CLAY LANDFILL LINERS SUBJECT TO VARIABLE INTERFACIAL REDOX AND PH CONDITIONS – HEAVY METAL AND CLAY INTERACTIONS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Civil and Environmental Engineering

by

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Abstract

Municipal landfill leachate contains high levels of metal species, including Cu, Zn, Cd and Pb generating competitive interactions between these metal species and the landfill clay liner materials. Characterization of the clay fraction, physical and chemical characteristics of landfill clay liner materials, the competitive interaction of metal species with clay liner materials, the kinetic modeling of metal species transport in clay liner, and the effect of cyclic interfacial redox potential on the structural changes to the clay liner and leachate metal transport were investigated in this study. The clay liner materials studied included Na-bentonite, kaolinite and Amite soil (sandy silty clay). Results indicate metal species interaction with bentonite is predominantly an ion exchange process. Competitive Freundlich isotherms were utilized to describe the interaction of metal species with the clay liner materials. The affinities of the three clay materials with metal species decreased in the order of: bentonite > Amite Soil > kaolinite while the relative affinities with the three clays followed a consistent trend of Pb > Cu > Zn > Cd. A surface complexation model (the diffuse-double layer model) was applied to model the interaction of Cu, Zn, Cd and Pb with the three clay liner materials. The complexation constants of each metal species with the clay liner materials were determined. The introduction of Mg or Ca in rainfall-runoff residual leachate decreased the metal species adsorption capacities by up to 50%. First order reaction could be utilized to describe the rate of metal species binding onto uncompacted clays. A shrinking-core model and pore and surface diffusion model were also tested to model the binding of metal species onto compacted clays. The clay liners were exposed to cyclic redox potentials (-200 mV, 0 mV and +300 mV) and the experimental results indicated that pore size distribution and hydraulic conductivity were changed for bentonite and Amite soil clay liners. However, kaolinite clay liner showed little changes either in porosity or hydraulic conductivity.
Chapter 1. Introduction

METAL SPECIES IN URBAN RAINFALL-RUNOFF

The Effects of Metal Species Toxicity

Metals are some of the most abundant elements in the earth and about 80% of elements in the periodic table are classified as metals (Novotny 1995). Of the various metals, as many as 75% are defined as heavy metals. Metal species are generally considered to be those whose density exceeds 5 grams per cubic centimeter. Some of the trace metals are necessary elements for mammals since they are important components of co-enzymes which are essential to the metabolism of organisms (Forstner and Wittman 1981). However, human activity has drastically changed the biogeochemical cycles and balance of some metal species and the metal species in excessive quantity are proven to be catastrophic to human beings. Metal species are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Therefore, they tend to be accumulated in environment. The toxicity of metal species has been recognized and during the last 2-3 decades considerable attention has been given to problems concerning negative effects of metal species (Vernet 1991).

Metal species are not easily discharged from the human body and instead they linger and accumulate while exerting their toxic effects and the damage of heavy metal is likely to be permanent and irreversible. On the basis of experimental and statistical research, the effects of metal species on human health have been ascertained and it was found that toxic metals may interfere with the normal function of any system of the body. For example, once absorbed, Cu and Zn are distributed primarily to the liver, kidneys, spleen, heart, lungs, stomach, intestines, nails, and hair and individuals with copper toxicity show an abnormally high level of copper in the liver, kidneys, brain, eyes and bones (www.epa.org). Animal studies on copper toxicity have
also shown varying degrees of liver and kidney damage (necrosis of the kidney; sclerosis, necrosis, and cirrhosis of the liver), decreased total weight, brain weight and red blood cell count, increased platelet counts and the presence of gastric ulcers (Rana and Kumar 1978). Cd was classified by USEPA as a probable human carcinogen (Harte et al. 1991). Chronic exposure to Cd is also associated with a wide range of other diseases, including heart disease, anemia, skeletal weakening, depressed immune system response, and kidney and liver disease. The target tissues suffering from Cd attacking include: appetite and pain centers (in brain), brain, heart and blood vessels, kidneys, and lungs (Pouls 2002). Pb affects human nervous system, the production of blood cells, kidneys, the reproductive system, and behavior at relatively low levels of exposure. Pb has also been attributed as a factor in the decline of the Roman Empire.

**Metal Species in Transportation Land Use Rainfall-runoff**

Urban storm runoff and snowmelt typically carry a mixture of metal species, entrained particulate matter, inorganic and organic constitutes. In urban transportation corridors, infrastructure and traffic generate metal species through leaching processes and vehicular and tire-pavement abrasion mechanisms. Treadware, paint, brake abrasion, and car body corrosion are well-documented heavy metal sources associated with normal highway traffic. Treadware can generate a wide gradation of particulate materials which contains metals. These metals are commonly used as additives in the tires. When the paint is sanded or scraped, some metals can be distributed in the highway. The metal species used in many paints include: cadmium, zinc, titanium, chromium, cooper, antimony and strontium chromate. In the same way, brake abrasion and car body corrosion can produce many metallic materials since either the parts or the body of car are made of metals. These dissolved and particulate materials are trans-located from their
mobile and infrastructure sources and can be wet or dry deposited in surrounding surficial environment.

As a result of anthropogenic activities, high concentrations of metal species such as Pb and Cd have been detected in the bodies of wild city pigeons in the high traffic density area (Schilderman et al. 1997) and it was found that the higher traffic density, the higher heavy metal concentrations. Valiulis et al. (2000) found that there were enrichments of heavy metal in the road dust and these metals were due to traffic emission. These heavy metal enriched dusts could be swept by precipitation and made the runoff contaminated with metal species. Metal species are an important group of anthropogenic constituents that exhibits persistence, bioaccumulation, toxicity and non-degradability in the environment. The transportation sources of metal species include brake linings, tire abrasion, vehicular parts abrasion, and infrastructure degradation and leaching (Sansalone and Buchberger 1997 and David et al. 2001). Particulates can also be generated from traffic activities, pavement and infrastructure degradation and maintenance, and littering (Sansalone et al. 1998). These particulate materials can be in a wide gradation ranging in size from smaller than 1 µm (colloidal material) to greater than 10,000 µm (silt or gravel). As a result, rainfall-runoff and snowmelt have been recognized as the “wastewater” of the next decade.

In response to the Clean Water Act (CWA), the USEPA developed the National Pollutant Discharge Elimination System (NPDES) Rainfall-runoff Program. As a goal of this program, sources of rainfall-runoff runoff that had the greatest potential to negatively impact water quality were to be permitted and controlled. During the past 20 years, extensive research has been conducted to characterize both the quality and quantity of urban rainfall-runoff (Smith et al. 2001, Wu et al. 1998, Line et al. 1996, Tsihrintzis and Hamid. 1997, Lee and Bang 2000 and Thomson et al. 1997, Tomanovic and Maksimovic 1996, Sansalone and Buchberger 1997, and Sansalone
et al. (1998). For example, a hydraulic model considering the flow hydrograph was used to estimate the loads of Cu, Zn and Pb to the river by Smith et al. 2000. Wu et al. (1998) monitored three highway segments typical of urban, semi-urban and rural settings in North Carolina. They found that runoff from both of the sites generated significant TSS loading associated with nitrogen and phosphorous. Similarly, COD, SS, T-N and T-P, in rainfall-runoff were also evaluated for both combined and separate type sewer systems by Uchimura et al (1997) and Lee and Bang (2000). It was found that there were high concentrations of T-N and T-P in the rainfall-runoff. The water quality of rainfall-runoff runoff from the industrial sites was also studied by Line et al. (1996). A wide range of pollutants, such as metal species (Cu and Zn), organic compounds and pesticides were detected. Some models such Soil Conservation Service hydrology method and empirical equations developed by USEPA were used to perform urban rainfall-runoff quantity and quality modeling (Tsihrintzis and Hamid 1997). Bertrand-Krajewski et al. (1998) used a dimensionless curve of the cumulative pollutant mass vs the cumulative discharged volume to compare pollutant discharge from different rainfall event. It was found that the curves were variable and dependent on the pollutant, the site, the rainfall event and the functioning of the sewer system. Tomanovic and Maksimovic (1996) measured the rainfall intensity, suspended solids, pH, conductivity and temperature in two urban areas in Sweden and Yugoslavia, respectively. A mathematical model was developed to describe suspended solids wash-off. Sansalone and Buchberger (1997) and Sansalone et al. (1998) studied the partition and first flush of metals and the physical characteristics of urban rainfall-runoff solids. They found that Zn, Cd, Cu were mainly in dissolved form while Pb, Fe and Al were mainly particulate-bound.
RAINFALL-RUNOFF BMPS

The significance of rainfall-runoff in affecting water quality in USA has become an increasing concern in recent years, as further improvements are made in controlling other point sources such as municipal sewage and industrial waste (USEPA 1999). As the number of treatment plants providing secondary treatment continues to increase, the importance of rainfall-runoff treatment in limiting the quality of the nation’s streams and rivers is increasing (Metcalf and Eddy 1991). In many river basins, additional treatment beyond secondary treatment will have essentially no impact on stream quality until the rainfall-runoff discharge is controlled. Today, Best Management Practices (BMPs) are being developed and utilized on a site-specific basis all over the country to remove these pollutants from transportation land rainfall-runoff and to improve water quality in downstream.

BMP is defined as a technique, measure or structural control that is used for a given set of conditions to manage the quantity and improve the quality of rainfall-runoff in the most cost-effective manner (USEPA 1999). BMPs can be either engineered and constructed systems (structural BMPs) that improve the quality and/or control the quantity of runoff such as detention ponds and constructed wetlands, or institutional, education or pollution prevention practices designed to limit the generation of rainfall-runoff or reduce the amounts of pollutants contained in the runoff (non-structural BMPs).

The engineered or constructed BMPs are capable of capturing a wide gradation of particulate materials if the BMPs are appropriately designed. Consequently there is an increasing accumulation of metal species in the sludge generated either from the engineered or constructed BMP practice. Table 1.1 is a summary of the properties of rainfall-runoff residuals collected from several site-specific studies (USEPA 1999).
Table 1-1 Properties of urban rainfall-runoff solids/residuals

<table>
<thead>
<tr>
<th>Properties of Residuals</th>
<th>Wet Ponds¹</th>
<th>Sedimentation Basin²</th>
<th>Swirl and Helical Bend In-Line Upsized Solids Separators³</th>
<th>Storm Conduit⁴</th>
<th>Urban Rainfall-runoff Runoff Residuals⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VSS</td>
<td>6%</td>
<td>104-155 mg/L</td>
<td>107-310 mg/L</td>
<td>25,800 mg/L</td>
<td>90 mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>43%</td>
<td>233-793 mg/L</td>
<td>344-1,140 mg/L</td>
<td>161,000 mg/L</td>
<td>415 mg/L</td>
</tr>
<tr>
<td>Nutrients</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorous</td>
<td>583 mg/kg</td>
<td>&lt;5 mg/L</td>
<td>&lt;5 mg/L</td>
<td>0.3-2,250 mg/L</td>
<td>502-1,270 mg/kg</td>
</tr>
<tr>
<td>T-KN</td>
<td>2,931 mg/kg</td>
<td>&lt;5 mg/L</td>
<td>&lt;5 mg/L</td>
<td>0.3-2,250 mg/L</td>
<td>1,140-3,370 mg/kg</td>
</tr>
<tr>
<td>Metal Species</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>6-3,171 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>302-353 mg/kg</td>
</tr>
<tr>
<td>Pb</td>
<td>11-748 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>251-294 mg/kg</td>
</tr>
<tr>
<td>Cr</td>
<td>4.8-120 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>168-458 mg/kg</td>
</tr>
<tr>
<td>Ni</td>
<td>3-52 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>69-143 mg/kg</td>
</tr>
<tr>
<td>Cu</td>
<td>2-173 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>251-294 mg/kg</td>
</tr>
<tr>
<td>Cd</td>
<td>ND-15 mg/kg</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>6.1-2,970 mg/L</td>
<td>6.1-2,970 mg/L</td>
<td>6.1-2,970 mg/L</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Schueler and Yousef, 1994
² Marquette University, 1982 (Racine, Wisconsin)
³ Marquette University, 1982 (Boston, Massachusetts)
⁴ Marquette University, 1982 (Lansing, Michigan)
⁵ Field and O’Shea, 1992.

It can be seen from Table 1-1 that the residuals in the rainfall-runoff runoff may contain a variety of pollutants such as metal species and the proper handling and disposal of these materials is essential and critical.

**LANDFILL CLAY LINER**

**Landfill and Landfill Leachate**

Landfills are the most widely used method of solid waste disposal around the world. This process has been practiced for centuries and will continue to be an important component of municipal solid waste management across the USA. However, with increasing concerns about
landfill leachate as a potential source of soil and groundwater pollution, landfill practices have come under increasing scrutiny in recent decades (Bagchi 1989).

![Figure 1-1 Cross section of an idealized landfill system.](image)

A schematic of landfill is illustrated in Figure 1-1. Typically, a landfill system is composed of clay liner system, leachate collection system, and cover system.

Landfills can receive sludge from wastewater treatment plants generated by treating a mixture of wastewater and urban rainfall-runoff which contains a variety of pollutants such as metal species and rainfall-runoff residuals from rainfall-runoff BMP practices. Under anaerobic condition which is typical inside landfill, organic matter in the residual will first undergo anaerobic digestion and metal species will be released subsequently from the residuals under acidic environment. Therefore, clay-lined landfill systems for the disposal of urban rainfall-runoff and snow melt runoff residuals often contain leachate with high concentrations of metal species, including Cu, Zn, Cd and Pb.

The typical range of concentrations of different contaminants in leachate of municipal waste is listed in Table 1.2 (Bagchi 1989, McGinley and Kmet 1984).
Table 1-2 The Range of concentration of different parameters in leachate of municipal waste.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of Concentration (mg/L except as indicated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>584—55000</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>2—140900</td>
</tr>
<tr>
<td>BOD</td>
<td>ND—195000</td>
</tr>
<tr>
<td>COD</td>
<td>6.6—99000</td>
</tr>
<tr>
<td>pH</td>
<td>3.7—8.9 units</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>ND—15050</td>
</tr>
<tr>
<td>Hardness</td>
<td>0.1—225000</td>
</tr>
<tr>
<td>Chloride</td>
<td>2—11375</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.0—2500</td>
</tr>
<tr>
<td>Sodium</td>
<td>12—6010</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen</td>
<td>2—3320</td>
</tr>
<tr>
<td>Iron</td>
<td>ND—4000</td>
</tr>
<tr>
<td>Potassium</td>
<td>ND—3200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4.0—780</td>
</tr>
<tr>
<td>Sulfate</td>
<td>ND—1850</td>
</tr>
<tr>
<td>Aluminum</td>
<td>ND—85</td>
</tr>
<tr>
<td>Zinc</td>
<td>ND—731</td>
</tr>
<tr>
<td>Manganese</td>
<td>ND—400</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>ND—234</td>
</tr>
<tr>
<td>Boron</td>
<td>0.87—13</td>
</tr>
<tr>
<td>Barium</td>
<td>ND—12.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>ND—7.5</td>
</tr>
<tr>
<td>Nitrate-nitrogen</td>
<td>ND—250</td>
</tr>
<tr>
<td>Lead</td>
<td>ND—14.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>ND—5.6</td>
</tr>
<tr>
<td>Antimony</td>
<td>ND—3.19</td>
</tr>
<tr>
<td>Copper</td>
<td>ND—9.0</td>
</tr>
<tr>
<td>Thallium</td>
<td>ND—0.78</td>
</tr>
<tr>
<td>Cyanide</td>
<td>ND—6.0</td>
</tr>
<tr>
<td>Arsenic</td>
<td>ND—70.2</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.01—1.43</td>
</tr>
<tr>
<td>Tin</td>
<td>ND—0.16</td>
</tr>
<tr>
<td>Nitrite-nitrogen</td>
<td>ND—1.46</td>
</tr>
<tr>
<td>Selenium</td>
<td>ND—1.85</td>
</tr>
<tr>
<td>Cadmium</td>
<td>ND—0.4</td>
</tr>
<tr>
<td>Silver</td>
<td>ND—1.96</td>
</tr>
<tr>
<td>Beryllium</td>
<td>ND—0.36</td>
</tr>
<tr>
<td>Mercury</td>
<td>ND—3.0</td>
</tr>
</tbody>
</table>
Metal species in leachate are an important group of constituents of concern. The occurrence and potential threat of metal species in landfill leachate have been well understood. Since the migration of leachate is often a slow process and the dangerous effects of heavy metal will typically become evident after a long period of time, the prediction of the fate of heavy metal in the leachate is challenging. Metal species are the most frequently detected constitutes in urban rainfall-runoff, snowmelt and various transported urban residual materials. Of the various metal species commonly detected in runoff from transportation land uses, Cu, Zn, Cd and Pb are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA).

**Clay Liner and Clay Mineral**

It can be said that more energy, effort, and resources have gone into the development of clay liner system for hazardous waste disposal facilities than any other technical aspect of landfill (LaGrega et al. 1994). A clay liner consists of one or more layers of cohesive soil that have been compacted to achieve a low permeability. The purpose of a clay liner in a landfill is to serve as a barrier between waste materials and the environment by limiting seepage from the landfill.

Soils may be viewed as a three-phase system composed of solids, liquids and gases. Clays are important constituents of the solid phase in soil, which can be referred as all soil particles with size less than 2 µm (Mitchell 1976). Clay minerals are hydrous silicates with layer structures and they belong to the group of phyllosilicates (Brown 1984, Langmuir 1997). Table 1-3 summarizes some important physical and chemical characteristics of the clay minerals commonly occurring in the soils (Mitchell 1976) while Figure 1-2 is illustrations of the structures of two clay minerals, kaolinite and smectite. It can be seen from Table 1-3 that kaolinite and
smectite represent two extremes: small specific surface area (SSA) with low cation exchange capacity (CEC) and high SSA with high CEC, respectively.

Table 1-3 Clay mineral characteristics.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Basal Spacing (Å)</th>
<th>CEC (meq/100g)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>7.2</td>
<td>3-15</td>
<td>10-20</td>
</tr>
<tr>
<td>Halloysite</td>
<td>7.2</td>
<td>5-10</td>
<td>35-70</td>
</tr>
<tr>
<td>Illite</td>
<td>10</td>
<td>10-40</td>
<td>65-100</td>
</tr>
<tr>
<td>Vermiculate</td>
<td>10.5-14</td>
<td>100-150</td>
<td>40-80</td>
</tr>
<tr>
<td>Smectite</td>
<td>9.6-C-S</td>
<td>80-150</td>
<td>700-840</td>
</tr>
<tr>
<td>Chlorite</td>
<td>14</td>
<td>10-40</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1-2 Diagrams showing the structures of (a) kaolinite and (b) smectite.

Because of their high surface charge and specific surface area, clay can profoundly influence the interfacial chemistry of clay liner materials and the underground environment, such as groundwater and landfill leachate. Clays are commonly used landfill liner materials and their interaction with metal species is critical in understanding the mobility of metal species in the underground environment.

ISOTHERM

An isotherm is a graphic representation describing the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration of the solute (Roy et al. 1991). Isotherm models represent effective tools to predict metal species equilibrium partitioning capacity and the strength by which a metal species is bound onto the clay (Morera et al. 2001). Since empirical
isotherms are experimentally determined, different researchers have obtained a range of results. For example, Lee at al. (1996) and Malakul et al. (1998) conducted equilibrium batch experiments for the partitioning of metal species on soils and clays. The soils examined were 15 native New Jersey soils, described as sandy loam, silt loam, stony loam and silt clay loam. The clay minerals were hectorite and montmorillonite, and the soils contained a range of organic contents from 0.2 % to 8.6 % by mass. Results indicated that the Langmuir isotherm was an appropriate model to describe the adsorption data for their soils and clays. On the other hand, Zehetner and Wenzel (2000) found that the partitioning of Ni and Cu onto acidic forest soils could be represented by the Freundlich isotherm. The differences in model applicability may be explained by the differences in the soil phase materials and metal species concentration applied.

**CYCLIC REDOX POTENTIAL AND PH CHANGES**

Many issues related to engineering behavior of landfill liners have been investigated over the last 30 years. These issues include the effect of organic matter on hydraulic properties of clay liners, the effect of compaction on clay properties and the influence of clay type on hydraulic properties of clay liners. However, to data there has been no research on the impact of cyclic interfacial anaerobic-aerobic conditions and coupled redox potential and pH changes on the structure of the landfill clay liners that are subject to variable high groundwater conditions. In some gulf coast regions in USA there exist variably high groundwater tables with relatively high organic content soil. The elevation of groundwater table can occur due to the wet weather precipitation in summer or spring seasons. In these cases, groundwater can have more opportunities to come into contact with the microorganisms and organic matter. The activities of microorganism can be stimulated and the degradation of organic matter in the upper soil will deplete oxygen and reduce redox potential of groundwater consequently. As a result, the oxygen
diffusion into the clay liner is drastically curtailed. Gascoyne (1997) confirmed that the groundwater redox potential changed from oxidizing to reducing conditions due to rapid consumption of dissolved oxygen by organics in the upper soils in Canadian. Organic acid can be generated by anaerobic fermentation and as a result pH is decreased. On the other hand, the redox potential of groundwater will restore to aerobic condition due to the decrease in groundwater table in arid weather. Because there is less organic matter available in the depth of soil, where both the activities and number of microorganism become less, the biodegradation rate slows down and both dissolved oxygen and pH in groundwater will ascend. Therefore, the landfills constructed in these areas can be subject to cyclic redox potential and coupled pH changes.

There is a regional need to examine the effect that in-situ redox conditions have on the long-term structure and transport of leachate through the clay liner. Results from such an examination can provide guidance for a risk management assessment and evaluate what potential solution or mitigation strategies are feasible under such conditions.

**OBJECTIVES**

Since the reactions at leachate – clay liner – groundwater interfaces are critical in assessing the fate of heavy metal in landfill system, it is important to model this processes. An investigation of heavy metal transport in landfill clay liners and influence of cyclic interfacial redox conditions on the structure of landfill clay liners requires a comprehensive knowledge of aqueous chemistry, soil physics and chemistry and clay mineralogy. Three kinds of clay, sodium montmorillonite (bentonite), kaolinite and Amite soil will be used as clay liner matrix in this study. Two of these materials are pure clay minerals, bentonite and kaolinite and the third is a
natural clayey soil used for landfill liners in Louisiana. There are several major objectives included in this research.

