welke slechts zwak gebonden is aan de kleideeltjes. Opgeloste Al-citraat complexen worden belangrijk wanneer de citraat:Al verhouding toeneemt, een klein gedeelte van de Al is dan nog slechts aanwezig als ALHO.

De Al concentratie in de evenwichtsoplossing kan worden berekend door de Al-citraat complexerings- en de citroenzuur dissociatieconstanten van Motekaitis en Martell (1984) en Öhman and Sjöberg (1983) te gebruiken.

De binding van Zn tijdens de vorming van een klei/ALHO/citraat systeem wordt bediscussieerd in hoofdstuk 6. In zo'n systeem vormt citraat Al- en Zn-citraat complexen. De verdeling van Zn over de verschillende species wordt berekend m.b.v. het speciatiemodel dat gebruik maakt van de constanten van de opgeloste complexen in combinatie met een ionenomwisselingsvergelijking. In de literatuur kunnen verschillende series complexeringsconstanten worden gevonden. De constanten van de Al-citraatcomplexering en de citroenzuurdissociatie van Motekaitis en Martell (1984) leiden tot een redelijke goede interpretatie van de resultaten.

De berekende hoeveelheden Zn gebonden aan de ALHO, welke gevormd werden in de aanwezigheid van citraat (lage citraat:Al verhoudingen), zijn vergeleken met de Zn binding aan CALHO in afwezigheid van citraat. Wanneer de molfractie van Zn gebonden aan de omwisselingsplaatsen kleiner is dan 0,5, is slechts een kleine hoeveelheid minder Zn gebonden aan de ALHO welke gevormd is in de aanwezigheid van citraat in vergelijking met Zn gebonden aan de ALHO in afwezigheid van citraat. Hierdoor blijkt dat de binding van Zn aan de ALHO nog steeds een belangrijk proces is, ondanks de aanwezigheid van citraat. Voor Zn molfracties groter dan 0,5, neemt in aanwezigheid van citraat, de Zn binding sterk toe. Dit suggereert de vorming van een co-precipitaat of "solid solution" tussen ALHO, Zn-hydroxyde en citraat. Met toenemende citraat:Al verhoudingen neemt de Zn adsorptie sterk af. Dit wordt veroorzaakt door complexatie van Zn en Al met citraat.

Dankwoord

Hierbij wil ik iedereen bedanken die een bijdrage in de totstandkoming van dit proefschrift hebben geleverd. Enkele wil ik met name noemen.

Allereerst wil ik mijn begeleider, co-promotor en initiator van het onderzoek beschreven in dit boekje, Theo Bruggenwert bedanken. Hij heeft altijd met zeer veel enthousiasme en toewijding dit onderzoek begeleid.
Mijn promotor, Willem van Riemsdijk bedank ik voor zijn begeleiding, enorme inzet en belangstelling.
Bert Wittich bedank ik voor de analytische ondersteuning en goede ideeën, Peer Keizer voor theoretische ondersteuning en het kritisch doorlezen van het proefschrift.
De vakgroep Bodemkunde & Plantevoeding wil ik bedanken voor de gastvrijheid en de ondersteuning, en het Speerpuntprogramma Bodemonderzoek voor het scheppen van de financiële mogelijkheden voor het project.
In het kader van een afstudeervak heeft Grietje van Dijk meegewerkt aan ons onderzoek. Ik bedank haar voor haar bijdrage en inzet.
Tenslotte wil ik mijn ouders, Léon en Annelies bedanken voor hun overall support gedurende de gehele promotietijd.

René Janssen
Wageningen, mei, 1995.

Levensloop

René Janssen werd geboren op 22 december 1962 in Roermond. Hij doorliep de H.A.V.O. aan het St. Ludgercollege in Doetinchem. Hierna startte hij in 1980 met de opleiding tot laboratoriumassistent aan de O.L.A.N. in Arnhem. In 1983 behaalde hij hiervoor het diploma en begon hierop aansluitend met een éénjarige V.W.O. avondopleiding aan de scholengemeenschap Oost-Gelderland in Doetinchem. In 1984 startte hij met de studie Milieuhygiëne aan de Landbouwuniversiteit in Wageningen. Als afstudeervakken werden gedaan bodemkwaliteitsbeheer (hoofdvak), grond- en gewasanalyse en hydrogeologie. Het doctoraalexamen werd afgelegd in september 1989. In de periode van december 1989 tot september 1994 werd het in dit boekje beschreven promotieonderzoek uitgevoerd aan de vakgroep Bodemkunde en Plantevoeding van de Landbouwuniversiteit in Wageningen. Sinds 1 september 1994 is hij aangesteld als tijdelijk wetenschappelijk medewerker bij het Laboratorium voor Ecotoxicologie van het Rijksinstituut voor Volksgezondheid en Milieuhygiëne (R.I.V.M.) in Bilthoven.