The first objective is to investigate the physical and chemical characteristics of the clay liner materials. The application of clayey materials or clay minerals in the construction of landfill liner requires an understanding of the properties of the clay liners since the incorporation of chemicals such as metal species into the clay liner materials may change the morphology or even the structure of the clays. The second objective is to study the competitive adsorption of metal species onto clay liner materials based on the adsorption isotherms. It is believed that the behavior of heavy metal adsorption with the presence of other metal(s) will be changed in the multiple-element system. Therefore, competition will be dominant in landfill system. The method of determining the competition coefficients will be developed and the interactions between metal species and clays will be evaluated. The third objective is to study the competitive adsorption of metal species onto clay liner materials based on the surface complexation model. In this study, another different approach will be employed to evaluate competitive adsorption. The intrinsic surface reaction constants of the metal species with the clays will be calculated and the three-dimensional graphics describing the decrease of heavy metal adsorption as functions of pH and initial metal concentration will be developed. The fourth objective is to study heavy metal adsorption kinetics. Both uncompacted and compacted clays will be tested and the best kinetic model to represent adsorption will be selected and discussed. The fifth objective is to study the influence of cyclic interfacial redox conditions and resulting pH changes that result from variably groundwater and induced redox changes. The sixth objective is to examine changes to the structure and mineralogy of clay liner materials under different redox and pH
conditions with the help of spectroscopic methods, such as SEM (Scanning Electronic Microscopy) and EXAFS (Extended X-ray Absorption Fine Structure).

REFERENCES


Chapter 2. Interaction of Clay Liner Materials with Metals Species from Urban Rainfall-runoff Residual Leachate: Physical and Chemical Characteristics

SUMMARY

NPDES Storm Water Phase I and II regulations have led to a proliferation of suggested structured best management practices (BMPs) to capture storm water and snowmelt particulate residual material that contains metal species. As these BMPs are maintained such residual material will be managed in landfills isolated by clay liners. Physical and chemical characteristics of landfill clay liner materials contributes significantly to their heavy metal isolation performance, and the understanding of these characteristics is critical to evaluation of the isolation processes and the viability of the clay as a landfill liner material. In this study, basic indices of the three clay materials, Na-bentonite, kaolin and Amite soil (sandy silty soil), were investigated. The results indicate that bentonite has the highest specific surface area and surface charge while Amite soil has the lowest specific surface area and surface charge. Surface complexation models, including the constant capacitance model, the diffuse-layer model and the triple-layer model, were use to model the potentiometric titration processes of the clay materials. A series of geochemistry algorithms were employed to examine surface phenomena. It was found that the surface complexation model could explain the experimental data and quantify the acidity constants of the clays. For the three clay materials tested, the constant capacitance model and the double-layer model could develop very similar acidity constant values. Although ionic strength had little effect on the protonation and deprotonation of kaolin, the protonation and deprotonation of bentonite and Amite soil increased with increasing ionic strength. SEM spectral analyses suggest that heavy metal adsorption by bentonite is predominantly an ion exchange process.
INTRODUCTION

Over the last decade there has been a significant proliferation of stormwater Best Management Practices with the recent enactment of the NPDES Phase II Stormwater requirements, this proliferation will continue. Management of residuals that contain metal species, captured by such BMPs will eventually grow into a unique industry that will rival the size of the biosolids industry. Many metal species are essential components of metallic and non-metallic parts in motor vehicles. In urban and transportation corridors, metal species are generated primarily from the abrasion of metal-containing vehicular parts, including the abrasive interaction of tires against pavement, leaching of metal species from infrastructure, and oil and grease leakage (Armstrong 1994). These released metal species are associated to varying degrees with anthropogenic particulates of varying physical and chemical properties. It is reported that pavement wear accounts for 40-50% and tire wear for 20-30% of particulates generated on a mass basis (Kobriger and Geinopolos 1984). Vehicular parts abrasion from the engine and brakes accounts for approximately an additional 15% of the total particulate mass generated from vehicular activities, while deposition from background urban atmospheric sources generates less than 3% of the total particulate mass that is dry deposited. Anthropogenic particulate matter in the urban environment (< 1 µm to > 10,000 µm) is a major source of metal species contamination.

Urban storm water runoff can carry a wide gradation of particulates along with a variety of metal species. As a result, urban and transportation land use storm water levels of Zn, Cu, Cd and Pb are significantly above ambient background levels, and for many transportation land uses, Zn, Cu, Pb and Cd often exceed surface water discharge criteria on an event basis (Sansalone et al. 1998 and Sansalone and Buchberger 1997). In areas with combined sewers, wastewater
treatment plants can receive a mixture of wastewater and rainfall-runoff which contains metal species. Many structured storm water best management practices (BMPs) are intended to capture particulate material that often contains metal species. Such species are not degraded in BMPs and therefore require removal and long-term management. Since metal species are not destroyed or degraded, during the treatment process, there is an accumulation of metal species in the sludge and residuals generated from the wastewater treatment process. In many cases this sludge or residual material can be classified as a hazardous waste with sufficient exposure in the urban environment or BMP. Landfills are commonly used method for disposal of the sludge and residuals and therefore, landfills can become a sink and potentially a source for metal species.

Clay is the most commonly used material in constructing landfill liners (Goldman 1990). These clay liners act as compacted isolation barriers to separate solid waste, hazardous waste, and leachate from the local soil and groundwater environment. The clay liner surface can act as a reactive barrier, attenuating metal species migration by a series of mechanisms including complexation, adsorption, ion exchange, precipitation, diffusion and dispersion through the clay matrix. Effective control of metal species in leachate requires a detailed investigation of the interaction of clay materials with metal species.

Clayey soil and clay minerals are hydrous silicates, and contain significant levels (as opposed to trace levels) of aluminum, magnesium, or iron, which lose adsorbed and constitutional water to potentially yield refractory material at high temperatures (Goldman et al. 1990). Most clay particles fall into the size range that defines larger colloids; particles small enough to have significant interfacial forces that influence the fate of metal species in leachate. Because of their electrochemical surface activity and high specific surface area, clay minerals can profoundly influence the engineering behavior of a soil. Due to their unique interfacial
properties, clay materials are important in many areas of scientific endeavor, including environmental science and engineering (Wilson 1994).

On a granulometric basis, clay can be defined as the soil fraction with particles $\leq 5 \, \mu m$ (Bagchi 1989) in size. Clay is of importance in the fate and transport of leachate, since clays have a surface chemistry different from that of the larger granulometric materials. Due to high specific surface area and surface charge per mass as compared to silt or sand, clay materials have a greater propensity to undergo surface phenomena such as adsorption and ion exchange phenomena. Such surface phenomena by colloidal suspended particles or sediments in the aquatic environment has been an interesting topic, and many researchers have studied such phenomena with respect to interacting with metal species under a wide range of conditions associated with the aquatic environment (Mellah and Chegrouche 1997, Kayabali and Kezer 1998, Cells et al. 2000, Eick and Fendorf 1998).

In past, the mobility of metal species at the clay liner interface depends on their association with clay liner materials. Modeling surface phenomena such as adsorption between clay liner materials and metal species in leachate is important in evaluating the migration of metal species in groundwater. Physical and chemical characteristics of clays, such as surface charge, protonation, deprotonation and specific surface area play an important role in determining metal species speciation and surface interactions. For example, the adsorption capacity of minerals is proportional to their surface areas and surface-site densities (Langmuir 1997). Langmuir (1997) examined the properties of materials that exhibit significant surface interactions, as such properties influence adsorption-desorption reactions. The properties included particle size, surface area, surface charge, surface-site density, and cation exchange capacity (CEC). Langmuir results indicated that the size effect was most important for kaolin and
decreasingly important for illite and smectite. Surface complexation models (Davis and Leckie 1978a, b) have been proposed for modeling clay or soil surface chemistry and pollutant transport in aqueous system. These results suggested that the competitive effective was weaker than expected since the relative binding strengths of various sites for metals were different. The application of a complexation model requires knowledge of acidity constants for protonation and deprotonation of clay surface sites (Jenne 1998). As a result, many researchers (Wen et al. 1998, Sarkar 1999, Sarkar 2000, Manning and Goldberg 1997, Arizian and Nelson 1998) have conducted studies on properties of materials which significant surface interactions before beginning the investigation of phenomena by clay or soil. Wanner et al. (1994) studied alkalimetric and acidimetric titrations of montmorillonite at ionic strengths varying from 0.005 to 0.5 M NaNO₃. In their study, a diffuse double layer model was used to determine model parameters based on experimental data.

In addition to metal species, clay minerals and the fate and transport of organic matter compounds such as pesticides are influenced by surface interactions (Cox et al. 1998). Cox et al. found that surface interactions were important for the clay fraction containing a high content of montmorillonite and relatively high organic carbon content.

In order to better understand the change in the surface after adsorption, Laperche and Traina (1998) employed different spectroscopic methods, including X-ray Diffraction, Scanning Electronic Microscopy and Extended X-ray Absorbance Fine Structure, to determine the structure of the precipitated Pb-phosphates and the process of formation of adsorption products in a solution of aqueous Pb and hydroxylapatite at pH of 5 to 6. Results indicated that at low Pb concentrations the predominant mineral was pyromorphite and not (Pb, Ca)-apatite that was formed when Pb reacts with apatite. Fendorf et al. (1997) used EXAFS to studied the local
coordination environment of As and Cr on goethite. Based on the oxyanion-Fe distance, it was concluded that three different surface species, a mono-dentate complex, bidentate-binuclear complex and bidentate-mononuclear complex exist on goethite for both oxyanions.

The utilization of clayey soils or clay minerals in the construction of landfill liner requires an understanding of the clay liner surface structure since the interaction of metal species with the clay liner material may change the morphology or even the structure of the clay liner surface. When examining the capacity of clay to interact with metal species utilizing the concept of adsorption, a number of isotherm forms can be potentially useful. However, the use of such models becomes complicated when the solid phase exhibits a pH-dependent surface charge. Under such conditions, the adsorption of metal or trace ionic species often takes place against a solid phase net surface charge that is of the same sign as the species (EDS).

**OBJECTIVES**

This study had three objectives and utilized three clay materials in this study. Two of these materials were pure clay minerals, bentonite and kaolin, and the third was a natural clayey soil used for landfill liners in Louisiana. The first objective of this paper was to characterize physical properties of the clay liner materials. The second objective was to investigate acid/base chemistry of the clays based on surface complexation models (SC), considering both protonation and deprotonation. The third objective was to examine changes in surface characteristics of the clay materials as a result of the adsorption process, with the aid of Scanning Electronic Microscopy (SEM) and energy dispersive spectra (EDS).

**BACKGROUND**

**Surface Complexation Models**

Three common surface complexation (SC) models including the constant capacitance (CC) model, the diffuse-layer (DL) model and the triple-layer (TL) model have been proposed to
model the binding of protons, cations and anions onto mineral surfaces (Mouvet and Bourg 1983, Fu and Allen 1992). These three models differ in how they conceptualize the structure of the double layer and describe the changes in surface potential and surface charge from the solid surface to the bulk solution (Langmuir 1997). If a clay liner material is assumed to have a conceptualized surface functional group, the surface protonation and deprotonation reactions that are basic to the three SC models are expressed in Equations (1) and (2):

\[
\text{SOH} + \text{H}^+(S) = \text{SOH}_2^+ \quad (1)
\]

\[
\text{SOH} = \text{SO}^- + \text{H}^+(S) \quad (2)
\]

In these experiments SOH, SOH$_2^+$ and SO$^-$ represent neutral, positively charged and negatively charged functional groups on the solid surface, respectively, and H$^+(S)$ is hydrogen ion (proton) species at the solid surface. Corresponding mass-action expressions and their intrinsic constants are written as shown in Equations (3) and (4).

\[
K_{a1}^{\text{int}} = \frac{\{\text{SOH}\}\{\text{H}^+\}_S}{\{\text{SOH}_2^+\}} \quad (3)
\]

\[
K_{a2}^{\text{int}} = \frac{\{\text{SO}^-\}\{\text{H}^+\}_S}{\{\text{SOH}\}} \quad (4)
\]

In these expressions $K_{a1}^{\text{int}}$ and $K_{a2}^{\text{int}}$ are intrinsic acidity constants of protonation and deprotonation, $\{\text{H}^+\}_S$ is hydrogen ion activity at the adsorption surface, $\{\text{SOH}\}$ is functional group activity at the adsorbent surface, and $\{\text{SOH}_2^+\}$ and $\{\text{SO}^-\}$ are activities of protonated and deprotonated surface sites. Estimation of acidity constants is critical to the modeling of metal species surface interaction as a function of pH using a surface complexation model.

The value of $\{\text{H}^+\}_S$ at the solid surface which can not be directly measured is related to bulk H$^+$ activity $\{\text{H}^+\}$.

\[
\{\text{H}^+\}_S = \{\text{H}^+\}\exp(-\psi_0F/RT) \quad (5)
\]
In this expression $\psi_0$ is the potential at the solid surface, $F$, $R$ and $T$ are the Faraday constant, the ideal gas constant and the absolute temperature, respectively. All three SC models assume protons are exchanged at the surface of the solid. However, because the three models assume different structures for the electrical double-layer surrounding the solid surface and different locations of adsorbed ions, values of intrinsic acidity constants in each model will generally be different.

**Constant Capacitance (CC) Model**

In this model the electrical double layer is compared to a capacitor with a constant capacitance $C_1$ and only one plane of interaction or exchange (surface of solid) is considered in this model. This assumption implies that all ions are exchanged on this plane. The CC model has three specific parameters, $C_1$, $pK_{a1}^{\text{int}}$ and $pK_{a2}^{\text{int}}$. The surface charge density versus potential relationship is written as shown in Eq. (6).

$$\sigma = C_1 \psi$$

(6)

In this expression $\sigma$ is surface charge and $\psi$ is the potential. This model has been applied to the interaction of transition metal species, including Cd$^{2+}$, Pb$^{2+}$, and to anions such as borate and phosphate that complex hydrous oxide surfaces of Al, Fe and Si suspended in aqueous solution (Davis and Kent 1990, Brady 1992).

**Diffuse-Layer (DL) Model**

The DL model assigns two planes in the interfacial region: a zero plane (surface plane) and a diffuse-layer plane. $H^+$, $OH^-$ and all specifically complexed ions are assigned to the surface plane while all nonspecifically adsorbed counter-ions are assigned to the diffuse layer (Dzombak and Morel 1997). It is assumed that potentials measured at the zero plane and the diffuse-layer plane are equal. The distribution of ions, charge and potential in the diffuse-layer is described by
the Poisson-Boltzmann equation (Wen 1998). For a symmetrical electrolyte of charge \( z \), the charge density at some distance away from the surface can be described by the Gouy-Chapman theory (Dzombak and Morel 1997).

\[
\sigma = 0.1174 I^{1/2} \sinh \left( \frac{z \psi F}{2RT} \right) \tag{7}
\]

In this expression \( I \) is the ionic strength in units of M and 0.1174 arises from the product of ideal gas constant, dielectric constant of water (78.4) and the permittivity of free space at 25 °C (8.854×10^{-12} F/m). Dzombak and Morel (1990) have published an extensive treatment of the DL model, including a compilation of measured or estimated intrinsic constants for the exchange of \( \text{H}^+ \), metal cations and anions by hydrous ferric oxide. Only two parameters, \( pK_{a1}^{\text{int}} \) and \( pK_{a2}^{\text{int}} \) are required in this model. These parameters are typically determined by the relationship between pH and metal species uptake by the solids.

**Triple Layer (TL) Model**

The TL model was developed by Davis and Leckie (1978a, 1978b). There are three planes in the interfacial region: a zero plane (surface plane) for exchange of \( \text{H}^+ \), \( \text{OH}^- \) and specifically bound ions, a middle plane (\( \beta \) plane) for weakly bound alkali and alkaline earth cations (for example electrolyte ions) and a diffuse layer (d layer). Integral capacitances \( C_1 \) and \( C_2 \) are assigned to zones between zero plane and \( \beta \) plane and \( \beta \) plane and d plane, respectively. Typically, \( C_3 \) is assumed constant at 0.2 F/m^2, with \( C_2 \), \( pK_{a1}^{\text{int}} \) and \( pK_{a2}^{\text{int}} \) values adjusted to optimize the fit of the TL model to experimental data (Langmuir 1997). In modeling protonation and deprotonation of the clay liner materials, the following parameters are required: \( C_2 \), \( C_3 \), \( pK_{a1}^{\text{int}} \), \( pK_{a2}^{\text{int}} \) and \( pK_{el}^{\text{int}} \) (intrinsic constants for electrolyte cations and anions). Smith and Jenne (1988, 1991) evaluated published TL modeling for the interaction of ferric oxyhydroxide solids...
and MnO₂. Their analysis led to a set of intrinsic constants based on experimental measurement and estimation (Langmuir 1997).

**METHODOLOGY**

**Clay Materials**

The clays used in this study included non-treated natural Na-bentonite (having a trade name of Aquagel Gold Seal, Baroid Drilling Fluids, Inc., Houston, TX), kaolin (having a trade name of EPK, Feldspar Corporation, Atlanta, GA), and a native clayey soil (Amite soil) commonly found in the Tangipahoa basin of South Louisiana and commonly used for landfill liners.

**Clay Particle Size Gradation**

For bentonite and kaolin, particle size distribution was analyzed using a laser diffraction particle analyzer (Model LISST, Sequoia Scientific Inc., Seattle, WA) for a dilute suspension of these clays in water, while a mechanical sieve analyses (Model SS-15, Gilson Company, Lewis Center, OH) was used to separate particle size gradation of Amite soil. All analyses were replicated. Since particle size distributions of Amite soil were analyzed on a mass basis, while particle size distributions of bentonite and kaolin were analyzed on a volume (calculated number basis) basis it is necessary to inter-convert the two methodologies for comparison purposes. The following equations were used to make the conversion:

\[
N_i = \frac{M_i}{\rho \left( \frac{\pi}{6} d_i^3 \right)} \quad (8)
\]

\[
\text{Number,\%} = \frac{M_i / (\rho_i d_i^3)}{\sum M_i / (\rho_i d_i^3)} \times 100 \quad (9)
\]

\[
\text{Mass,\%} = \frac{\rho_i N_i d_i^3}{\sum (\rho_i N_i d_i^3)} \times 100 \quad (10)
\]
In these expressions $\rho_i$, $M_i$ and $N_i$ are the density, mass of particles and the number of particles with diameter of $d_i$, respectively.

**Elemental Analysis of Clay**

A measured mass of dry clay particles (approximately 1 gram) was digested in a mixture of 9 mL of 70% HNO$_3$ and 3 mL of 37% HCl for two hours using microwave digestion as outlined in SW-486 Method 3015 (USEPA 1990). Once cool, the samples were diluted to 100 mL with deionized water, and a filtered 50 mL sample was withdrawn for metal analysis. Metal analysis was performed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, ELAN 6000) instrument. The following metals were examined: Na, Al, Ca, Mg, Cu, Zn, Cd and Pb. The measuring conditions were 100 ms dwell time, 50 sweeps/reading and 3 replicates for each sample. The internal standard was Rh which was pumped into the plasma with the sample, giving a concentration of 10 mg/L. The elements were measured at m/z values of 63 for Cu, 64 for Zn, 114 for Cd and 208 for Pb. QA/QC included checking a standard solution with concentration of 50 $\mu$g/L for each metal every 8 samples. Analyses were accepted only if the measured value was within 45 to 55 $\mu$g/L for each metal. Triplicate samples were measured for each sample.

**Organic Matter**

The Walkley-Black Method (Nelson and Sommers 1996) was used to determine the organic matter content of the clay materials. A measured amount of dry clay (approximately 0.5 g of dry clay sample) was transferred into a 500-mL Erlenmeyer flask. 10 mL of 0.167 M K$_2$Cr$_2$O$_7$ and 20 mL of concentrated H$_2$SO$_4$ (98%) were added and the flask was mixed for 1 minute. After 30 minutes, 200 mL of water was added to the flask. Acid resistant filter paper was used to separate the residual from the solution, which was titrated with 0.5 M FeSO$_4$. The
result was calculated according to the following formula, using a correction factor $f = 1.3$ (Nelson and Sommers 1996).

$$\text{Organic C \%} = \frac{(v_{\text{blank}} - v_{\text{sample}})(M_{\text{Fe}^{2+}}) \times 0.3}{W_s} \times f$$  \hspace{1cm} (11)

In this expression $v_{\text{blank}}$ and $v_{\text{sample}}$ are the volume of FeSO$_4$ used in titration, $M_{\text{Fe}^{2+}}$ is concentration of FeSO$_4$ solution and $W_s$ is weight of sample clay. Triplicate sampling and analyses were conducted.

**Specific Surface Area**

The EGME (Ethylene Glycol Monoethyl Ether) method (Sansalone et al. 1998) is a gravimetric method utilized for the determination of clay specific surface area (SSA). This method determines the amount of EGME adsorbed at a constant vapor pressure, by measuring the increase in clay weight due to the adsorbed monolayer of EGME. A representative measured amount of dry clay (approximately 0.5 g – 1.0 g) was first saturated with EGME, by completely wetting all particle surface area, and then placing glass petridishes of the EGME-wetted clay in a glass dessicator over 600 grams mixture of an EGME-ground CaCl$_2$ solvate. A constant vapor pressure was produced from this solvate. The EGME to CaCl$_2$ ratio was 1.5:1. Samples were weighed at 4-hour intervals after 24 hours in the dessicator until a constant weight (less than 1 mg across 4 hours) for each sample was obtained. Based on the assumption of a monolayer surface coverage of EGME, molecular weight and molecular diameter of EGME, specific surface area (SSA) of clay was calculated.

$$\text{SSA} = \frac{W_a}{0.000286(W_s)}$$  \hspace{1cm} (12)

$W_a$ is the weight of EGME adsorbed by clay while $W_s$ is the weight of clay. Granular activated carbon with a SSA of 1100 m$^2$/g was used as quality control.
**Particle Density**

The particle density of clay was measured using a pycnometer (Quanta Chrome Corporation, Boynton Beach, FL). The methodology followed ASTM D 5550-94 (ASTM 1994). The pycnometer is an instrument designed to measure the volume of particulate sample. The pycnometer determines the volume of solid by measuring the pressure difference when a known quantity of inert gas (UHP helium in this case) is allowed to flow under pressure from a precisely known reference volume ($V_R$) into a sample cell containing clay material. The true solid volume can be calculated using Eq. (13).

$$VS = VC - VR\left[\left(\frac{P_1}{P_2}\right)-1\right]$$

(13)

In this expression, $V_S$ is true sample volume, $V_C$ is cell volume, $V_R$ is reference volume, $P_1$ is initial pressure and $P_2$ is final pressure. Particle density can be obtained by dividing weight of sample ($M_S$) by the true volume of sample ($V_S$). Triplicate analyses were conducted for each sample.

**Scanning Electronic Microscope**

Scanning Electronic Microscope (SEM) examination was carried out to obtain clay surface topography and morphology information, as well as qualitative chemical composition. SEM samples were glue-mounted and gold-coated by a vacuum electric arc. Standard qualitative elemental analysis of the clay materials was carried out using an energy dispersive X-ray spectrometer system (EDS) and associated JSM-840A Scanning Microscope (Liu et al. 2001).

**X-Ray Diffraction**

X-Ray Diffraction (XRD) technology was employed to identify the composition of the clay materials. The analyses were carried out on a Siemens D5000 diffractometer. Cu K$_\alpha$ was employed, with a tube current of 40 mA and a tube voltage of 45 kV. The detector was Kevex
solid psi. All results were analyzed with a Siemens Diffrac AT V3.1. The identification of the clay mineral was based on the values of d-spacing (Griffin 1971) and the percentage of each mineral in the clay fraction is calculated based on Eq. (14).

\[
\% \text{ mineral } i = \frac{A_i}{\sum A_i}
\]  

(14)

In this equation \( A_i \) is the peak area of mineral \( i \) and \( \sum A_i \) is the total peak area. The peak areas were determined through discrete summation of differential areas.

**Surface Charge**

Surface charge was analyzed using a potentiometric titration method described by Van Raij and Peech (1972). A representative measured amount of dry clay (approximately 0.2 g of clay) was suspended in 20 mL of 0.01 M NaNO\(_3\). The suspension was purged with nitrogen gas, sealed and kept mixed using a reciprocating shaker at room temperature for 24 hours after which the pH values of the supernatant were recorded. During the titration process, the suspension was continuously bubbled with N\(_2\) to eliminate the effect of CO\(_2\). Surface charge values were calculated by the amounts of H\(^+\) or OH\(^-\) (addition of 0.01 N HCl or 0.01 N NaOH) required to bring the samples to the final equilibrium pH, minus the amount necessary to bring 20 mL of a blank solution to the same pH. Triplicate analyses were conducted for each sample. The surface charge of the sample is calculated as (Wen 1998):

\[
\sigma_H = \frac{[(v_{HCl}N_{HCl} - v_{NaOH}N_{NaOH})_{\text{sample}} - (v_{HCl}N_{HCl} - v_{NaOH}N_{NaOH})_{\text{blank}}]/W_S}{S}
\]  

(15)

where \( v \) and \( N \) are the volume and normality of acid or base added, respectively.

**Measurement of Intrinsic Acidity Constant**

The interaction of protons and hydroxyl ions with the clay surface was investigated using potentiometric titration. 400 mg of kaolin, 400 mg of Amite soil, or 200 mg of bentonite was added into 100 mL DI water in a 150-mL Erlenmeyer flask. The background electrolyte was kept
at either 0.001, 0.01 and 0.1 N NaNO₃. Known amounts of 0.1 N HNO₃ were titrated into the suspension at increments of 0.02 mL to reduce the pH value to less than 3.5. NaOH solution with concentration of 0.1 N was titrated at an increment of 50 or 100 µL to increase the pH value. The stable pH values after each addition of acid were recorded after an equilibrium time of 2 hours. During the process of titration, nitrogen gas was continuously supplied to purge CO₂ from the solution so that the effect of CO₂ was eliminated. The titrations of blanks without the addition of clay materials were also conducted under the same experimental conditions. The data sets of pH versus the net consumption of H⁺ or OH⁻ due to surface complexation were used to obtain intrinsic acidity constants in the surface complexation model with the aid of FITEQL algorithms (Herbelin and Westall 1999).

**Modeling of Intrinsic Acidity Constant**

A multi-component chemical equilibrium model (FITEQL) and titration data were utilized to determine the intrinsic acidity constants. Surface complexation modeling requires the solution of a number of simultaneous equations. In the case of protonation and deprotonation of clay liner material, these equations include protonation and deprotonation equations, mass balance equations and charge balance equations. The first step was to set up in tabular form the chemical equilibrium of the protonation and deprotonation for the clay liner materials as were indicated in Eqs. (1) and (2) (Morel and Hering 1993). In the table, the species included SOH, SOH₂⁺, SO⁻ and H⁺ while H⁺ and SO⁻ were chosen as components. This table is shown in table 1. The intrinsic acidity constant expressions can be shown in Eqs. (16) and (17).

\[
K_{a1}^{\text{int}} = \frac{\{SOH\} \{H^+\} \exp\{-\psi_F R F / RT\}}{\{SOH_2^+\}} \tag{16}
\]

\[
K_{a2}^{\text{int}} = \frac{\{SO^-\} \{H^+\} \exp\{-\psi_F R F / RT\}}{\{SOH\}} \tag{17}
\]
Table 2-1. Table showing the equilibrium of protonation and deprotonation of the clay liner materials.

<table>
<thead>
<tr>
<th>Species</th>
<th>H_{2}O</th>
<th>H^{+}</th>
<th>SO^{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{2}O</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H^{+}</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>SO^{-}</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>OH^{-}</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>SOH</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SOH_{2}^{+}</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

The mass balance equations for the four metal species in aqueous solution are expressed in the following equations.

\[
\text{TOTH} = C_{H^{+}} + \{\text{SOH}\} + \{\text{SOH}_{2}^{+}\} \tag{18}
\]

In this expression, TOTH is total hydrogen concentration (M) and \( C_{H^{+}} \) is hydrogen ion concentration in bulk solution (M). \( C_{H^{+}} \) can be calculated using the activity and the relationship between hydrogen activity and concentration can be expressed in Eq. (19).

\[
\{H^{+}\} = C_{H^{+}} \gamma \tag{19}
\]

In this expression, \( \gamma \) is activity coefficient which can be calculated from the Davies equation (Morel and Hering 1994) at temperature of 298 K.

\[
\log \gamma = 0.509Z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \tag{20}
\]

In this expression, \( Z \) is valence of ion and \( I \) is ionic strength (N).

The surface charge balance of the clay can be given by different expressions based on different surface complexation models. In CC model, \( \sigma_0 \) is calculated in Eq. (21) which is a special case of Eq. (6).

\[
\sigma_0 = C_1 \psi_0 \tag{21}
\]

In DL model, \( \sigma_0 \) is calculated in Eq. (22) which is a special case of Eq. (7).
\[
\sigma_0 = 0.1174I^{1/2} \sinh\left(\frac{z \psi_0 F}{2RT}\right) \tag{22}
\]

In TL model, \(\sigma_0\) is calculated in Eq. (23).

\[
\sigma_0 = \frac{F}{SSA \times C_s} \left[ \{SOH_2^+\} - \{SO^{-}\} \right] \tag{23}
\]

In this expression, \(C_s\) is solid concentration (g/L). The net change of \(\beta\)-plane is given by Eq. (24).

\[
\sigma_\beta = \frac{F}{SSA \times C_s} \left[ 2\{SOHNa^+\} - 2\{SOH_2NO_3^-\} \right] \tag{24}
\]

In this expression, \(\{SOHNa^+\}\) and \(\{SOHNO_3^-\}\) represent the activities of clay-Na and clay-NO\(_3^-\) complex activities, respectively. In TL model, the background electrolyte such as Na NO\(_3\) is assigned to the \(\beta\)-plane. The overall charge balance equation is written in Eq. (25).

\[
\sigma_0 + \sigma_\beta + \sigma_d = 0 \tag{25}
\]

In this expression, \(\sigma_d\) is the net charge at \(d\)-plane. The TL model calls for the capacitances \(C_2\) and \(C_3\), corresponding to zones between the zero- and \(\beta\)-planes and \(\beta\)- and \(d\)-planes, respectively. The capacitances are related to the net charge and potentials of those planes through the following expressions.

\[
\sigma_0 = C_2(\psi_0 - \psi_\beta) \tag{26}
\]

\[
\sigma_\beta = C_2(\psi_\beta - \psi_0) + C_3(\psi_\beta - \psi_d) \tag{27}
\]

\[
\sigma_d = C_2(\psi_d - \psi_\beta) \tag{28}
\]

These equations are solved simultaneously and the intrinsic surface complexation constants are obtained from the solution.

The three surface complexation models, the CC model, DL model and TL model, were applied separately using the FITEQL algorithms. For the application of CC model, the value of capacitance was selected based on previous studies (Herbelin and Westall 1999, Dzombak and
Morel 1990) and values of 1.0 to 2.0 F/m^2 were chosen to fit the experimental data at different ionic strengths for the three clay liner materials. The initial estimates for \( \log K_{\nu_1}^{\text{int}} \) and \( \log K_{\nu_2}^{\text{int}} \) were set at 7.0 and -9.0, respectively. In the DL model, the input data were similar to those for the CC model except for the specifying characteristics of the background electrolyte such as concentration and charge. In the case of the TL model, the input data were also similar to those for the CC model with \( C_3 \) fixed at 0.2 F/m^2. However, three additional components were required. The three initial estimates for \(-F\psi(0)/RT\ln 10\), \(-F\psi(\beta)/RT\ln 10\) and \(-F\psi(d)/RT\ln 10\) were -1.0, -0.5 and -0.2, respectively.

In the calculation, the maximum number of iteration in the optimization procedure was set at 30 for each of the three surface complexation models.

**Metal Species Interaction with Clays**

Four metal species, Cu, Zn, Cd and Pb were employed as reactants in this study. These species with their respective concentrations were chosen because these metals are very common in the leachate of focus in this study. The metal species and clay interaction experiment involved the equilibration of 200 mg of bentonite, 400 mg of kaolin or 400 mg of Amite soil in 40 mL of metal species solution with initial concentrations of 100 mg/L for each metal in capped 50 mL centrifuge tubes. The metal species solution was composed of a combination of the four metal species. The initial pH value for the bentonite suspension was adjusted to 3.0, while the initial pH values for kaolin or Amite soil were adjusted to 5.0 so that the equilibrium pH for the three suspension were kept at 5.0 to 5.5. The centrifuge tubes were placed on a shaking table for 24 hours at room temperature to obtain equilibrium. The clays were separated from the solution by sedimentation after the adsorption test and were smeared on glass slides. The samples on the slides were put into an oven at 60 °C for 30 minutes in preparation for SEM analysis.
RESULTS AND DISCUSSION

Clay Composition

The physical and chemical properties of the clays are summarized in Table 2-2. Na is a major component of the bentonite examined in this study, and has an important effect on the surface exchange processes. Compared with kaolin and Amite soil, bentonite has a much higher Na content and also a much higher specific surface area (SSA) of 625 m$^2$/g. Among the three clays investigated, Amite soil has the smallest specific surface area of 14 m$^2$/g. It is also worthwhile to note that Amite soil had the highest relative organic matter content among the three clay materials, although the absolute magnitude of organic content was small (≤ 0.34 %).

Table 2-2. Measured characteristic of the sorbent materials as arithmetic means, (standard deviation), $m = 3$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Amite Soil 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (%)</td>
<td>1.3 (0.08)</td>
<td>0.0145 (0.0009)</td>
<td>0.0184 (0.001)</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.055 (0.01)</td>
<td>0.0131 (0.0010)</td>
<td>0.0252 (0.005)</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.0067 (0.004)</td>
<td>0.0071 (0.003)</td>
<td>0.0051 (0.004)</td>
</tr>
<tr>
<td>Al (%)</td>
<td>7.0 (0.75)</td>
<td>17.2 (1.51)</td>
<td>2.1 (0.11)</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>0.00045 (0.00005)</td>
<td>0.0006 (0.0002)</td>
<td>0.00124 (0.0001)</td>
</tr>
<tr>
<td>Zn (%)</td>
<td>0.01 (0.0008)</td>
<td>0.0044 (0.0003)</td>
<td>0.0032 (0.0003)</td>
</tr>
<tr>
<td>Cd (%)</td>
<td>0.00002 (0.00002)</td>
<td>0.00000 (0)</td>
<td>0.00018 (0.00001)</td>
</tr>
<tr>
<td>Pb (%)</td>
<td>0.0024 (0.0009)</td>
<td>0.0044 (0.0004)</td>
<td>0.00072 (0.00005)</td>
</tr>
<tr>
<td>Organic Matter (%)</td>
<td>0.23 (0.05)</td>
<td>0.18 (0.04)</td>
<td>0.34 (0.05)</td>
</tr>
<tr>
<td>pH (10g/100ml H$_2$O)</td>
<td>9.10 (0.05)</td>
<td>5.10 (0.01)</td>
<td>6.12 (0.02)</td>
</tr>
<tr>
<td>$d_{50}$ (µm) *</td>
<td>7 (2)</td>
<td>15 (4)</td>
<td>12 (5)</td>
</tr>
<tr>
<td>$d_{50}$ (µm) **</td>
<td>1.6 (0.4)</td>
<td>1.5 (0.5)</td>
<td>16 (6)</td>
</tr>
<tr>
<td>Specific Surface Area (m$^2$/g)</td>
<td>625 (8)</td>
<td>52 (2)</td>
<td>14 (2)</td>
</tr>
<tr>
<td>Particle Density (g/cm$^3$)</td>
<td>2.72 (0.01)</td>
<td>2.75 (0.16)</td>
<td>2.75 (0.01)</td>
</tr>
</tbody>
</table>

$d_{50}$* is based on particle mass.
$d_{50}$** is based on particle number.
The numbers in parenthesis are standard deviations.
1: Designated as a sandy silty clay soil.
XRD Diffraction

Figure 2-1. X-ray diffractograms (XRD) of bentonite, kaolin and Amite soil. θ is diffraction angle (degree). S, K and Q represent for smectite, kaolinite and quartz, respectively.

X-ray diffraction (XRD) was used to examine the mineralogy of the clay materials. Diffractogram results are shown in Figure 2-1. The XRD patterns of bentonite (B) and kaolinite (K) indicated no other significant diffraction peaks other than those characteristic of bentonite and kaolinite. Results indicated that the dominant components of the clay fraction of the Amite
soil were bentonite and kaolinite, Illite, goethite and quartz (Q) in particle sizes of < 5 µm were also identified in the clay fraction of Amite soil by XRD spectra. The mineral composition of the Amite soil is illustrated in Table 2-3.

Table 2-3. Composition of clay fraction (-5 µm) of Amite soil. m = 2.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Illite</th>
<th>Goethite</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>38.52</td>
<td>56.32</td>
<td>1.39</td>
<td>1.84</td>
<td>1.92</td>
</tr>
</tbody>
</table>

**Particle Size Gradation**

The metal species interaction behavior with clayey materials arise from a combination of size gradation, surface charge and surface area (SA). Therefore, it was important to investigate particle size gradation and surface charge of the clay in addition to surface area as a prerequisite for examining metal species adsorption. Particle size gradations of the three types of clayey materials are illustrated in Figure 2-2. Compared with Amite soil, bentonite and kaolin have gradations dominated by the smaller particle fractions. The particle size distributions of bentonite and kaolin indicate that the d50 (number) is 7 µm for bentonite and 15 µm for kaolin, respectively. Although the particle size of bentonite is a factor of two smaller than kaolin (on a number basis), bentonite has a specific surface area that is an order of magnitude higher than kaolin. The structure of bentonite is characterized by thin flakes which have high surface area while those for both kaolin and Amite soil are described by discrete and aggregated particles.

**Surface Charge**

The relationships between pH and surface charge of the clays are shown in Figure 2-3, in which the H⁺ or OH⁻ adsorption onto the three clay materials was measured as a function of pH with the background electrolyte fixed at 0.01 N NaNO₃. It can be seen from the figure that different clay surfaces demonstrated different relative affinities for H⁺ and OH⁻ as shown by the
values of points of zero charge (PZC). Kaolin and Amite soil had net positive charges at low pH values and net negative charges at higher pH values. The PZC values of kaolin and Amite soil are 4.6 and 5.25, respectively. This indicates that the net surface charge at a pH above these PZC values is negative and that cationic metal species surface interaction may be significantly
increased if the pH is greater than 4.6 for kaolin and 5.25 for Amite soil. In contrast, the surface charge of bentonite was permanently negative and demonstrated only a slight dependence on pH, resulting in no PZC for bentonite.

Figure 2-3. Surface charges of bentonite, kaolin and Amite soil as a function of pH when background electrolyte is 0.01 (mole/L) NaNO₃. There is no PZC for bentonite.

The surface charge of bentonite arises primarily from isomorphous substitution in the crystal lattice where Al³⁺ replaces Si⁴⁺ in the tetrahedral layer. This results in an excess of O²⁻ bonds. Therefore, bentonite is a permanently-charged mineral which does not have a PZC since the negative charge is too great to be balanced by the small amount of positive charge that may develop on the edge of layer-silicate plates (McBride 1989). The surface charge values of kaolin
and bentonite obtained in this study were consistent with those in the literature where it was found that the PZC value for kaolin was 4.3 while there was no PZC value for bentonite (McBride 1989). Of the three clay materials investigated, bentonite had a much higher surface charge than kaolin and Amite soil. It has been reported that the typical cation exchange capacity (CEC) values for kaolin and montmorillonite (Na-bentonite) are 3-15 and 60-150 meq/100 g, respectively (Wilson 1994). The experimental data in this research match the reported values well with measured values of around 3 and 60 meq/100 g for kaolin and bentonite, respectively.

The surface charge versus pH curve in Figure 2-3 illustrates that the magnitude of negative surface charge increases with pH (the surface charge of clay becomes more negative), indicating that the potential for cationic metal species interaction increases with pH. On the other hand, cationic metal species interaction decreases with decreasing pH. This is because the increasing H\(^+\) will compete with metal species in solution for exchange sites on the clay surface.

**Acid-Base Chemistry of Clay Materials**

The proton excess or deficiency is the key to the understanding of acid-base chemistry of these clay materials. The surface proton excess or deficiency, designated as TOTH, was plotted against pH, as seen in Figure 2-4 where the modeling results of surface complexation models are also represented. TOTH was calculated with the following expression (Dzombak 1990).

\[
\text{TOTH} = C_A - C_B - (H^+) + K_w/(H^+) \tag{29}
\]

In this expression \(C_A\) is the molar concentration of acid added, and \(C_B\) of base added. \((H^+)\) is hydrogen activity and \(K_w\) is the ion product of water \((10^{-14})\).

The results of acid-base titration provide macroscopic information about the surface chemistry of the clay surface. TOTH is positive due to protonation, the complexation of H\(^+\) with clay surface, and negative due to deprotonation of surface functional sites.
Figure 2-4. Simulation of titration curves of bentonite, kaolin and Amite soil. CC, DL and TL models represent constant capacitance (CC) model, diffuse-layer (DL) model and triple-layer (TL) model, respectively. Note the TOTH scale difference for bentonite compared to kaolin and Amite soil.
It can be seen from Figure 2-4 indicates that ionic strength has different effects on the three different clay materials. The protonation and deprotonation of kaolin is reproducible for the three different background electrolyte concentrations which have little effect on the clay surface complexation with $H^+$. On the other hand, ionic strength can significantly influence on sorption and desorption of protons on Amite soil. At the same time, ionic strength has a moderate effect on bentonite. The data of bentonite and Amite soil further indicate that the degree of protonation increases with ionic strength.

The three complexation models were examined with respect to the experimental data by using FITEQL software. With the exception of the TL model applied to bentonite, the three models simulate the protonation and deprotonation of the clay materials well since the values of WSOS were smaller than 10(m-1) and m is the number of experimental data points. It was also found that the CC model, DL model and TL model could generate very similar results when applied to kaolin. Therefore, only one curve was presented to indicate the results of the three models. However, the application of the TL model to Amite soil generated different results compared to those of the CC model and the DL model. A goodness of fit test was adopted to compare the three models to experimental data and to identify the best-fit model (Ko et al. 2001). The goodness of fit equation is expressed as follows.

$$RMSE = \sqrt{\frac{1}{m} \sum_{i=1}^{m} (\hat{Y}_i - Y_i)^2}$$  \hspace{1cm} (30)

RMSE is root-mean-square-error, m is the number of experimental data points and $\hat{Y}_i$ and $Y_i$ are the model prediction value and experimental value, respectively. For a model selection criteria it was decided that the model that provided the least RMSE was considered as the best model.
Table 2-4. The Values of RMSE ($\times 10^5$) for the fit of the three surface complexation model forms.

<table>
<thead>
<tr>
<th></th>
<th>I=0.001 M</th>
<th></th>
<th></th>
<th>I=0.01 M</th>
<th></th>
<th></th>
<th>I=0.1 M</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC Model</td>
<td>DL Model</td>
<td>TL Model</td>
<td>CC Model</td>
<td>DL Model</td>
<td>TL Model</td>
<td>CC Model</td>
<td>DL Model</td>
</tr>
<tr>
<td>Bentonite</td>
<td>6.66</td>
<td>7.69</td>
<td>NA*</td>
<td>8.16</td>
<td>9.13</td>
<td>NA*</td>
<td>10.30</td>
<td>9.02</td>
</tr>
<tr>
<td>Kaolin</td>
<td>1.73</td>
<td>1.82</td>
<td>1.45</td>
<td>1.62</td>
<td>1.66</td>
<td>1.66</td>
<td>2.00</td>
<td>1.92</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>6.68</td>
<td>5.42</td>
<td>3.21</td>
<td>8.80</td>
<td>6.12</td>
<td>2.49</td>
<td>10.92</td>
<td>8.91</td>
</tr>
</tbody>
</table>

*NA: Not Available. The potentiometric data of bentonite did not converge using TL model in FITEQL.

Based on the values of RMSE (Table 2-4), it was found that the TL model was the best model to describe the acid-base titration of Amite soil. Just like kaolin and Amite soil, the applications of the CC model and the DL model made virtually no difference.

The values of intrinsic acidity constants were obtained by using FITEQL, and these values are tabulated in Table 2-5. For the CC model, the $C_1$ or $C_2$ adjustment procedure was based on minimizing the sum of squares of the difference of experimental data and modeling results over all the titration points. It can be seen from the table that the intrinsic acidity constants were similar to the CC model and the DL model. However, the differences in the intrinsic acidity constants based on the TL model and the CC model or the DL model were much larger than those between the CC model and the DL model. Usually, $C_2$ is assumed constant at 0.2 F/m$^2$ (Langmuir 1997) while $C_1$ is varied to optimize the fit of the TL model to experimental data. Published values of $C_1$ for hydrous ferric oxide have ranged from 0.90 to 1.4 F/m$^2$ (Hsi and Langmuir 1985). Riese (1982) suggested $C_1 = 1.3$ F/m$^2$ for quartz and $C_1 = 2.4$ for kaolin. On the other hand, Silva and Yee (1981) used $C_1 = 0.9$ F/m$^2$ for quartz. In this experiment, the $C_1$ values ranged from 1.4 to 2 F/m$^2$. Since the dominant component of Amite soil is quartz on a mass basis, it is reasonable to have $C_1$ values of 1 to 1.5 F/m$^2$ for Amite soil.

For measurement over a range of ionic strengths, the CC model requires the input of $C_1$ values at different ionic strength, and it is found in this study that the optimum $C_1$ value depends
on ionic strength. Since the CC model conceptualizes the complexation layer as a capacitor filled with electrolyte, it is reasonable to imagine that the value of “electrical capacitance” increases with increasing electrolyte. The DL model is both simpler and more flexible in that the DL model allows modification of complexation for ionic strength using Gouy-Chapman theory and does not demand an input of capacitance (Langmuir 1997). The TL model has the most parameter requirements, but exhibits the greatest flexibility and accuracy.

Table 2-5. Intrinsic Acidity Constants of Clay Materials.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Parameter</th>
<th>CC Model</th>
<th>DL Model</th>
<th>TL Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log K_a^{\text{int}}$</td>
<td>$\log K_a^{\text{int}}$</td>
<td>$\log K_a^{\text{int}}$</td>
<td>$\log K_a^{\text{int}}$</td>
</tr>
<tr>
<td></td>
<td>I=0.001 N</td>
<td>I=0.01 N</td>
<td>I=0.1 N</td>
<td>I=0.001 N</td>
</tr>
<tr>
<td>Bentonite</td>
<td>10.49</td>
<td>10.67</td>
<td>10.55</td>
<td>12.39</td>
</tr>
<tr>
<td>Kaolin</td>
<td>9.44</td>
<td>9.22</td>
<td>9.72</td>
<td>9.74</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>9.74</td>
<td>9.49</td>
<td>9.15</td>
<td>9.08</td>
</tr>
<tr>
<td></td>
<td>-29.1</td>
<td>-28.79</td>
<td>-29.1</td>
<td>-26.95</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>1.1</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

CC Model: Constant Capacitance Model  
DL Model: Diffuse-layer Model  
TL Model: Triple Layer Model. The data for bentonite did not converge in TL modeling
Figure 2-5. Schematic distribution of charged surface species on bentonite, kaolin and Amite soil. Since the three complexation models generate very similar surface species distribution, only the result based on CC model is presented here.
Based on the surface complexation model, the fraction of surface species of the three clay materials as a function of pH are plotted in Figure 2-5. It can be seen from the figure that the surface of kaolin and Amite soil is positively charged at low pH value due to the dominance of SOH$_2^+$ while negatively charged at high pH value due to prevalence of SO$. However, it is found that the SOH$_2^+$ percentage is always negligible compared with SO$^-$ on the bentonite surface over the pH range tested. This is an illustration of why PZC was not observed during the potentiometric titration of bentonite, as demonstrated in Figure 2-3. At the same time, the PZC of kaolin and Amite soil can also be obtained from the points where SOH$_2^+$ and SO$^-$ have the same concentration. The comparison of Figures 3 and 5 indicates that the complexation model gives a similar PZC value compared to the potentiometric titration method results illustrated in Figure 2-3.

**SEM Investigation of Clay Materials**

Scanning electron micrographs (SEM) of the three clay materials before and after subjected to metal species solution are shown in Figures 2-6 through 2-8. Virgin bentonite minerals are composed of interconnected, small, distorted flakes which form a homogeneous texture. On the other hand, kaolin contains discrete fine particles, aggregated as large particles and stacks. Fine particles are the dominant form of kaolin. Amite soil contains large discrete particles (quartz) which are covered with clay mineral coating. However, large aggregates of particles or fine particles were not found for Amite soil. Comparing SEMs of the three clays also provides a qualitative indication that bentonite has a much higher specific surface area than kaolin.

The comparison of SEM images before and after interaction with metal species indicate that clay morphology did not significantly change, for kaolin and Amite soil. Energy spectra of
kaolin and Amite soil also indicate that the composition of the two clay materials did not significantly change after the adsorption process, as illustrated in Figures 2-6 and 2-7. This is reasonable since the total amount of metal species adsorbed on the clays amounted to less than 0.05 % of the total solid mass.

Figure 2-6. SEM image and associated energy spectra of bentonite before and after interaction with metal species. In the SEM image sodium crystal build up can be observed. The energy spectra indicate a high sodium content at the clay surface suggesting sodium was released from interlayers of the clay and exchanged for metal species.
However, this was not the case for bentonite since it was found that there was a build-up of crystals on the bentonite surface. Energy spectra summarized in Figure 2-6 were further employed to identify the composition of the crystal. The result indicates that the crystals were high in sodium. Therefore, it was speculated that unlike complexation reactions occurring on kaolin and Amite soil surfaces, metal species interaction by bentonite was governed by ion
exchange reactions. Na\(^+\) ions in bentonite were replaced by the metal species when bentonite came into contact with the metal species and Na\(^+\) ions were released into the solution thereafter. When the sample was prepared for SEM analysis, they were dried, and therefore sodium salts crystallized.

Figure 2-8. SEM image and associated energy spectra of Amite soil before and after interaction with metal species.
CONCLUSIONS

The physical and chemical characteristics of bentonite, kaolin and Amite soil were investigated since it was hypothesized that these characteristics have a significant effect on their surface interaction with metal species in stormwater residual landfill leachate. Results indicate that of the three clay materials investigated, bentonite has the highest specific surface area and surface charge while Amite soil has the smallest specific surface area and surface charge. The PZC values are 4.6 and 5.25 for kaolin and Amite soil, respectively based on the experimental results. However, the surface of bentonite was always negatively charged over the pH range (3.5 to 9) of this study. The surface complexation models of constant capacitance form (CC), the diffuse-layer form (DL) and triple-layer form (TL) were used successfully with the aid of the FITEQL algorithms to model protonation and deprotonation processes on the clay surface. The CC model and DL model result in very similar acidity constants. Based on the result of potentiometric titration, it was concluded that ionic strength had little effect on the protonation and deprotonation for kaolin while the degree of protonation of bentonite and Amite soil increased with ionic strength. SEM and energy spectra were also employed to investigate the change of clay surface caused by the clay surface interactions with metal species. It was found that no significant change occurred in the surface morphology of kaolin and Amite soil. However, sodium-containing crystals were built up on the bentonite surface, suggesting that metal species interaction with bentonite is a process of ion exchange.

REFERENCES


Herbelin, A. L. and Westall, J. (1999) “A computer program for the determination of chemical equilibrium constants from experimental data.” Report 99-01, Department of Chemistry, Oregon State University, Corvallis, USA.


NOMENCLATURE

The following symbols are used in this paper:

- $A_i$ = peak area in XRD diffractogram
- $C_A$ = molar concentration of acid added (M)
- $C_B$ = molar concentration of base added (M)
- $C_1$ = capacitance in constant capacitance model (F/m$^2$)
- $C_2$ = capacitance constant between zero plane and $\beta$ plane (F/m$^2$)
- $C_3$ = capacitance constant between $\beta$ plane and d plane (0.2 F/m$^2$)
- $C_j$ = free concentration of species j (M)
- $d_i$ = particle diameter ($\mu$m)
- $F$ = Faraday constant (96480 C/mol)
- $f$ = correction factor in calculating soil organic content (1.3)
- $H^+(s)$ = hydrogen ion at solid surface
- $\{H^+(s)\}$ = hydrogen ion activity at solid surface (M)
- $I$ = ionic strength (M)
- $K_{a1}^{\text{int}}$ = intrinsic acidity constants of protonation of clay
- $K_{a2}^{\text{int}}$ = intrinsic acidity constants of deprotonation of clay
- $K_{el}^{\text{int}}$ = intrinsic constants for electrolyte cations and anions
- $K_w$ = ion product of water ($10^{-14}$)
- $m$ = number of measurement
- $M_i$ = mass of particles with diameter of $d_i$ (g)
- $M_{Fe^{2+}}$ = concentration of FeSO$_4$ solution (M)
- $N_i$ = number of particles with diameter of $d_i$
- $v_{NaOH}$ = concentration of base added (N)
- $N_{HCl}$ = concentration of acid added (N)
- $P_1$ = initial pressure in particle density measurement (lb/in$^2$, 1 b/in$^2$ = 6.9 kPa)
- $P_2$ = final pressure in particle density measurement (lb/in$^2$, 1 b/in$^2$ = 6.9 kPa)
- $pK_{a1}^{\text{int}}$ = negative logarithm of intrinsic acidity constants of protonation of clay
- $pK_{a2}^{\text{int}}$ = negative logarithm of intrinsic acidity constants of deprotonation of clay
- $pK_{el}^{\text{int}}$ = negative logarithm of intrinsic constants for electrolyte cations and anions
- $R$ = ideal gas constant (8.314 J/mol·K)
- $SOH$ = neutral function group on clay surface
- $\{SOH\}$ = neutral function group activity on clay surface (M)
- $SOH_2^+$ = positively charged functional group on adsorbent surface
- $\{SOH_2^+\}$ = positively charged functional group activity on adsorbent surface (M)
- $SO^- = negatively charged functional group on adsorbent surface
- $\{SO^-\}$ = negatively charged functional group activity on adsorbent surface (M)
- $T$ = absolute temperature (K)
- $TOTH$ = surface proton excess or deficiency (M)
- $v_{\text{blank}}$ = volume of FeSO$_4$ used in titration of blank solution (ml)
- $v_{\text{sample}}$ = volume of FeSO$_4$ used in titration of sample (ml)
- $v_{HCl}$ = volume of acid added (ml)
- $v_{NaOH}$ = volume of base added (ml)
- $V_C$ = cell volume of pycnometer (cm$^3$)
VR = reference volume (cm³)
VS = true sample volume (cm³)
Wa = weight of EGME adsorbed by clay (g)
Ws = dry weight of sample clay (g)
Yi = value obtained experimentally
\( \hat{Y_i} \) = value predicted from the model
z = ionic valence
\( \psi_0 \) = potential at clay surface (V)
\( \psi \) = potential at adsorption zone (V)
\( \theta \) = diffraction angle (degree)
\( \rho_i \) = particle density with diameter i (g/cm³)
\( \sigma \) = surface charge density (C/m²)
\( \varepsilon_r \) = dielectric constant of water (78.4)
\( \varepsilon_0 \) = permittivity of free space (8.85×10⁻¹² F/m)
CC Model = constant capacitance model
DL Model = diffuse-layer model
EGME = ethylene glycol monoethyl ether
Organic C = organic content (%)
RMSE = root-mean-square-error
PZC = point of zero charge
SA = surface area (m²)
SEM = scanning electronic microscopy
SCM = surface complexation model
SSA = specific surface area (m²/g)
TL Model = triple-layer model
XRD = X-ray diffraction
Chapter 3. Interaction of Clay Liner Materials with Metal Species from Urban Rainfall-Runoff Residual Leachate: Competition and Isotherms

SUMMARY

Clay-lined landfill systems for urban storm water and snow melt runoff residuals often contain leachate with high concentrations of metal species, including Cu, Zn, Cd and Pb. The competitive interactions of Cu, Zn, Cd and Pb with bentonite, kaolin and a native (sandy silty clay) soil (Amite soil) was investigated and Freundlich isotherms were utilized to describe the experimental data. The results indicated that the adsorption capacities of the three clay materials decreased in the order: bentonite > Amite Soil > kaolin. The relative affinities of the four metals for the three clays followed a consistent trend with Pb > Cu > Zn > Cd. The analysis of interaction parameters of metal species on the clay materials indicates that Cu was preferentially adsorbed compared to Zn and Cd while Pb was preferentially adsorbed compared to Cu for bentonite, kaolin and Amite soils. Metal species adsorption by bentonite exhibited an ion exchange behavior. Ion exchange isotherms were interpreted in terms of metal species exchange selectivity. Results indicate that the selectivity for Pb could be altered by the presence of Cu, Zn and Cd. However, the selectivity of the exchange reactions for Cu, Zn and Cd exhibited little change for combinations of these metals. This research indicates that with respect to selection and use of clay materials for landfill liners to contain metal species leachate, competitive adsorption must be considered. In addition to functioning as a physical separation barrier, clay materials can function as reactive barriers that exhibit selectivity for metal species.

INTRODUCTION

Rainfall-Runoff and Snowmelt Leachate

Cu, Zn, Cd and Pb are the most frequently detected metal species in urban rainfall-runoff, snowmelt and urban residual materials captured by recent proliferation of best management
practices (BMPs). Urban rainfall-runoff and snowmelt typically carry a mixture of metal species, entrained particulate matter and inorganic constituents (Glenn and Sansalone 2002, Sansalone and Buchberger 1997). As a result, rainfall-runoff and snowmelt and residuals captured by BMPs have been recognized as “wastewater” distinct from more traditional waste streams such as domestic wastewater. Figure 3-1 illustrates typical distributions of residual mass, granulometric surface area, specific surface area and solid-phase metal species mass as a function of particle diameter for residuals collected from a BMP loaded by urban rainfall-runoff in an urban transportation land use corridor. It can be seen from the figure that the mass of metal species in sludge taken from rainfall-runoff BMPs can be relatively high with a distribution across the particulate gradation. The predominance of metal species mass can be associated with the coarser size particle fraction (>250-µm). This trend is similar to that for residual mass retained and total SA where the predominance of both is associated with the coarser fraction of particles. A simple example illustrates the magnitude of the problem for solid residuals. Assume a typical urban area with a population of a 10^6 residents and interstate/major arterial roadway area of 50 km^2, annual precipitation of 1000 mm, mean suspended solids level of 200 mg/L in rainfall-runoff, and an average runoff volume coefficient of 0.70 for urban transportation land use only (Sansalone et al 1998). Even if 50% effectiveness is assumed for separation of suspended solids and associated metal species the quantity of potentially hazardous solid waste residual generated is 5 ×10^6 kg or approximately 2140 m^3 of solid hazardous waste on an annual basis. This excludes the liquid volume from the sludge.

As the number of treatment plants providing advanced treatment continues to increase, the relative importance of rainfall-runoff treatment for improvement of the nation’s streams and rivers is increasing (Metcalf and Eddy 2003).
Figure 3-1. Typical distribution of characteristics for urban residuals recovered from a transportation land use storm water control.
In many river basins, additional treatment beyond secondary treatment may have essentially marginal impact on stream quality until rainfall-runoff discharges are controlled. Today, current practices for “Best Management Practice” (BMP) application development and BMPs utilization is on a site-specific basis all over the country whether on a site-specific or regional basis. There is an increasing accumulation of metal species in the sludge generated from the proliferation of such BMPs, and therefore a greater impact to manage this sludge.

**Landfill as Management Tool from Residuals**

Landfills are the most widely used method of solid waste and sludge disposal around the world. This method of waste management has been practiced for centuries and will continue to be an important component of municipal solid waste management across the USA. However, with increasing concerns about landfill leachate as a potential source of soil and groundwater pollution, landfill practices have come under increasing scrutiny in recent decades (Bagchi 1989). Due to the variations in solid waste composition, landfill age and moisture content, metal species constituents and concentration can exhibit large concentration variations in leachate. For example, landfill leachate concentrations of Cu, Zn, Cd and Pb can range from 0.01 to 16 mg/L, 0 to 40 mg/L, 0.05 to 8.2 mg/L and 0.3 to 19 mg/L, respectively. (LaGrega et al. 1994). Of the various metal species encountered in landfill leachate, Cu, Zn, Cd and Pb are listed as priority pollutants by USEPA, are commonly found in landfill leachate (Qasim and Chiang 1994) and are the most commonly detected metals in urban runoff and snowmelt (Sansalone and Buchberger 1997, Sansalone and Glenn 2002).

Specific aspects of the occurrence and potential impacts of metal species in landfill leachate have been investigated by various researchers (Papini 2001, Qasim and Chiang 1994, Schroth and Sposito 1998 and Kayabali and Kezer 1998). Since the migration of leachate is often
a slow process and the deleterious impacts of metal species may become evident only after a long period of time, the prediction of the fate of metal species in the leachate is critical. Clays are commonly used landfill liner materials for separation of metal species leachate from the subsurface environment, and clay interaction with metal species is critical in understanding the mobility of metal species in the subsurface environment.

The removal of metal species, including Cd, Ni and Cu, from three leachates collected from landfill sites at different fermentation stages onto kaolin was studied by Papini et al. (2001). They found that metal species speciation played an important role in determining the equilibrium partitioning behavior onto kaolin. Results from their research also demonstrated that strong complexing capacity of leachate containing high organic matter (1379 to 9155 mg/L of COD) that was capable of altering the equilibrium partitioning of metal species with the solid phase. No isotherms were developed from this research. Mellah and Chegrouche (1997) investigated the removal of Zn from aqueous solution by bentonite. It was found that the Zn isotherm could be represented by both Freundlich and Langmuir models. However, only Zn was investigated and no information was provided on the solid phase partitioning of other metal species found in landfill leachate.

Kayabali and Kezer (1998) examined the ability of natural zeolites to remove metal species (Pb, Zn, Cu, Ni, As, Mn and Fe) from aqueous solutions. Leachate from a conventional landfill was used as the percolation fluid. In their study, information was provided on the temporal breakthrough of metal species and exchangeable ions (Ca, Na, K and Mg) in the effluent. However, no isotherm, selectivity or mathematical modeling was presented. Modified clays (montmorillonite) grafted with organic ligands have also been tested to partition Hg, Zn and Pb from aqueous solution (Rafael Cells et al. 2000). Results indicated that the Langmuir
The Langmuir equation was a good approximation of the experimental data. Dong et al. (2000) investigated Pb and Cd partitioning onto Fe and Mn oxides that existed in lake biofilms. The Langmuir equation was used to model the partitioning process. The partitioning of metal species from aqueous solution onto various clay minerals is controlled by speciation aqueous chemistry and the physical-chemical characteristics of the clays, such as Na or Ca content. (Weiss et al. 1998). Consequently, different mathematical models have been developed to simulate the various partitioning processes such as adsorption or ion exchange processes onto clay. Of the various models proposed, ion exchange type models (such as simple ion exchange models and power exchange functions) and electrostatic complexation models (such as diffuse-layer and constant capacitance models and the triple-layer model) are the two main categories of models (Langmuir 1997). Van et al. (1993) studied Ca-Cd and Ca-Zn exchange on different clay minerals and the thermodynamic equilibrium constants for ion exchange reactions were calculated. More recently, Sarkar et al. (1999) and Sarkar et al. (2000) reported the influence of pH, ionic strength, ligands (Cl\(^-\), SO\(_4^{2-}\), PO\(_4^{3-}\)) and metals (Ni and Pb) on the surface complexation of Hg by quartz and gibbsite. The triple layer model was used successfully to simulate the surface complexation process by these researchers.

OBJECTIVES

Metal species interaction with clay has been studied by numerous researchers. While there is some agreement that multiple species interaction with the solid surface is influenced by species competition, there remains uncertainty about the isotherm, interactions and selectivity of different metal species in competitive surface process for common clay liner materials. Some researchers have investigated metal species adsorption on clay in terms of ion exchange (Bladel et al. 1993, Weiss et al. 1998) and the ion exchange isotherms often refer to binary exchange
systems. However, there has been little investigation of higher order exchange systems (for example, quaternary systems). Although several ion exchange studies have been undertaken for multiple element systems (Colella 1996 and Galindo and Bingham 1997), the effect of the presence of other metal species on the selectivity for a given metal species over another metal species has not been fully investigated. Because of the importance of metal species interaction with clay materials in determining metal species overall mobility and fate in soil and groundwater, competitive interaction of Cu, Zn, Cd and Pb with clay, a commonly used material in landfill liner, was investigated in this research. Investigations of interactions between single and multiple metal species and selected clay liner materials are the focus of this paper. For urban residual landfill leachate the presence of multiple competing cations will be more frequently encountered than the existence of only one metal species.

Interactions among four metal species, Cu, Zn, Cd and Pb were examined in this research. Although numerous metal species may be detected in landfill leachate, these four metal species are the most frequently detected elements associated with urban residual materials and in sludge from rainfall-runoff and snowmelt best management practices (BMPs). These metals are also designated as priority pollutants under the Clean Water Act (LaGrega et al. 1994). Three clay soil materials were investigated. Two of these materials were pure clay minerals, bentonite and kaolin and the third was a natural clayey soil used for landfill liners. Results from the characterization of the clay liner materials were described in elsewhere.

The first objective of this study was to study the differences in clay behavior for single metal species interactions. The second objective was to investigate the competitive metal species interaction for multiple-element systems. The competitive isotherms for each metal species were developed based on the investigation and comparison of the metal-clay interactions in mono-
element and multiple-element systems. The third objective was to simulate the uptake of metal species on bentonite in terms of an ion exchange model and analyze the selectivity of exchange reactions between Cu, Zn, Cd and Pb.

BACKGROUND

Competitive Isotherm

To date, numerous studies have been conducted to investigate the interaction of metal species with soils or clays, and various approaches have been used to quantify adsorption equilibria, through the use of isotherms (Malakul et al. 1998, Zehetner and Wenzel 2000, Lee et al. 1996, Dong et al. 2000 and Manning and Goldberg 1997). For example, Malakul et al. (1998) found that several modified clays with long-chain alkyldiamines, dialkklamines and carboxylic acid could have the comparable partitioning capacity as those of some commercial chelating resin. Langmuir isotherms were employed to model the process. Five acid forest soils of east Austria were used to study the Ni and Cu partitioning to soils and the distribution coefficients were calculated (Zehetner and Wenzel 2000). Lee et al. (1996) used a partition coefficient model of Cd interaction with 15 New Jersey soils. The interactions of Pb and Cd by biofilms and associated minerals extracted from surface water was examined and Langmuir isotherm was tested to fit the experimental data by Dong et al. (2000). Both Freundlich and Langmuir isotherms were examined to evaluate the interaction of arsenic with 3 California soils (Manning and Goldberg 1997).

Isotherm equations can represent the experimental data in a concise manner and such equations can also be used to predict behavior under conditions that have not been investigated. An isotherm model that has been commonly utilized to model clay as a suspended material in aquatic systems is the Freundlich isotherm (Yong and MacDonald 1998, Wang et al. 1998,

\[ q = kC^n \]  

In this equation \( q \) is adsorption density defined as mass of solute partitioned per unit mass of solid, \( C \) is the equilibrium concentration of solute, and both \( k \) and \( n \) are constants.

For example, Yong and MacDonald (1998) employed Freundlich isotherm to study the interaction of Pb and Cu with illite. Wang et al. (1998) evaluated the applicability of Freundlich isotherm to the interaction of Cd, Ni and Sr with surface soils. At the same time, Zehetner and Wenzel (2000) studied the interaction of Ni and Cu while Manning and Goldberg (1997) examined the interaction of As with soils. The Freundlich expression has the form of a power law expression and was initially regarded as a completely empirical isotherm (Roy et al. 1991). However, for a mono-component system, the Freundlich isotherm can be obtained theoretically when an exponential distribution of adsorption energy is assumed (Sheindorf et al. 1981). Alternatively, isotherm equations could also be developed from theory, based on kinetics for the interactions with the solid surface, dissolved species and surface-complexed as shown below.

It is conceptually imagined that the adsorption process consists of two processes occurring simultaneously; these are adsorption and desorption reactions. The net rate of adsorption from aqueous solution is the difference of adsorption rate and desorption rate (Sposito 1994).

\[ r_{\text{net}} = r_{\text{ads}} - r_{\text{des}} \]  

In this expression \( r_{\text{net}} \) is the net rate of adsorption, \( r_{\text{ads}} \) is the rate of adsorption and \( r_{\text{des}} \) is the rate of desorption. It is further assumed that the adsorption reaction rate is first order with respect to adsorption sites which are unoccupied on clay and \( n/\)th order in metal species concentration in
aqueous solution, while the desorption reaction rate is first order with respect to adsorbed metal species on clay. Based on the above assumptions, Equation (3) is derived:

\[ r_{net} = k_1 C_S C^n - k_2 C_{SA} \]  

(3)

In this expression \( C_S \) is the concentration of unoccupied adsorption sites on the clay, \( C_{SA} \) is the concentration of occupied adsorption sites and \( k_1 \) and \( k_2 \) are reaction coefficients of adsorption and desorption reactions, respectively. At equilibrium, \( r_{net} \) is zero so Equation (3) can be rewritten as shown in Equation (4).

\[ k' = \frac{k_1}{k_2} = \frac{C_{SA}}{C_S C^n} \]  

(4)

In this expression \( k' \) is the adsorption equilibrium constant and all the other parameters have been previously defined.

In a mono-element system, a mass balance on adsorption sites, including both the occupied and unoccupied, the following equation can be generated:

\[ C_{Stot} = C_S + C_{SA} \]  

(5)

In this equation, \( C_{Stot} \) is total concentration of adsorption sites on clay. Substituting Equation (5) into Equation (4) results in Equation (6).

\[ C_{SA} = \frac{k' C_{Stot} C^n}{1 + k' C^n} \]  

(6)

Equation (7) is equivalent to Equation (6) if both sides of Equation (6) are divided by adsorbent concentration.

\[ q = q_{max} \frac{k' C^n}{1 + k' C^n} \]  

(7)

In this expression \( q_{max} \) is maximum adsorption density. Under conditions where \( k' C^n \ll 1 \), Equation (7) becomes
\[ q = q_{\text{max}}k'C^n = kC^n \]  

(8)

It can be seen from Equation (8) that \( n \) can also be regarded as the adsorption reaction order with respect to the adsorbate in aqueous solution while \( k \) is the product of maximum adsorption density and adsorption equilibrium constant.

In a multiple-element system, competitive effects can be significant even if a small portion of another metal species exists. Under such circumstances, interaction parameters are required to model such systems. In the general case where \( j \) adsorbates compete for the surface sites, the corresponding expression for the Freundlich adsorption isotherm of any particular species \( i \) is presented in Equation (9) (Sheindorf et al. 1981).

\[ q_i = k_iC_i\left(\sum_j a_{ij}C_j\right)^{n_{ij}^{-1}}, \quad a_{ii} = 1 \]  

(9)

In this expression \( a_{ij} \) is interaction coefficient of metal species \( j \) to \( i \). It can be seen from Equation (9) that this equation reduces to the conventional Freundlich isotherm when there is only one adsorbate in the system (mono-element system).

For a two-component system, Equation (9) results in Equation (10).

\[ q_1 = k_1C_1(C_1 + a_{12}C_2)^{n_{11}^{-1}} \]  

(10)

Algebraic re-arrangement of Equation (10) yields Equation (11).

\[ \frac{C_1}{C_2} = \frac{\beta_1}{C_2} - a_{12} \]  

(11)

In Equation (11)

\[ \beta_1 = \left(\frac{k_1C_1}{q_1}\right)^{\frac{1}{1-n_i}} \]  

(12)
Plotting of $\frac{C_1}{C_2}$ versus $\frac{\beta_1}{C_2}$ will yield a line with slope of unity and an intercept of $-a_{12}$. In the same way, the isotherm of the metal species in question in a three-component system is:

$$q_1 = k_1 C_1 (C_1 + a_{12} C_2 + a_{13} C_3)^{n_1-1} \quad (13)$$

Rearrangement of Equation (13) leads to Equation (14).

$$\frac{C_1}{C_3} = \left( \frac{\beta_1 - a_{12} C_2}{C_3} \right) - a_{13} \quad (14)$$

The interaction coefficient of metal species 3 to 1, $a_{13}$, can be determined by plotting $\frac{C_1}{C_3}$ versus $\left( \frac{\beta_1 - a_{12} C_2}{C_3} \right)$.

Similarly, the isotherm of the metal species in question in a four-component system is written as follows in Equation (15).

$$q_1 = k_1 C_1 (C_1 + a_{12} C_2 + a_{13} C_3 + a_{14} C_4)^{n_1-1} \quad (15)$$

From this expression the following equation can be drawn.

$$\frac{C_1}{C_4} = \left( \frac{\beta_1 - a_{12} C_2 - a_{13} C_3}{C_4} \right) - a_{14} \quad (16)$$

The interaction coefficient of metal species 4 to 1, $a_{14}$, can be determined by plotting $\frac{C_1}{C_4}$ versus $\left( \frac{\beta_1 - a_{12} C_2 - a_{13} C_3}{C_4} \right)$.

It can be seen from Equation (9) that competitive adsorption is a fundamental component of multi-element systems and to ignore such competitive nature can lead to significant error even at low species concentrations for Freundlich type adsorption.
**Ion Exchange Isotherm**

If Na$^+$ is the interlayer exchangeable cation for Na-bentonite, stoichiometrically binary ion exchange reactions for Na and divalent metal species on clay can be expressed by the following equation (Sposito 1994):

\[
2 \text{NaX(s)} + \text{Me}^{2+}(\text{aq}) \leftrightarrow \text{MeX}_2(\text{s}) + 2\text{Na}^+(\text{aq})
\]  

(17)

In this expression X(s) represents anion exchange sites on the clay and Me$^{2+}$ is a divalent metal species, such as Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ or Pb$^{2+}$.

The equilibrium constant, $K_c$, can be formulated to describe the reaction in Equation (17) (Sposito 1994).

\[
K_c = \frac{x_{\text{Me}}[\text{Na}^+]^2}{x_{\text{Na}}^2[\text{Me}^{2+}]} 
\]  

(18)

In this expression $x_{\text{Me}}$ and $x_{\text{Na}}$ are the mole fractions of exchanged metal species and Na on the clay, respectively, and [Na$^+$] and [Me$^{2+}$] are ion activities of the aqueous ionic species Na$^+$ and Me$^{2+}$, respectively. Either $x_{\text{Me}}$ or $x_{\text{Na}}$ can be expressed in the following form.

\[
x_i = \frac{\Gamma_i}{\Gamma_{\text{Na}} + \Sigma \Gamma_{\text{Me}}} \quad (i = \text{Na}^+ \text{ or Me}^{2+})
\]  

(19)

In this expression, $\Gamma_i$ is mole of exchanged metal species (Me$^{2+}$) per unit dry mass of clay. $\Sigma \Gamma_{\text{Me}}$ is the sum of moles of exchanged metal species on a unit mass of dry clay. $K_c$ is also defined as ion exchange selectivity, which is a measure of the preference that the exchanger exhibits for one ion compared with another. If $K_c = 1$, the exchange reaction described in Equation (17) indicates no preference while the exchange reaction is selective for a metal species if $K_c > 1$ (Sposito 1994). The rearrangement of Equation (18) yields the nonpreference exchange isotherm equation (Sposito et al. 1981).
\[ E_{Me} = 1 - \left[ 1 + \frac{2~E_{Me}}{\sim S Q(1 - \sim E_{Me})^2} \right]^{-1/2} \] (20)

In this expression \( E_{Me} \) is the charge fraction of adsorbed the exchanged divalent metal species, \( \text{Me}^{2+} \) (e. g., Cu, Zn, Cd and Pb). \( \sim E_{Me} \) is the charge fraction of \( \text{Me}^{2+} \) in aqueous solution. \( S \) is a ratio of the single ion activity coefficient \( (\gamma) \) of the aqueous cation \( \text{Na}^+ \) squared to the metal species of interest, \( \text{Me}^{2+} \). \( E_{Me} \) can also be expressed in the following terms.

\[ E_{Me} = \frac{q_{Me}}{Q} \] (21)

In this expression \( q_{Me} \) is the adsorbed charge of ion \( \text{Me}^{2+} \) and \( Q \) is the cation exchange capacity (CEC) of the clay. \( \sim E_{Me} \) can be calculated with the following expression.

\[ \sim E_{Me} = \frac{Z_{Me} m_{Me}}{\sim Q} \] (22)

In this expression \( Z_{Me} \) is the valence and \( m_{Me} \) is the molality of metal species \( \text{Me}^{2+} \). \( \sim Q \) is defined in the following terms.

\[ \sim Q = \sum (Z_{Me} m_{Me}) \] (23)

\( S \) is defined in the following terms.

\[ S = \left( \frac{\gamma_{Na}^2}{\gamma_{Me}} \right) \] (24)

In a multi-component ion exchange system with Cu, Zn, Cd and Pb where clay is used as an ion exchange medium, the following cation exchange reactions are expected to exist in addition to Equation (17).

\[ \text{CuX}_2 + \text{Zn}^{2+} \leftrightarrow \text{ZnX}_2 + \text{Cu}^{2+} \] (25)
The non-preference exchange isotherm for the homovalent exchange reactions which are representative of Eqs. (25) through (30) can be expressed as follows (Sposito et al. 1981).

$$E_i = \tilde{E}_i$$  \hspace{1cm} (31)

This equation has been used extensively to model the exchange of $\text{Ca}^{2+}$-$\text{Zn}^{2+}$ and $\text{Ca}^{2+}$-$\text{Cd}^{2+}$ on montmorillonite, bentonite, illite and vermiculite (Bladel et al. 1993), $\text{K}^+$-$\text{Na}^+$ and $\text{Ca}^{2+}$-$\text{Mg}^{2+}$ on soils (Galindo and Bingham 1977) and $\text{NH}_4^+$-$\text{Na}^+$ on zeolite (Colella 1996).

**METHODOLOGY**

**Clay Materials**

The clays used in this study included non-treated natural Na-bentonite (having a trade name of Aquagel Gold Seal, Baroid Drilling Fluids, Inc., Houston, TX), kaolin (having a trade name of EPK, Feldspar Corporation, Atlanta, GA), and a native soil (Amite soil) commonly found in the Tangipahoe basin of South Louisiana. The physical and chemical characteristics of these clays were examined in elsewhere.

**Competitive Isotherms**

There were 4 specific metal species (Cu, Zn, Cd and Pb) investigated in this study. As a result, there existed 15 ($C_1^4 + C_2^4 + C_3^4 + C_4^4$) possible metal species combinations which included either one, two, three or four of the metal species.
Mono-element and multiple-element isotherms were obtained in batch-type experiments using 50-mL polypropylene centrifuge tubes. 200 mg of bentonite, 400 mg of kaolin or 400 mg of Amite soil were equilibrated with 40 mL of metal species solutions with different composition and concentration for 24 h at 25 ºC using a reciprocating shaker. The metal species solutions were obtained by diluting 1000 mg/L metal species stock solutions of Cu(NO₃)₂, Zn(NO₃)₂, Cd(NO₃)₂ and Pb(NO₃)₂. The initial concentrations were 1, 10, 20, 30, 40, 50, 60 and 70 mg/L for each metal species. NaNO₃ was used as background electrolyte and the ionic strength was kept at 0.01 M throughout the experiment (Lee et al. 1996). The initial pH values were adjusted to 3.5 so that the equilibrium pH values were maintained at 5.0 to 5.9. Equilibrium speciation modeling (MINTEQA) was used to ensure that there was no metal species precipitation within the experimental pH range and the predominant species in solution are their uncomplexed divalent forms. Table 3-1 is a summary of metal species speciation when the metal species concentration was 70 mg/L for each metal at pH 5.9. Nearly all metal species exist in the form of uncomplexed ions and no precipitate occurs when pH was less than 5.9 and metal species concentrations were 70 mg/L or less than 70 mg/L for each. After equilibration, the solution was separated from the clay by a syringe membrane filter (cellulose, 0.45 µm) and 0.1 or 0.2 mL of the filtered solution was removed and acidified with 5% trace metal HNO₃ for metal species analyses using ICP-MS. Five-point calibration was employed to construct the standard curve. The concentrations of the standard solution used included 0, 10, 20, 100 and 500 µg/L. The measuring conditions were 100 ms dwell time, 50 sweeps/reading and 3 replicates for each sample. The internal standard was Rh which was pumped into the plasma with the sample, giving a concentration of 10 mg/L. The elements were measured at m/z values of 63 for Cu, 64 for Zn, 114 for Cd and 208 for Pb. QA/QC included checking a standard solution with
concentration of 50 µg/L for each metal every 8 samples. The reliability of the results was checked to ensure that the measured value was within 45 to 55 µg/L for each metal. The amount of exchanged metal species was calculated as the difference between the amount added initially and that remaining in solutions.

Table 3-1. Metal species speciation at pH 5.9 and concentration of 70 mg/L for each metal. At lower pH values and lower concentrations the divalent species were all higher.

<table>
<thead>
<tr>
<th></th>
<th>Species Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Species</td>
</tr>
<tr>
<td></td>
<td>Cu^{2+}</td>
</tr>
<tr>
<td></td>
<td>Cu(OH)^+</td>
</tr>
<tr>
<td></td>
<td>Cu_2(OH)_2^{2+}</td>
</tr>
<tr>
<td></td>
<td>Cu(NO_3)^+</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Species</td>
</tr>
<tr>
<td></td>
<td>Zn^{2+}</td>
</tr>
<tr>
<td></td>
<td>Zn(NO_3)^+</td>
</tr>
<tr>
<td></td>
<td>Zn(OH)^+</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Species</td>
</tr>
<tr>
<td></td>
<td>Cd^{2+}</td>
</tr>
<tr>
<td></td>
<td>Cd(NO_3)^+</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Species</td>
</tr>
<tr>
<td></td>
<td>Pb^{2+}</td>
</tr>
<tr>
<td></td>
<td>Pb(OH)^+</td>
</tr>
<tr>
<td></td>
<td>Pb_2(OH)_3^{3+}</td>
</tr>
<tr>
<td></td>
<td>Pb(NO_3)^2 (aq)</td>
</tr>
<tr>
<td></td>
<td>Pb(NO_3)_2 (aq)</td>
</tr>
</tbody>
</table>

RESULTS

Competitive Isotherms

The isotherms for metal species under different experimental conditions are summarized in Figures 3-2 through 3-7, where the amount of metal species exchanged per unit dry weight of clay is plotted as a function of equilibrium metal species concentration. Over the entire range of metal species concentrations considered, the degree of metal species adsorption onto bentonite is greater than that observed for the other two clay materials studied, indicating that bentonite has the largest affinity for Cu, Zn, Cd and Pb. This is not surprising because bentonite has a much
higher surface charge and much higher specific surface area compared with kaolin and Amite soil.

Figure 3-2. Competitive exchange of Cu and Zn on bentonite. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 
Figure 3-3 Competitive exchange of Cd and Pb on bentonite. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 
Figure 3-4. Competitive exchange of Cu and Zn on kaolin. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 

Metal Species: Cu
Clay: Kaolin

Metal Species: Zn
Clay: Kaolin
Figure 3-5. Competitive exchange of Cd and Pb on kaolin. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 

Metal Species: Cd
Clay: Kaolin

1. Cd, $q = 0.245C^{0.342}$, $R^2 = 0.943$
2. Cd+Zn, $q = 0.062C^{0.669}$, $R^2 = 0.950$
3. Cd+Cu, $q = 0.079C^{0.601}$, $R^2 = 0.965$
4. Cd+Pb, $q = 0.070C^{0.608}$, $R^2 = 0.967$
5. Cd+Cu+Zn, $q = 0.054C^{0.634}$, $R^2 = 0.973$
6. Cd+Zn+Pb, $q = 0.044C^{0.689}$, $R^2 = 0.937$

Metal Species: Pb
Clay: Kaolin

1. Pb, $q = 0.579C^{0.407}$, $R^2 = 0.984$
2. Pb+Cd, $q = 0.278C^{0.530}$, $R^2 = 0.991$
3. Pb+Cu, $q = 0.296C^{0.450}$, $R^2 = 0.904$
4. Pb+Zn, $q = 0.186C^{0.612}$, $R^2 = 0.963$
5. Pb+Cu+Cd, $q = 0.131C^{0.556}$, $R^2 = 0.976$
6. Pb+Zn+Cd, $q = 0.184C^{0.484}$, $R^2 = 0.876$
Figure 3-6. Competitive exchange of Cu and Zn on Amite soil. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 

Metal Species: Cu
Clay: Amite Soil

| 1 | Cu, $q = 0.380C^{0.522}$, $R^2 = 0.990$ |
| 2 | Cu+Cd, $q = 0.234C^{0.526}$, $R^2 = 0.983$ |
| 3 | Cu+Zn, $q = 0.104C^{0.723}$, $R^2 = 0.977$ |
| 4 | Cu+Pb, $q = 0.152C^{0.621}$, $R^2 = 0.971$ |

Metal Species: Zn
Clay: Amite Soil

| 1 | Zn, $q = 0.107C^{0.692}$, $R^2 = 0.991$ |
| 2 | Zn+Cd, $q = 0.083C^{0.734}$, $R^2 = 0.959$ |
| 3 | Zn+Pb, $q = 0.082C^{0.702}$, $R^2 = 0.981$ |
| 4 | Zn+Cu, $q = 0.062C^{0.767}$, $R^2 = 0.978$ |
| 5 | Zn+Cu+Cd, $q = 0.022C^{0.995}$, $R^2 = 0.991$ |
| 6 | Zn+Cu+Pb, $q = 0.055C^{0.762}$, $R^2 = 0.979$ |
| 7 | Zn+Cd+Pb, $q = 0.066C^{0.733}$, $R^2 = 0.979$ |
| 8 | Zn+Cu+Cd+Pb, $q = 0.032C^{0.855}$, $R^2 = 0.975$ |
Figure 3-7. Competitive exchange of Cd and Pb on Amite soil. Initial aqueous metal species concentration: 1, 10, 20, 30, 40, 50, 60, 70 mg/L for each metal. Bentonite loading: 0.2 g/40 mL of aqueous solution. Ionic strength: 0.01 M NaNO₃. Equilibrium pH: 5.5 to 5.9. Draft fit to a Freundlich isotherm of form $q = kC^n$. 

Metal Species: Cd
Clay: Amite Soil

1. Cd, $q = 0.203C^{0.506}$, $R^2 = 0.983$
2. Cd+Zn, $q = 0.968C^{0.658}$, $R^2 = 0.980$
3. Cd+Cu, $q = 0.121C^{0.556}$, $R^2 = 0.992$
4. Cd+Pb, $q = 0.194C^{0.458}$, $R^2 = 0.979$
5. Cd+Cu+Zn, $q = 0.058C^{0.732}$, $R^2 = 0.992$

Metal Species: Pb
Clay: Amite Soil

1. Pb, $q = 0.816C^{0.436}$, $R^2 = 0.986$
2. Pb+Cd, $q = 0.530C^{0.409}$, $R^2 = 0.962$
3. Pb+Zn, $q = 0.460C^{0.463}$, $R^2 = 0.905$
4. Pb+Cu, $q = 0.553C^{0.401}$, $R^2 = 0.974$
5. Pb+Zn+Cd, $q = 0.567C^{0.365}$, $R^2 = 0.994$
6. Pb+Cu+Cd, $q = 0.439C^{0.428}$, $R^2 = 0.989$
7. Pb+Cu+Zn, $q = 0.483C^{0.382}$, $R^2 = 0.994$
8. Pb+Cu+Zn+Cd, $q = 0.380C^{0.405}$, $R^2 = 0.985$
However, although the Amite soil has a smaller surface charge and specific surface area than kaolin, it still has a higher affinity for metal species compared with kaolin. Of the three clay materials, Amite soil has the highest organic matter content, which may provide the additional exchange capacity. Therefore, the organic matter, although at a low level (0.34%) in clay, can have a significant effect on metal species interaction (Schroth and Sposito 1998).

These figures also illustrate that except for a few cases the Freundlich isotherm was a good model ($R^2 > 0.99$) to characterize the interaction of metal species with the three clay materials. At the same time, a comparison of mono-element metal species interaction with that of multiple-element demonstrates that the presence of other metals can alter the selectivity of a metal. The resultant competitive effects can be observed in Figures 3-2 through 3-7. The results summarized in these figures indicate that single-element systems had higher interaction than two-element systems, while two-element systems had higher interaction than three-element systems, and so on. In other words, metal species interactions were altered in the presence of other metal species, potentially allowing the preferential mobility of a particular metal species.

Table 3-2 is a summary of the Freundlich isotherm parameters. For the three clay liner materials, bentonite had the highest value of $k$ while Amite soil had the highest value of $n$. The $k$ value describes the capacity of the solid phase medium or the adsorption density under standard conditions ($q = k$ when $C = 1$), while $n$ indicates how dramatically the exchange or interaction affinity changes as the adsorption density or equilibrium concentration changes (Suffet and McGuire 1980). Since the interaction of metal species follow the Freundlich isotherms, it is assumed that the adsorption energy on clay materials is exponentially distributed (Sheindorf and Rebhun 1981). In other words, the clay materials behaved as if they contain very few sites with strong affinity for metal species and increasing numbers of sites with decreasing affinities. With
the increase of metal species concentration, the strong affinity sites would be rapidly exhausted with subsequent attachment of metal species to increasingly weaker interaction sites. As a result, the average adsorption affinities decrease with increasing surface coverage.

Table 3-2. Freundlich isotherm parameters under different experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Amite Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k</td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.834</td>
<td>0.138</td>
<td>0.202</td>
</tr>
<tr>
<td>2</td>
<td>2.806</td>
<td>0.172</td>
<td>0.067</td>
</tr>
<tr>
<td>3</td>
<td>2.323</td>
<td>0.144</td>
<td>0.036</td>
</tr>
<tr>
<td>4</td>
<td>1.956</td>
<td>0.112</td>
<td>0.012</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.068</td>
<td>0.280</td>
<td>0.089</td>
</tr>
<tr>
<td>2</td>
<td>1.895</td>
<td>0.212</td>
<td>0.067</td>
</tr>
<tr>
<td>3</td>
<td>1.125</td>
<td>0.293</td>
<td>0.047</td>
</tr>
<tr>
<td>4</td>
<td>1.018</td>
<td>0.270</td>
<td>0.018</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.704</td>
<td>0.147</td>
<td>0.245</td>
</tr>
<tr>
<td>2</td>
<td>1.614</td>
<td>0.296</td>
<td>0.070</td>
</tr>
<tr>
<td>3</td>
<td>1.065</td>
<td>0.309</td>
<td>0.047</td>
</tr>
<tr>
<td>4</td>
<td>0.929</td>
<td>0.276</td>
<td>0.032</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.995</td>
<td>0.417</td>
<td>0.579</td>
</tr>
<tr>
<td>2</td>
<td>2.019</td>
<td>0.512</td>
<td>0.253</td>
</tr>
<tr>
<td>3</td>
<td>0.830</td>
<td>0.627</td>
<td>0.133</td>
</tr>
<tr>
<td>4</td>
<td>0.643</td>
<td>0.531</td>
<td>0.029</td>
</tr>
</tbody>
</table>

* 1: Mono-element system
2: Bi-element system
3: Tri-element system
4: Tetra-element system

Table 3-2 indicates that bentonite has the highest affinity while kaolin has the lowest affinity for metal species. On the other hand, the binding affinity of metal species to Amite soil had the smallest decreasing gradient compared to the other two clays, while the binding affinity of bentonite has the most dramatic decrease among the three clays. Unlike bentonite and kaolin, Amite soil is a mixture mainly containing three minerals (bentonite, kaolin and quartz) with different distributions of metal species affinities. It is speculated that the number of strong
affinity sites on Amite soil decreases more slowly than bentonite and kaolin, thus giving Amite soil a value of n closer to unity. Even though sites with high affinity in Amite soil are completely occupied by metal species, there still remain other reactive adsorption sites on other clay surfaces. These adsorption sites still have high affinity and are accessible to the remaining metal species. As a result, the competitive behavior on Amite soil is less significant as compared with bentonite and kaolin. This is verified by Figure 3-8 from which it can be seen that of the three clay materials Amite soil has the smallest overall affinity decrease in the multiple-element system. The overall affinity decrease is calculated as

\[
\text{Overall affinity decrease} \% = 1 - \frac{\text{Affinity in multiple-element system}}{\text{Affinity in mono-element system}}
\]

(32)

Figure 3-8 also indicates that of the four metals, as a result of multiple-element interactions Pb has the largest magnitude of decrease in affinity. As the numbers of metal species components increase, these metal species bind to increasingly weaker sites, so the mean values of k in the Freundlich model results decrease.

Alternatively, the parameter n in the Freundlich isotherm can also be explained as the surface reaction order based on Equation (3). It can be seen from Table 3-2 that of the four metals investigated Pb has a relatively constant surface reaction order (0.407 to 0.436) for the three clay materials. However, this is not the case for Cu, Zn and Cd. The surface reaction orders of Cu, Zn and Cd on bentonite have the smallest values while those on Amite soil have the highest values, suggesting that different interaction mechanisms of Cu, Zn and Cd may exist on the three clay materials.

Figures 3-9 through 3-12 illustrates the determination of a_{ij}, the interaction coefficient of metal species j with respect to i. Based on Equations (11), (14) and (16), each line is expected to have a slope of unity and an intercept of -a_{ij}. 
Figure 3-8. Metal species affinity decrease for multiple-element systems. Overall affinity decrease is calculated as the difference of affinity in the mono-element system and that in the multiple-element system divided by the affinity in the mono-element system. The affinity decrease was obtained with C = 25 mg/L for each metal. Overall affinity decrease % = \frac{1 - Affinity in multiple-element system}{Affinity in mono-element system}. Results indicate that as a result of multiple-element interactions Pb has the largest magnitude of decrease in affinity.

However, the slopes of the lines in Figures 3-9 through 3-12 range from 0.70 to 1.63. Statistical analysis indicated that the mean and standard deviation of the values of slopes in Figure 3-6 were 1.02 and 0.20, respectively. T-tests were further employed and demonstrated that the slopes were not significantly different from unity at a 95% confidence interval. It can also be seen from the y-axes in Figure 3-6 that in the multiple-element system, there exists the following relationship for the three clay materials: $C_{Cu} < C_{Zn}$, $C_{Cu} < C_{Pb}$ and $C_{Zn} < C_{Cd}$. Based on
Figure 3-9. Determination of interaction parameter of Cu with other species for bentonite, kaolin and Amite soil.
Figure 3-10. Determination of interaction parameter of Zn with other species for bentonite, kaolin and Amite soil.
Figure 3-11. Determination of interaction parameter of Cd with other species for bentonite, kaolin and Amite soil.
Figure 3-12. Determination of interaction parameter of Pb with other species for bentonite, kaolin and Amite soil.
this information, and while the mechanisms may be different the relative affinity of the four metals for bentonite, kaolin and Amite soil is consistently Pb > Cu > Zn > Cd.

Table 3-3. Interaction coefficient of different metal species on clay materials

<table>
<thead>
<tr>
<th></th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Amite Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{Cu,Zn}$</td>
<td>0.22</td>
<td>0.36</td>
<td>0.16</td>
</tr>
<tr>
<td>$a_{Zn,Cu}$</td>
<td>0.41</td>
<td>0.53</td>
<td>0.40</td>
</tr>
<tr>
<td>$a_{Cu,Cd}$</td>
<td>0.38</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>$a_{Cd,Cu}$</td>
<td>1.53</td>
<td>0.59</td>
<td>1.21</td>
</tr>
<tr>
<td>$a_{Cu,Pb}$</td>
<td>1.22</td>
<td>1.02</td>
<td>0.96</td>
</tr>
<tr>
<td>$a_{Pb,Cu}$</td>
<td>0.42</td>
<td>1.09</td>
<td>0.55</td>
</tr>
<tr>
<td>$a_{Zn,Cd}$</td>
<td>0.32</td>
<td>0.94</td>
<td>0.42</td>
</tr>
<tr>
<td>$a_{Cd,Zn}$</td>
<td>0.53</td>
<td>0.94</td>
<td>0.47</td>
</tr>
<tr>
<td>$a_{Zn,Pb}$</td>
<td>1.49</td>
<td>1.01</td>
<td>1.38</td>
</tr>
<tr>
<td>$a_{Pb,Zn}$</td>
<td>1.42</td>
<td>0.98</td>
<td>0.83</td>
</tr>
<tr>
<td>$a_{Cd,Pb}$</td>
<td>1.26</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>$a_{Pb,Cd}$</td>
<td>0.74</td>
<td>0.97</td>
<td>0.80</td>
</tr>
</tbody>
</table>

$q_i = k_i C_i \left( \sum_{j} a_{ij} C_j \right)^{n_i-1}$, $a_{ii} = 1$

$q_i$: adsorption density of metal species $i$
$C_i$: equilibrium concentration of species $i$
$C_j$: equilibrium concentration of species $j$
$k_i$ and $n_i$: Freundlich constants.
a$_{ij}$: interaction coefficient of heavy metal $j$ to $i$

Table 3-3 reports the values of the interaction coefficients for various combinations of metal species. Results indicate that values of $a_{ij}$ for bentonite and Amite soil are not necessarily equal to $a_{ji}$. In other words, the competitive effect exerted by metal species $i$ on $j$ might be different from that exerted by $j$ on $i$ on bentonite or Amite soil. However, it was found that the values of $a_{ij}$ are roughly equal to $a_{ji}$ for kaolin, suggesting that metal species $i$ and $j$ would interact with each other equally with kaolin. On the other hand, most metal species would not compete with each other to the same extent. Cu outcompeted Zn and Cd while Pb outcompeted Cu. The only exceptions are Zn and Cd. Zn has almost the same competitive effect on Cd adsorption as Cd has on Zn adsorption. It is worth noting that of the interaction coefficients,
a_{Cd,Cu}, a_{Zn,Pb} \text{ and } a_{Pb,Zn} \text{ on bentonite have the highest values while } a_{Cu,Zn} \text{ has the smallest values for bentonite, kaolin and Amite soil. Results indicate that Cu interfered with Cd complexation, Zn interfered with Pb complexation and Pb interfered with Zn complexation on bentonite. On the other hand, Zn had the least competitive effect on Cu.}

**Ion Exchange Isotherm**

![Ion Exchange Isotherm](image-url)

Figure 3-13. Sodium and metal species exchange isotherm on bentonite at pH 6.0. The solid curve represents the thermodynamic nonpreference isotherm.

Figure 3-13 summarizes ion exchange isotherms which represent Equation (17). Unlike adsorption isotherms, an ion exchange isotherm is a plot of equivalent fractions of a metal species, $\tilde{E}_{Me}$, present at equilibrium in the aqueous phase, against the equivalent fraction $E_{Me}$ of the same metal species on the clays. The curve is the thermodynamic nonpreference exchange isotherm of Na for the metal species ($K_c = 1$), which was plotted based on Equation (20). It can be seen from the figure that the experimental data of Cu, Zn, Cd and Pb lie above the
nonpreference isotherm. This indicates that the bentonite preferentially exchanges \( \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) over \( \text{Na}^+ \) under these experimental conditions. Since electrostatic forces are involved in ion exchange, generally ions with higher charge will be preferred (Sparks 1999) and divalent ions are usually held more strongly than monovalent metals. Therefore it is not surprising to find that bentonite has preference for \( \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+} \) and \( \text{Pb}^{2+} \) relative to \( \text{Na}^+ \).

Equations (25) through (30) are plotted in Figure 3-14 against measured data. These equations are the ion exchange isotherm of any dual combination of, Cu, Zn, Cd and Pb in a multiple element system. The line with a 45\(^\circ\) angle is the non-preference exchange isotherm. It was found that all the experimental data are located above the non-preference exchange isotherm. Based on this result the greater the deviation of the isotherm from the 45\(^\circ\)-angle non-preference exchange isotherm, the more selective is the clay for the ion whose charge fractions are plotted (Sposito 1994). It can be concluded from the figure that the decreasing selectivity pattern of bentonite for metal species appears to be: \( \text{Pb} > \text{Cu} > \text{Zn} > \text{Cd} \) under the experimental conditions. This conclusion is consistent with the result obtained from the analysis of the Freundlich isotherms. Of the six pairs of divalent metal species, it is found that the selectivity for \( \text{Zn} \leftrightarrow \text{Cd} \) has the smallest value as supported by the exchange isotherm for \( \text{Zn} \leftrightarrow \text{Cd} \) having the smallest deviation of the isotherm from 45\(^\circ\)-angle non-preference exchange isotherm.

Ion exchange equilibrium may be complicated by the presence of several competing ions. The selectivity of ion exchange for Pb or other metal species is reduced with the presence of other metals. This phenomenon is reflected in the decrease of the deviation of the isotherm from 45\(^\circ\)-angle non-preference exchange isotherm. However, it seems that the presence of other metals only has a small effect on the selectivity of the ion exchange reaction between Cu, Zn and Cd, indicating that higher order exchange systems (without Pb) can be understood in terms of
Figure 3-14. Exchange isotherms corresponding to multiple metal species on bentonite. $E_{Me}$ is charge fraction of adsorbed metal species on clay materials (-) and $\tilde{E}_{Me}$ is charge fraction of metal species in aqueous solution (-). The following reactions are included in the plot:

- $CuX_2 + Zn^{2+} \leftrightarrow ZnX_2 + Cu^{2+}$
- $CuX_2 + Pb^{2+} \leftrightarrow PbX_2 + Cu^{2+}$
- $ZnX_2 + Pb^{2+} \leftrightarrow PbX_2 + Zn^{2+}$
- $CuX_2 + Cd^{2+} \leftrightarrow CdX_2 + Cu^{2+}$
- $ZnX_2 + Cd^{2+} \leftrightarrow CdX_2 + Zn^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Zn^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Zn^{2+}$
- $CuX_2 + Pb^{2+} + Zn^{2+} \leftrightarrow PbX_2 + Zn^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
- $CuX_2 + Pb^{2+} + Cd^{2+} + Pb^{2+} \leftrightarrow PbX_2 + Cd^{2+} + Cu^{2+}$
binary exchange reactions. Sposito (1994) constructed the exchange isotherm for reaction $\text{Ca} \leftrightarrow \text{Mg}$ with and without the presence of Na on montmorillonite and illitic soil. Results indicated that within experimental precision, no effect of the Na charge fraction on the isotherm was apparent. However, it was emphasized at the same time that N-ary ion exchange must be examined carefully, on a case by case basis to determine whether they can be predicted from binary exchange data.

CONCLUSIONS

Urban rainfall-runoff and snowmelt residual leachate typically contains high levels of metal species. These metal species can be released from the storm water residuals or sludge and become dissolved into leachate under the acidic conditions commonly encountered in landfills. Four metal species, including Cu, Zn, Cd and Pb, which are most common in rainfall-runoff or snowmelt and three clay liner materials, bentonite, kaolin and Amite soil, were investigated.

Results from mono-element and multiple-element adsorption systems indicate that the adsorption of the metal species on the clay materials can be represented by Freundlich isotherms at pH of 5 to 6.0. Under these experimental conditions the interaction capacities of the three clay materials decrease in the order bentonite $>$ Amite Soil $>$ kaolin and the relative affinities of the four metals for the 3 clay materials were Pb $>$ Cu $>$ Zn $>$ Cd. Of the four metals Pb displayed a much higher affinity for clay materials than Cu, Zn and Cd. The high affinity of metal species for bentonite is attributed to its high surface charge and high specific surface area. Comparison of metal species adsorption in mono-element systems to those in multiple-element systems demonstrated that competitive interaction must be considered, since competition can significantly decrease metal species adsorption. Cu outcompetes Zn and Cd while Pb outcompetes Cu during the competitive adsorption on bentonite, kaolin and Amite soil. Metal
species tend to interact with each other equally on kaolin while exhibiting unequal interaction on bentonite and Amite soil.

Na from Na-bentonite was exchanged for divalent metal species. Bentonite demonstrates a preferential selectivity for Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ over Na$^+$. Under experimental condition of this study, the selectivity of the four metals can be described by the sequence Pb$^{2+} >$ Cu$^{2+} >$ Zn$^{2+} >$ Cd$^{2+} >>$ Na$^+$. It appears that the selectivities of the exchange reactions between Cu, Zn and Cd are not affected by the presence of other metals. However, the selectivity of Pb for the other three metals decreases with the presence of other metals.

REFERENCES


NOMENCLATURE

The following symbols are used in this paper:

\[ a_{ij} \] = interaction coefficient of metal species j to i (-)
\[ C \] = equilibrium metal species concentration in aqueous solution (mg/L)
\[ Cs \] = concentration of unoccupied adsorption sites on clay (g/L)
\( C_{SA} \) = concentration of occupied adsorption sites on clay (g/L)
\( C_{TOT} \) = concentration of total adsorption sites on clay (g/L)
\( E_{Me} \) = charge fraction of adsorbed metal species on clay materials (-)
\( E_{Me} \sim \) = charge fraction of metal species in aqueous solution (-)
k = parameter of Freundlich isotherm (-)
k_1 = reaction rate constant of adsorption (L^{n-a} mg^{1-n} L^{-1} h)
k_2 = reaction rate constant of desorption (h^{-1})
k' = k_1/k_2
\( K_c \) = equilibrium constant of ion exchange reaction (-)
m_{Me} = molality of metal species in aqueous solution (M)
\( MeX_2(s) \) = metal – clay complex
\( n \) = parameter of Freundlich isotherm (-)
q = mass of solute adsorbed per unit mass of adsorbent (mg/g)
\( NaX(s) \) = sodium-clay complex
\( q_{max} \) = maximum adsorption density (mg/g)
\( Q \) = CEC of clay (meq/100 g)
\( \sim \) = total equalities of adsorbed charge in aqueous solution (N)
r_{net} = net rate of adsorption (mg/L·h)
r_{ads} = adsorption rate (mg/L·h)
r_{des} = desorption rate (mg/L·h)
\( S = \gamma_{Na}^2/\gamma_{Me} \) (-)
\( W_a \) = weight of EGME adsorbed by clay (g)
\( W_s \) = weight of clay (g)
\( x_{Me} \) = mole fraction of adsorbed metal species on clay (-)
\( x_{Na} \) = mole fraction of adsorbed Na on clay (-)
\( Z_{Me} \) = valence of metal species Me (-)
\( \beta = \frac{kC}{q^{1-n}} \)
\( \gamma \) = ion activity coefficient (-)
\( \Gamma_{Me} \) = moles of adsorbate per unit mass of clay (mole/g)
\( \Gamma_{Na} \) = moles of Na per unit mass of clay (mole/g)
\( \Gamma_i \) = moles of species i per unit mass of clay (mole/g)
\( \sum \Gamma_{Me} \) = total moles of metal species per unit mass of clay (mole/g)
CEC = cation exchange capacity (meq/100 g)
ICP-MS = inductively coupled plasma –mass spectroscopy
Chapter 4. Competitive Interactions of Rainfall-Runoff Sludge Metal Species by Clay Materials: Application of the Surface Complexation Model

SUMMARY

Storm water best management practices can generate large amount of sludge with high contents of metal species. These metals can be accumulated in the landfill and there exist interactions between metal species and clay liner materials. A surface complexation model (the diffuse-layer model) has been applied to model the complexation of Cu, Zn, Cd and Pb on to three clay liner materials, including bentonite, kaolin and Amite soil at constant ionic strength (0.01 NaNO$_3$). By using the previously determined acidity constants of the clay liner material, the complexation constants of each metal species with the clay liner materials were determined under different experimental conditions, including mono-element and multiple-element systems. The parameters determined from the mono-element systems were then compared with those obtained from the multiple-element system including a mixture of the four metal species. The result indicated that there is little variation of the intrinsic surface complexation constants. Based on the analysis of $K_{Me}^{int}$ values, it was found that the affinities of the clays for metal species increased in the order kaolin < Amite soil < bentonite while the affinities of the metals for the clays increased in the order Cd < Zn < Cu < Pb. Metal species speciation was also investigated and it was found that the distributions of metal concentration in aqueous phase and solid were pH dependent and they changed relatively slowly when kaolin was used as adsorbent. The prediction of complexation decrease due to competitive complexation was carried out with the aid of the three-dimensional graphs that were functions of pH and initial metal concentration. It was suggested that the effect of competitive complexation was not significant at high pH and low initial metal concentration for the complexation of the four metals on bentonite. However, competitive complexation could reduce metal complexation in multiple-element system when pH
was low or initial metal concentration was high. Complexation decrease was very sensitive to the change of initial concentration at low pH value.

INTRODUCTION

Metal Species in Landfill

Enactment of the NPDES Storm Water Phase II regulations have led to the proliferation of Best Management Practices (BMPs) and structural controls that generate rainfall-runoff and snow sludge containing metal species such as Cu, Zn, Cd and Pb. The solutions of how to deal with the significant volumetric quantities of this hazardous waste will include management of such volumes in hazardous waste landfill. Metal species in storm water sludge landfill leachate are of great concern due to the potential to cause contamination of soils and groundwater. Metal species are mobile under acidic environment that is commonly encountered in such landfill leachate. Of the many metal species found in storm water sludge, Cu, Zn, Cd and Pb are defined as priority pollutants by USEPA because of their toxicity, persistence and bioaccumulation (Sansalone and Buchberger 1997, Glen and Sansalone 2002). A landfill clay liner can be constructed of native soil that contains appreciable amounts of clayey materials or materials such as bentonite or kaolin are utilized when the native soil is not suitable as a liner. Since the clay liner can be a reactive barrier of low hydraulic conductivity the interaction of metal species with clay liner materials is crucial and controlled by the fate of both metal species in the solid and aqueous phase. In large part, metal species in rainfall-runoff and snow sludge captured by BMPs can account for toxicity of the leachate. It has been reported that toxicity depends on the speciation more so than total concentration (Sunda et al. 1978).

Isotherms

There are a number of mass transfer phenomena that play an important role with respect to the fate and transport of metal species. The commonly applied mass transfer processes for
metal species in environmental engineering are shown in Figure 4-1. In the general category of sorption, there exist several specific mechanisms including surface complexation, ion exchange, differential precipitation, diffusion into solid and hydrolysis (Schindler and Stumm 1987, Davis and Hayes 1986). Metal species sorption from leachate is an important category of mass transfer which has received extensive attention in assessing the fate and transport of metal species in the presence of clay. While equilibrium isotherms are an important tool to describe the equilibrium between aqueous and solid phases for a solute, isotherms cannot provide much more than a qualitative indication of more fundamental mechanisms. While isotherms are an effective tool to describe metal species interaction as a function of equilibrium concentration of solid and aqueous phases, isotherms will yield only indirect information on the effects of pH and adsorbent characteristics. Therefore, isotherms alone are not sufficient when modeling complex and variable natural or engineered systems. This is particularly true when the species of interest are minor or trace ionic species and the solid phase substrate exhibits a pH-dependent surface charge (Langmuir 1997).

Figure 4-1. The general category of mass transfer for metal species.
In contrast, surface complexation (SC) model based on double-layer theory, belongs to another group of models that take a mechanistic and molecular-scale approach to surface interaction. As a result, the surface complexation model is both versatile and has a fundamental physical-chemical basis for predicting metal species surface interaction phenomena over a wide range of experimental and natural conditions.

**Surface Complexation Models**

SC models have been used successfully for describing metal species interaction onto mineral surfaces. The SC model typically requires knowledge of the properties of the solid-phase surface and assumptions regarding the location (such as zero plane, δ plane or β plane) and form of the surface-complexed ions in the envisioned electrical layers near the surface. Of the SC models, the most commonly utilized models include: the constant capacitance (CC) model (Ikhsan et al. 1999 and Wanner et al. 1994, Goldberg et al. 2000 and Lutzenkirchen 1999), the diffuse-layer (DL) model (Lee and Davis 2001, Marmier and Fromage 2000 and Ravat et al. 2000) and the triple-layer (TL) model (Jung et al. 1998, Smith 1997, He et al. 1997 and Sarker et al. 2000). The SC models differ in how the surface and ionic layers are conceptualized and how the models describe the potential gradient as a function of distance from the solid-phase surface. Specifically, the constant capacitance and diffuse-layer models assume that all species are complexed at the zero plane while for the triple-layer model species are assumed to be located on either zero plane or β plane. In the diffuse-layer model, the relationship between charge density and the distance from the surface is estimated based on the Gouy-Chapman theory.

Several researchers (Ikhsan et al. 1999, Sarker 2000 and He et al. 1997) investigated the surface complexation of inorganic ions, including Hg, Cu, Pb, Zn, Co, Mn, SO_4^{2-} and PO_3^{3-} on kaolin, a clay mineral frequently found component in sediments and soils. In their study, kaolin
was considered to be composed of silanol and aluminol surface functional groups and the study proposed that the binding of the ions on kaolin could be described by the triple-layer model or the constant capacitance model that assumed two different types of binding sites having different surface complexation constants. In the first type of binding site, the ions were held by electrostatic forces to permanent-charge sites on the tetrahedral silanol group while the second type of complex involved inner-sphere coordination to the variable-charge surface hydroxyl groups at the edges of kaolin and on the octahedral aluminol face. A comparative study of Cu complexation on goethite, hematite and kaolin was carried out by Jung et al. (1998). This study concluded that goethite and hematite demonstrated a complexation behavior independent of ionic strength while complexation on kaolin surface was ionic-strength dependent. The triple-layer model was used to explain the experimental results. Marmier and Fromage (2000) utilized the constant capacitance (CC) model and the diffuse-layer (DL) model to simulate Cs complexation on magnetite in the presence of silicate. Their work demonstrated that dissolved silicates can bind on the surface of magnetite for a wide pH edge and appeared to be responsible for the binding of Cs on the magnetite.

In recent years, there has been a shift of interest in the application of the SC model for metal species binding onto pure minerals to heterogeneous natural and anthropogenic materials. These materials include soil, sediment, rainfall-runoff BMP sludge and residuals, waste materials and recycled substance. The surfaces of these materials contain some functional groups such as –OH, –SH and –COOH. These functional groups can undergo protonation and deprotonation processes and react with metal ions under natural and engineered conditions. Therefore the applicability of SC models has been investigated with respect to the complexation of metal species on these materials. Goldberg et al. (2000) investigated the complexation of boron on soils.
and a regression model was developed for predicting soil surface complexation constants from easily measured soil chemical characteristics such as cation exchange capacity, surface area, organic carbon content and inorganic carbon content. Wen et al. (1997) and Wang and Chen (1997) investigated the complexation of metal species, including Cu, Zn, Pb and Cd, on a variety of natural aquatic sediment based on the SC model. Wen concluded that the three SC models including CC, DL and TL models could simulate the experimental data well while Wang and Chen only tested the DL model. Aside from soil and sediment, the SC models can also be applied to the simulation of metal species complexation by other materials. For example, the DL model was used to describe the sorption of Cu\(^{2+}\) on a lignocellulosic substrate extracted from wheat bran (Ravat et al. 2000). The surface complexation constants derived from the experimental data were then used to predict the sorption for increasing metal loading, different solid to solution ratio or ionic strength. Results indicated that the parameters deduced from the single-metal data could be used to predict metal binding under different experimental conditions. Lee and Davis (2001) tested the applicability of the DL model to complexation of Cu\(^{2+}\) and Cd\(^{2+}\) by waste sludge generated from seafood processing factory. The surface complexation constants were first determined in single metal solution and the study also applied the surface complexation constants to predict the results in binary-adsorbate system. A complicated model in which the adsorbent surface was conceptualized to be consisted of two amphoteric sites and one monoprotic site was suggested by Papini et al. (1999) based on a SC model to describe the binding of Pb\(^{2+}\) onto an Italian volcanic soil. Theoretical surface speciation showed that Pb complexation occurred mostly onto monoprotic sites at low pH value and onto the two amphoteric sites at higher pH value.
The binding of metal species in landfill leachate plays a significant role in determining the mobility of metal species through clay liner material. However, although study on metal complexation on natural materials has been documented, the application of SC models to the complexation of metal species with natural and anthropogenic materials is still relatively sparse due to the complicated nature and enormous diversity of these materials. While the literature is replete with investigations of metal species complexation using isotherm models, there are few studies that utilize SC modeling to predict competitive complexation. The ability to predict change in metal complexation over a range of pH and metal concentration is important to when evaluating the interaction of metal species with clay liner materials.

OBJECTIVES

This paper has three objectives. The first objective was to investigate metal species complexation to clay liner materials based on the DL model and determine the surface complexation constants between metal species and the clay liner materials. The second objective was to evaluate competitive complexation based on the DL model. In the past the competitive interactions of metal species in the presence of other metal species was investigated by some of the researchers either from the point view of complexation (Sheindorf and Rebhun 1981) or ion exchange isotherms (Colella 1996, Galindo and Bingham 1997). However, there has been no investigations on the competitive interaction of rainfall-runoff metal species in the presence of other metals such as Mg and Ca on the basis of surface complexation models. Typically, Mg and Ca are at higher concentrations than metal species such as Pb, Cu, Zn and Cd in urban rainfall-runoff sludge leachate. It is hypothesized that these two metals can have significant influence on the complexation of some metal species such as Cu, Zn, Cd and Pb on the clay liner materials. In this study, the influence of Ca and Mg on the competitive complexation of other metals under a
range of pH conditions was studied. The third objective was to predict the decrease of metal binding as functions of pH and initial metal concentration. Although complexation isotherm and ion exchange isotherm are capable of correlating metal species concentration in the solid phase with that in aqueous phase, such isotherms cannot predict metal species binding when either pH or initial concentration is changed. This limitation restricts their application in predicting the change of metal species binding under different experimental and in-site conditions. On the other hand, the SC model can predict metal species binding as function of pH and initial concentration while requiring that some intrinsic constants such as surface complexation constants are determined or available.

**BACKGROUND**

It has been reported that ion complexation onto heterogeneous materials was largely controlled by electrostatic interaction between ions and charged surface of these materials (De Wit et al. 1993). For modeling purpose, the charged surface of clay liner materials is considered as identical and the following surface complexation reaction can be expressed to describe the complexation of divalent metal ions onto the clay liner materials.

\[
\text{SOH} + \text{M}_s^{2+} = \text{SOM}^+ + \text{H}_s^+ 
\]

where SOH is neutral functional groups on the adsorbent surface, M\(_s^{2+}\) and H\(_s^+\) are metal ion and hydrogen ion at the solid surface and SOM\(^+\) is metal-complexation site complex. The intrinsic surface complexation constant \(K_{\text{Me}^{2+}}^{\text{int}}\) can be expressed as Eq. (2).

\[
K_{\text{Me}^{2+}}^{\text{int}} = \frac{\{\text{SOM}^+\} \{\text{H}_s^+\}}{\{\text{SOH}\} \{\text{M}_s^{2+}\}} 
\]

where \{\} indicates activity.
The surface activities of \( M_s^{2+} \) and \( H_s^+ \), which cannot be measured directly, are assumed to be related to the bulk \( M^{2+} \) and \( H^+ \) activities through a Boltzmann factor (Langmuir 1997):

\[
\{M_s^{2+}\} = \{M^{2+}\} \exp\left(-\frac{\psi_0 F}{RT}\right) \tag{3}
\]

\[
\{H_s^+\} = \{H^+\} \exp\left(-\frac{\psi_0 F}{RT}\right) \tag{4}
\]

In this expression \( \{M^{2+}\} \) and \( \{H^+\} \) are metal and \( H^+ \) activities in bulk solution, \( \psi_0 \) is the potential at the solid surface, \( F \), \( R \) and \( T \) are the Faraday constant, the ideal gas constant and the absolute temperature, respectively. The substitutions of Eqs. (3) and (4) into Eq. (2) yield the following expression:

\[
K_{int}^{Me^{2+}} = \frac{\{SOM^+\} \{H^+\}}{\{SOH\} \{M^{2+}\} \exp(-\psi_0 F / RT)} \tag{5}
\]

In the DL model, assuming Gouy-Chapman theory for a symmetrical electrolyte of valence \( z \) and 25 °C, the charge density, \( \sigma \) (C/m²), at some distance away from the surface, is approximated by the following expression.

\[
\sigma = 0.1174I^{1/2} \sinh\left(\frac{z\psi F}{2RT}\right) \tag{6}
\]

In this equation \( I \) is ionic strength and all other terms have previously been defined.

**METHODOLOGY**

**Acid-base Titration**

The purpose of acid-base titration was to determine the intrinsic acidity constants of the clay liner materials. These constants are required to apply the surface complexation model to predict the metal species competitive complexation. In this process, 400 mg of kaolin or Amite soil, or 200 mg of bentonite was suspended in 100 mL DI water in a 150-mL Erlenmeyer flask. Known amount of 0.1 N HNO₃ was added to the suspension to reduce the pH value to less than 3.5. NaOH solution with concentration of 0.1 N was titrated at an increment of 50 or 100 µL to
increase the pH value. The stable pH values were recorded after an equilibrium time of 2 hours. During the process of titration, nitrogen gas was continuously supplied to purge CO₂ from the solution and the Erlenmeyer flasks were sealed with parafilm so that the effect of CO₂ was eliminated. The titrations of blanks without the addition of clay materials were also conducted under the same experimental conditions. The data sets of pH versus the net consumption of H⁰ or OH⁻ due to surface complexation were used to obtain intrinsic acidity constants in the surface complexation model with the aid of FITEQL algorithms (Herbelin and Westall 1999).

For a negative charged surface, the site density and cation exchange capacity (CEC) are related through the expression (Langmuir 1997):

$$N_s = \frac{CEC \times 6.02}{SSA}$$  \hspace{1cm} (7)

where $N_s$ is binding site density (sites/nm²), CEC is cation exchange capacity (meq/100g) and SSA is specific surface area (m²/g). 6.02 came from Avogadro’s number. The concentration of sorbing surface sites can be calculated using the following equation:

$$\Gamma_{SOH} (mol \ sites / L) = \frac{N_s (sites / nm^2) \times 10^{18} \times SSA (m^2 g) \times C_s (g / L)}{N_A}$$  \hspace{1cm} (8)

where $\Gamma_{SOH}$ is sorbing surface sites (mol sites/L), $C_s$ is sorbent concentration (g/L) and $N_A$ is Avogadro’s number ($6.02 \times 10^{23}$).

**Complexation Edge (pH Dependence)**

Six metals, including Cu, Zn, Cd, Pb, Mg and Ca, and three clay liner materials, including bentonite, kaolin and Amite soil (a natural soil commonly found in the Tangipahoe basin of South Louisiana and used in landfill in Amite, Louisiana) were tested in this study. Three groups of experiment were carried out. The first set of experiments was carried out in a mono-element system where only one metal species such as Cu, Zn, Cd or Pb was in the aqueous
solution. In the second set of experiments, a multiple-element system that included a mixture of the four metal species, Cu, Zn, Cd and Pb was examined. In the third set of experiment, a solution of six metal species was reacted with one of the three clay liner materials, separately and the complexation of each metal species with the clays was evaluated. The competitive interaction of the metals were investigated based on the comparisons of the results obtained from the first set of mono-element experiments.

Typically, Metal species complexation tests as a function of pH are performed in batch mode in which the chemical equilibrium can be attained within 24-hour reaction period (Daughney and Fein 1998, Davis et al. 1998 and Ravat et al. 2000). On the other hand, column study is seldom employed to study surface complexation problem for two reasons. First, columns are neither an ideal continuous-flow stirred tank reactors (CSTR) nor plug-flow reactors (PFR). Therefore, there exists a residence time distribution for a fluid element (Missen et al. 1999) and the mathematical model considering the fluid dispersion is required. Second, the chemical equilibrium is not achieved for some of the fluid elements since their residence time is very short.

Each metal species or a solution of Cu, Zn, Cd and Pb or of Cu, Zn, Cd, Pb, Ca and Mg in a volume of 40-mL was mixed with the three clay liner materials in 50-mL polypropylene centrifuge tubes. In order to investigate the effect of clay concentration on complexation performance, 2-g/L and 6-g/L of clay liner materials were applied, respectively. The pH of the initial suspension was adjusted with HCl or NaOH and the final pH values were kept at about 2, 2.5, 3, 3.5, 3.75, 4, 4.5, 5 and 6 respectively. To evaluate and compare the complexation capacities of Cu, Zn, Cd and Pb, the initial concentrations were equal for each metal species. In this study, the initial metal species concentration was 2-mg/L for Cu, Zn, Cd and Pb since this is a possible. In the third set of experiments, initial Mg and Ca concentrations were maintained at
10 and 200 mg/L, respectively, typical of Mg and Ca concentrations captured by rainfall-runoff BMPs in the urban environment (Sansalone et al. 1998) in storm water environment. The samples were shaken for 24 hours at 25 °C using a shaker table under the assumption that complexation equilibrium was reached (Rhee and Dzombak 1998, Lee and Davis 2001). The equilibrium pH values were recorded and the suspension was filtered using 0.45-µm nylon syringe filter.

**Elemental Analysis**

The fractions of dissolved metal species concentrations in the filtrate were measured using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS, ELAN 6000, Perkin-Elmer Company). Five-point calibration was employed to construct the standard curves. The concentrations of the standard solution used included 0, 10, 20, 100 and 500 µg/L. The measuring conditions were 100 ms dwell time, 50 sweeps/reading and 3 replicates for each sample to check reproducibility. The internal standard was Rh which was introduced into the plasma with the sample, giving a concentration of 10 µg/L. The elements were measured at m/z values of 63 for Cu, 64 for Zn, 114 for Cd and 208 for Pb. QA/QC included checking a standard solution with concentration of 50 µg/L for each metal to confirm the results. The criteria of precision included ≤ 5% relative standard deviation (RSD) of instrumental precision and ≤ 10% relative percent difference (RPD) for the precision of duplicate samples.

The amounts of adsorbed metal species were obtained from the difference between initial and final concentrations. The test was run in duplicate so that the error bars could be presented in the complexation edge.
Determination of Intrinsic Surface Complexation Constants

FITEQL algorithms (v. 4.0) (Herbelin and Westall 1999) were used to calculate surface complexation constants for Cu, Zn, Cd and Pb onto the clay liner materials under different experimental conditions. FITEQL algorithms combine a nonlinear least-square fitting with a chemical equilibrium model. The surface of the clay liner materials were considered as homogeneous and a single metal surface complexation reaction was employed (Wen et al 1998). The optimized values of $K_{Me^2+}^{int}$ were obtained by minimizing the difference between experimental data and predicted data using a nonlinear least-square regression. In this study, the DL model was employed since the DL model was regarded as more versatile compared to CC model and TL model because the DL model corrected complexation for ionic strength using Gouy-Chapman theory (Stumm and Morgan 1996) and did not require the input of capacitance. For the application CC model, the inputs of capacitance, and the intrinsic acidity constants of protonation and deprotonation are required. For the TL model, the inputs of the capacitances in the regions between the 0 and $\beta$ and $\beta$ and d planes, and the intrinsic acidity constants of protonation and deprotonation are required. However, as indicated by Dzombak and Morel (1990), the DL model requires only the intrinsic acidity constants of protonation and deprotonation to model the complexation behavior. Therefore, the DL model required the least number of input parameters (Langmuir 1997). Therefore, of the three SC models, the DL model requires the least model parameters and producing fewer subjective factors, making the DL model more attractive.

Double-layer Complexation Modeling

Surface complexation modeling requires the solution of a number of simultaneous equations. These equations include intrinsic complexation constant equations, metal species
hydrolysis of metal species equations, mass balance equations and charge balance equations. In the DL model, metal species are assumed to be specially adsorbed at the zero plane and the intrinsic constant expressions were written as:

\[
K^\text{int}_{\text{Cu}^{2+}} = \frac{\{\text{SOCu}^+\}\{\text{H}^+\}}{\{\text{SOH}\}\{\text{Cu}^{2+}\}\exp(-\psi_0 F / RT)}
\]  
(9)

\[
K^\text{int}_{\text{Zn}^{2+}} = \frac{\{\text{SOZn}^+\}\{\text{H}^+\}}{\{\text{SOH}\}\{\text{Zn}^{2+}\}\exp(-\psi_0 F / RT)}
\]  
(10)

\[
K^\text{int}_{\text{Cd}^{2+}} = \frac{\{\text{SOCd}^+\}\{\text{H}^+\}}{\{\text{SOH}\}\{\text{Cd}^{2+}\}\exp(-\psi_0 F / RT)}
\]  
(11)

\[
K^\text{int}_{\text{Pb}^{2+}} = \frac{\{\text{SOPb}^+\}\{\text{H}^+\}}{\{\text{SOH}\}\{\text{Pb}^{2+}\}\exp(-\psi_0 F / RT)}
\]  
(12)

In these equations, \(K^\text{int}_{\text{Cu}^{2+}}\), \(K^\text{int}_{\text{Zn}^{2+}}\), \(K^\text{int}_{\text{Cd}^{2+}}\) and \(K^\text{int}_{\text{Pb}^{2+}}\) are the intrinsic surface complexation constants of Cu, Zn, Cd and Pb while \{Cu\(^{2+}\), \{Zn\(^{2+}\), \{Cd\(^{2+}\) and \{Pb\(^{2+}\) are activities of Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) in bulk solution, respectively. The activity of each metal species is related to the concentration by the activity coefficient \(\gamma\) in the following equations.

\[
\{\text{Cu}^{2+}\} = C_{\text{Cu}} \gamma
\]  
(13)

\[
\{\text{Zn}^{2+}\} = C_{\text{Zn}} \gamma
\]  
(14)

\[
\{\text{Cd}^{2+}\} = C_{\text{Cd}} \gamma
\]  
(15)

\[
\{\text{Pb}^{2+}\} = C_{\text{Pb}} \gamma
\]  
(16)

In these equations, \(C_{\text{Cu}}\), \(C_{\text{Zn}}\), \(C_{\text{Cd}}\) and \(C_{\text{Pb}}\) are bulk concentrations of Cu, Zn, Cd and Pb. The activity coefficient can be calculated from the Davies equation (Morel and Hering 1994) at temperature of 298 K.

\[
\log \gamma = 0.509 z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)
\]  
(17)
In this expression, Z is valence of ion and I is ionic strength.

Eqs. (18) through (25) depict the hydrolysis of metal species in aqueous phase.

\[ K_{Cu(OH)} = \frac{[CuOH^+]\{H^+\}}{[Cu^{2+}]} \]  
(18)

\[ K_{Cu(OH)_2} = \frac{[Cu(OH)_2] \{H^+\}^2}{[Cu^{2+}]} \]  
(19)

\[ K_{Zn(OH)} = \frac{[ZnOH^+]\{H^+\}}{[Zn^{2+}]} \]  
(20)

\[ K_{Zn(OH)_2} = \frac{[Zn(OH)_2] \{H^+\}^2}{[Zn^{2+}]} \]  
(21)

\[ K_{Cd(OH)} = \frac{[CdOH^+]\{H^+\}}{[Cd^{2+}]} \]  
(22)

\[ K_{Cd(OH)_2} = \frac{[Cd(OH)_2] \{H^+\}^2}{[Cd^{2+}]} \]  
(23)

\[ K_{Pb(OH)} = \frac{[PbOH^+]\{H^+\}}{[Pb^{2+}]} \]  
(22)

\[ K_{Pb(OH)_2} = \frac{[Pb(OH)_2] \{H^+\}^2}{[Pb^{2+}]} \]  
(23)

In these expressions, both \( K_{Me(OH)} \) and \( K_{Me(OH)_2} \) are metal species hydrolysis constants.

The mass balance equations for the four metal species in aqueous solution are expressed in the following equations.

\[ \text{TOTCu} = C_{Cu} + \{SOCu^+\} + \{Cu(OH)^+\} + \{Cu(OH)_2\} \]  
(24)

\[ \text{TOTZn} = C_{Zn} + \{SOZn^+\} + \{Zn(OH)^+\} + \{Zn(OH)_2\} \]  
(25)

\[ \text{TOTCd} = C_{Cd} + \{SOCd^+\} + \{Cd(OH)^+\} + \{Cd(OH)_2\} \]  
(26)

\[ \text{TOTPb} = C_{Pb} + \{SOPb^+\} + \{Pb(OH)^+\} + \{Pb(OH)_2\} \]  
(27)
In these expressions, TOTCu, TOTZn, TOTCd and TOTPb are total Cu, Zn, Cd and Pb concentrations, respectively.

Charge-balance equations are the final group of equations used to complete the surface complexation solution. The surface charge of the clay can be given by the following equation.

$$\sigma_0 = \frac{F}{SSA \times C_s} \left[ \{SOH_2^+\} + \{SOCu^+\} + \{SOZn^+\} + \{SOCd^+\} + \{SOPb^+\} - \{SO^-\} \right]$$  \hspace{1cm} (28)

In the DL model, Eq. (6) can be used to correlate $\sigma_0$ and $\psi_0$. These equations (9 – 28) are solved simultaneously and the intrinsic surface complexation constants are obtained from the solution.

The precipitation edge can also be determined using the following equation.

$$\text{Me} + 2\text{OH}^- \rightarrow \text{Me(OH)}_2$$  \hspace{1cm} (29)

An equilibrium speciation model (MINTEQ) (Allison et al. 1991) was utilized to examine chemical precipitation across the pH range for the experiments in order to differentiate between surface complexation and precipitation.

RESULTS AND DISCUSSION

**Complexation Edge in Mono-element System**

The pH dependence of the metal species binding (complexation edge) onto the three clay liner materials in mono-element systems are illustrated in Figure 4-2 where symbols are representative of the experimental data while the solid curves are indicative of the predicted values based on the DL model. At the same time, the precipitation edge of each metal was also included. It can be seen that the binding of metal species are strongly dependent on pH and binding increases with increasing pH. However, the surface interactions are different for different clays and metal species. Results indicate that the binding of Cu, Zn, Cd and Pb on bentonite and Amite soil and the binding of Pb on kaolin show similarities as function of pH. Results indicate a significant increase in binding pH 2 and pH 4, resulting in an increase in
partitioning from the aqueous to solid-phase from 0 to 100% within 2 pH units. On the other hand, the binding of Cu, Zn and Cd on kaolin shows wider range of pH (from 3 to 6) where binding increases from near zero to almost 100%.

![Graphs showing metal species binding as a function of pH](image)

**Figure 4-2.** The dependence of metal species binding in the mono-element systems as a function of pH. The initial metal concentration was 2 mg/L for each metal and the clay concentration $C_s$ was 2 g/L. The solid curves represent DL model fits and the dashed curve indicates the metal precipitation edge without the addition of clay. Ionic strength was kept constant at 0.01 N NaNO₃.
The precipitation curves (precipitation edge) for each metal in the mono-element system are included in the Figure 4-2. The comparison of precipitation edge to the complexation edge illustrates that like precipitation, surface complexation could occur abruptly within a very narrow pH range when bentonite was used in the experiment. The comparison of the complexation edges for different clay liner materials indicates that the complexation edge shifted to a higher pH when bentonite was replaced by Amite soil as a partitioning medium while complexation edge moved to an even higher pH when Amite soil was replaced by kaolin. The results indicated that this trend was consistent for each metal. Dzombak and Morel (1990) regarded that this is an indication of the decrease of the binding affinity. Based on this suggestion, the binding affinity of the three clay liner materials for the multi-element solution matrix of Cu, Zn, Cd and Pb can be expressed in the order of bentonite > Amite soil > kaolin.

Table 4-1 summarizes the binding site densities and the mass and volume concentrations of the three clay liner materials. Results indicate that bentonite had the lowest site density and kaolin had the highest site density. However, since bentonite had a much higher total surface area than kaolin, bentonite still had the highest concentration of binding surface sites of the three clays. This suggests that the high affinity of bentonite for these metal species was in large part due to bentonite’s high total surface area. Although kaolin has the highest value of site density, it still had a weak affinity for metal species since it had a low total surface area.

If pH$_{50}$ is defined as the pH value at which 50% of the metal is adsorbed, it can be seen from the figure that pH$_{50}$ increased in the order Pb < Cu < Zn < Cd. A small value of pH$_{50}$ is an indication of high binding affinity of a solid medium for a metal species. It can be concluded that the binding affinity of metal species with the clay liner materials increased in the order Cd < Zn < Cu < Pb. This result is in agreement with that obtained from the previous isotherm studies.
Table 4-1. Characteristics of the clay liner materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Amite Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (%)</td>
<td>1.3 (0.08)</td>
<td>0.0145 (0.0009)</td>
<td>0.0184 (0.001)</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.055 (0.01)</td>
<td>0.0131 (0.0010)</td>
<td>0.0252 (0.005)</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.0067 (0.04)</td>
<td>0.0071 (0.003)</td>
<td>0.0051 (0.004)</td>
</tr>
<tr>
<td>Al (%)</td>
<td>7.0 (0.75)</td>
<td>17.2 (1.51)</td>
<td>2.1 (0.11)</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>0.00045 (0.00005)</td>
<td>0.0006 (0.0002)</td>
<td>0.00124 (0.0001)</td>
</tr>
<tr>
<td>Zn (%)</td>
<td>0.01 (0.0008)</td>
<td>0.0044 (0.0003)</td>
<td>0.0032 (0.0003)</td>
</tr>
<tr>
<td>Cd (%)</td>
<td>0.00002 (0.000002)</td>
<td>0.00000 (0)</td>
<td>0.00018 (0.00001)</td>
</tr>
<tr>
<td>Pb (%)</td>
<td>0.0024 (0.0009)</td>
<td>0.0044 (0.0004)</td>
<td>0.00072 (0.00005)</td>
</tr>
<tr>
<td>Organic Matter (%)</td>
<td>0.23 (0.05)</td>
<td>0.18 (0.04)</td>
<td>0.34 (0.05)</td>
</tr>
<tr>
<td>pH (10g/100ml H2O)</td>
<td>9.10 (0.05)</td>
<td>5.10 (0.01)</td>
<td>6.12 (0.02)</td>
</tr>
<tr>
<td>d50 (µm) *</td>
<td>7 (2)</td>
<td>15 (4)</td>
<td>12 (5)</td>
</tr>
<tr>
<td>Soil Type</td>
<td>Clay</td>
<td>Clay</td>
<td>Sandy Silty clay</td>
</tr>
<tr>
<td>PZC</td>
<td>No PZC</td>
<td>4.60</td>
<td>5.25</td>
</tr>
<tr>
<td>Specific Surface Area (m²/g)</td>
<td>625 (8)</td>
<td>52 (2)</td>
<td>14 (2)</td>
</tr>
<tr>
<td>Particle Density (g/cm³)</td>
<td>2.72 (0.01)</td>
<td>2.75 (0.16)</td>
<td>2.75 (0.01)</td>
</tr>
<tr>
<td>Ns(sites/nm²)</td>
<td>0.69</td>
<td>1.18</td>
<td>1.8</td>
</tr>
<tr>
<td>SOH(mol sites/L)</td>
<td>1.44</td>
<td>0.41</td>
<td>0.17</td>
</tr>
<tr>
<td>SOH(mol sites/g)</td>
<td>0.72</td>
<td>0.205</td>
<td>0.085</td>
</tr>
</tbody>
</table>

*d50 is based on particle number.
The numbers in parenthesis are standard deviations.

The DL model was applied to simulate the experimental data obtained from mono-element systems. The acidity constants of the clay liner materials were obtained from acid/base titration and the surface complexation constants were calculated for the complexation edges using FITEQL. Table 4-2 summarizes the equilibrium constants of the reactions, including surface acidity reaction, surface complexation reaction and metal species hydrolysis reactions.

Results indicate that bentonite has much higher values of surface complexation constants with metal species compared to Amite soil and kaolin. A higher value of the surface complexation constant means a higher affinity with metal species. Of the four metals investigated, Pb has the
highest surface complexation constant value and the binding affinity of metal species for clay liner materials can be consistently expressed as: Pb > Cu > Zn > Cd.

Table 4-2. Equilibrium constants for surface complexation and hydrolysis reactions in DL model

<table>
<thead>
<tr>
<th>Reaction*</th>
<th>Bentinone</th>
<th>Amite Soil</th>
<th>Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOH+H⁺ ↔ SOH₂⁺</td>
<td>11.58</td>
<td>9.97</td>
<td>9.63</td>
</tr>
<tr>
<td>SOH ↔ H⁺ + SO⁻</td>
<td>-29</td>
<td>-9.71</td>
<td>-10.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction**</th>
<th>Single Element</th>
<th>Multiple Element</th>
<th>Multiple Element</th>
<th>Single Element</th>
<th>Multiple Element</th>
<th>Multiple Element</th>
<th>Multiple Element</th>
<th>Multiple Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺ + SOH ⇔ SOCu⁺ + H⁺</td>
<td>Cₛ=2g/L</td>
<td>Cₛ=2g/L</td>
<td>Cₛ=6g/L</td>
<td>Cₛ=2g/L</td>
<td>Cₛ=2g/L</td>
<td>Cₛ=6g/L</td>
<td>Cₛ=2g/L</td>
<td>Cₛ=2g/L</td>
</tr>
<tr>
<td>Zn²⁺ + SOH ⇔ SOZn⁺ + H⁺</td>
<td>0.19</td>
<td>0.18</td>
<td>0.18</td>
<td>-1.85</td>
<td>-1.9</td>
<td>-1.88</td>
<td>-2.25</td>
<td>-2.26</td>
</tr>
<tr>
<td>Cd²⁺ + SOH ⇔ SOCd⁺ + H⁺</td>
<td>-0.33</td>
<td>-0.31</td>
<td>-0.37</td>
<td>-2.01</td>
<td>-2.05</td>
<td>-2.01</td>
<td>-2.84</td>
<td>-2.89</td>
</tr>
<tr>
<td>Pb²⁺ + SOH ⇔ SOPb⁺ + H⁺</td>
<td>1.92</td>
<td>1.97</td>
<td>1.94</td>
<td>-0.66</td>
<td>-0.7</td>
<td>-0.61</td>
<td>-1.57</td>
<td>-1.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cu²⁺ + H₂O ⇔ Cu(OH)⁺ + H⁺</th>
<th>-6.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺ + 2H₂O ⇔ Cu(OH)₂ + 2H⁺</td>
<td>-12.8</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺ + 3H₂O ⇔ Cu(OH)₃ + 3H⁺</td>
<td>-14.5</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺ + 4H₂O ⇔ Cu(OH)₄²⁻ + 4H⁺</td>
<td>-16.4</td>
<td></td>
</tr>
<tr>
<td>2Cu²⁺ + 2H₂O ⇔ Cu₂(OH)₂⁺⁺ + 2H⁺</td>
<td>-17.7</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺ + H₂O ⇔ Zn(OH)⁺ + H⁺</td>
<td>-9</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺ + 2H₂O ⇔ Zn(OH)₂ + 2H⁺</td>
<td>-17.9</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺ + 3H₂O ⇔ Zn(OH)₃ + 3H⁺</td>
<td>-28.4</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺ + H₂O ⇔ Cd(OH)⁺ + H⁺</td>
<td>-3.9</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺ + 2H₂O ⇔ Cd(OH)₂ + 2H⁺</td>
<td>-14.3</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + H₂O ⇔ Pb(OH)⁺ + H⁺</td>
<td>-7.71</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + 2H₂O ⇔ Pb(OH)₂ + 2H⁺</td>
<td>-17.12</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + 3H₂O ⇔ Pb(OH)₃ + 3H⁺</td>
<td>-28.06</td>
<td></td>
</tr>
</tbody>
</table>

(Morel and Hering 1976)

The acidity constants* of the clay liner materials were obtained from acid/base titration measurement. The surface complexation constants** were determined in this study.
Complexation Edge in Multiple-element System

To evaluate the competitive complexation of metal species onto clay liner materials, it is important to investigate how the binding interaction of certain metals will be influenced by the presence of other metals. The complexation edges of the four metal species on the three clay liner materials in the multiple-element system without the presence of Mg and Ca are shown in Figure 4-3 when solid-phase clay concentration was fixed at 2 g/L.

Compared to the pH edges in mono-element systems, the pH edges in multiple-element systems shifted to higher pH positions at the same sorbent concentration, indicating the decreases in individual metal species binding onto the clays. The presence of each metal species can reduce the binding of other metal species onto the clays and the evaluation of competitive behavior agrees with observations obtained in isotherm studies carried out previously.

The binding of metal species on bentonite was reduced the least for the three clays. For example, pH$_{50}$ changed from 2.9 to 3.04, from 3.25 to 3.40, from 3.40 to 3.60 and from 2.80 to 2.90 for Cu, Zn, Cd and Pb, respectively. In contrast, the decreases in the binding for each of the four metal species was significant for Amite soil and kaolin. The pH$_{50}$ on Amite soil changed from 3.30 to 3.60, from 3.50 to 4.24, from 3.42 to 4.5 and from 3.0 to 3.26, for Cu, Zn, Cd and Pb, respectively. The binding decreases were even more pronounced on kaolin and the values of pH$_{50}$ were even greater that 6 for Cu, Zn and Cd.

The surface complexation constants in the multiple-element system when the solid-phase clay concentrations were 2 g/L are also tabulated in Table 4-2. It can be seen from the table that there is little change in the surface complexation constants, suggesting that the competitive binding did not change the intrinsic surface complexation reaction constants.
Figure 4-3. The dependence of metal species binding in the multiple-element systems (without Mg and Ca) as a function of pH (Cs = 2 g/L). The initial metal concentration was 2 mg/L for each and adsorbent concentration was 2 g/L. The solid curves represent modeled trend based on the DL model. Ionic strength was kept constant at 0.01 N NaNO₃.
All metal species complexation edges increased with increasing pH, either in mono-element system or multiple-element system.

To investigate the effect of solid-phase dosage on the binding of metal species, clay concentrations were increased to 6 g/L and the complexation edges are illustrated in Figure 4-4. Compared to the binding at solid-phase concentration of 2 g/L, complexation edges stepped back to the positions of lower pH value, indicating the increase in binding to the solid-phase.

The DL model was employed to model the experimental data and the modeling results are presented as curves in Figures 4-2 to 4-5 and the intrinsic surface complexation constants are summarized in Table 4-2. Once again, it was observed that the values of $K_{Me^{2+}}^\text{int}$ demonstrated negligible differences between mono-element and multiple-element systems. In a similar manner to the chemical equilibrium constants, the intrinsic surface complexation constants depict the reaction between binding site and the metal species. Therefore, it is reasonable to find that $K_{Me^{2+}}^\text{int}$ does not change with the presence of other metal ions.

In order to investigate the influence of Mg and Ca on competitive metal species binding, two commonly detected metals in rainfall-runoff BMP residual sludge were included in the aqueous matrix. Figure 4-5 was constructed to illustrate the changes for the four metal species as a function of pH when 10 mg/L of Mg and 200 mg/L of Ca were presented in the multiple-element system. Results plotted in Figure 5 indicate that metal species binding was decreased with the introduction of Mg and Ca. However, the additional decrease of metal species binding was not as significant as those observed in the multiple-element system without Mg and Ca. This phenomena implies that the competitive binding of Mg and Ca with the solid-phase materials was not as strong as that of the binding of Cu, Zn, Cd and Pb.
Figure 4-4. The dependence of metal species complexation in the multiple-element systems (without Mg and Ca) as a function of pH (Cs = 6g/L). The initial metal concentration was 2 mg/L for each and adsorbent concentration was 6 g/L. The solid curves represent model fits based on the DL model. Ionic strength was kept constant at 0.01 N NaNO₃.
Figure 4-5. The dependence of metal species complexation in the multiple-element systems (including Mg and Ca) as a function of pH (2 g/L). The initial metal concentration was 2 mg/L for Cu, Zn, Cd and Pb and and 10 and 200 mg/L for Mg and Ca, respectively. Adsorbent concentration was 2 g/L. The solid curves represent model fits based on the DL model. Ionic strength was kept constant at 0.01 N NaNO₃.
Table 4-3. Coefficients of determination and goodness of fit for the application of the diffuse-layer model to experimental data summarized in Figures 4-2 through 4-5.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Experimental System</th>
<th>( R^2 )</th>
<th>( \chi^2 )</th>
<th>Bentonite</th>
<th>Amite Soil</th>
<th>Kaolin</th>
<th>Bentonite</th>
<th>Amite Soil</th>
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<td>10.41</td>
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<tr>
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<td>0.866</td>
<td>0.912</td>
<td>4.62</td>
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<tr>
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<td>0.874</td>
<td>0.933</td>
<td>23.12</td>
<td>3.64</td>
<td>0.278</td>
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</tr>
<tr>
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<td>34.23</td>
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<tr>
<td>Zn</td>
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<td>0.904</td>
<td>0.957</td>
<td>9.87</td>
<td>0.46</td>
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<td>Pb</td>
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</tr>
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<td>0.905</td>
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<td>3.76</td>
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<td>0.77</td>
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</tbody>
</table>

Experimental System 1: Mono-element system  
Experimental System 2: Multiple-element system without Mg and Ca  
Experimental System 3: Multiple-element system with Mg and Ca

Table 4-3 summarizes the agreement between fit of the experimental data and DL model results. In this table, \( R^2 \) is coefficient of determination and \( \chi^2 \) is the chi-squared result for computed goodness of the fit which can be expressed as the following equation (Buckland et al. 1993).

\[
\chi^2 = \sum_{i=1}^{n} \frac{(O(x_i) - E(x_i))^2}{E(x_i)}
\]  

(30)

In this expression, \( O(x_i) \) is the observation data, \( E(x_i) \) is the expected value (modeled data) and \( n \) is the number of data points. \( \chi^2 \) follows a chi-square distribution and the model that provided the least \( \chi^2 \) value was considered the best-fit model. The reasonable good fit between measured and modeled data suggests that the DL surface complexation model can be used to describe the metal species binding onto the clays.
**Metal Species Speciation**

In order to gain a better insight into the surface complexation behavior, metal speciation was examined. Speciation calculations were performed with the aid of MINTEQA algorithms. The species of the four metals in contact with different clay materials are depicted in Figures 4-6 through 4-8. Since the divalent metal ions (Me$$^{2+}$$) and the complex of metal and clay (SOMe$$^+$$) were the dominant species, the concentrations of other species such as Me(OH)$$^{2-n}$$ were negligible (< 0.1%) and were not included in these plots. Speciation results indicate that the distributions and predominance of metal species in the aqueous and solid phase varied on the type of clay materials examined. Figure 4-4 indicates that either in mono-element or multiple-element system, almost all the metal ions existed in the form of divalent metal ions at low pH values while SOMe$$^+$$ dominated at high pH values for bentonite. Me$$^{2+}$$ decreased sharply while SOMe$$^+$$ increased abruptly over a narrow pH range (from 3.5 to 4.5). This phenomenon was attributed to the high exchange capacity of bentonite for metal species. Compared to bentonite, both Cd$$^{2+}$$ and SOCd$$^+$$ profiles for Amite soil (2 g/L) changed more slowly with increasing pH in multiple-element systems indicating the role of competitive binding interactions caused by the presence of other metals. However, when the concentration of Amite soil was increased to 6 g/L, both Cd$$^{2+}$$ and SOCd$$^+$$ concentrations changed much more quickly with increasing pH in the multiple-element system. This result suggests that the increase of clay dosage could attenuate the effect of competitive complexation. Results for kaolin indicate that competitive interactions were significant at low kaolin concentration (2 g/L). As a result, divalent metal ions decreased while the complex of metal and kaolin increased very slowly with increasing pH. Even though kaolin concentration was increased to 6 g/L, the effect of competitive interaction was still significant for the binding of Cd on kaolin.
Figure 4-6. Metal species speciation as a function of pH when bentonite was used as exchange medium. This plot was constructed based on MINTEQ modeling.
Figure 4-7. Metal species speciation as a function of pH when Amite soil was used as complexation medium. This plot was constructed based on MINTEQ modeling.
Figure 4-8. Metal species speciation as a function of pH when kaolin was used as complexation medium. This plot was constructed based on MINTEQ modeling.
Decrease of Metal Complexation in Multiple-element System

Based on the values of $K_{Me^{2+}}^{int}$, the calculations of metal binding decrease in the multiple-element system were conducted and the results were plotted as 3-dimensional plots. In these plots, binding decrease is a function of pH and initial metal concentration (Figures 4-9 through 4-14). The average values of $K_{Me^{2+}}^{int}$ obtained from mono-element and multiple-element systems were used in the modeling. The binding decrease was calculated as the ratio of the difference of the binding in mono-element and multiple-element systems over the binding in mono-element system.

In the general case, there exists four regions in each graph: (i) low pH and low initial concentration; (ii) low pH and high initial concentration; (iii) high pH and low initial concentration and (iv) high pH and high initial concentration.

The binding decrease of bentonite in region (iii) was so small that the binding decrease could be neglected at high pH and low initial concentration. Results also indicate that the binding decrease in region (iv) was smaller compared to region (ii), suggesting that a higher pH value could attenuate the competitive binding decrease to some extent for bentonite. In region (i) where both low pH and initial concentration exist, although binding decrease was small when initial concentration was very small, the binding decrease rapidly became significant with increasing initial metal concentration. It can be inferred from this observation that binding decrease was very sensitive to the change of initial concentration at low pH value. For Amite soil and kaolin, the binding decrease was always sensitive to the increasing initial concentration along the whole pH range.

In modeling calculation, it was assumed that metal species ions were bound to the clay surface via surface complexation. However, with the increase of metal concentration, the clay
Figure 4-9. Decrease of metal species complexation in multiple-element system without Mg and Ca when 2 g/L of bentonite was used as exchange medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. \(C_0\) was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO₃.
Figure 4-10. Decrease of metal species complexation in multiple-element system without Mg and Ca when 2 g/L of Amite soil was used as complexation medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. $C_0$ was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO$_3$. 
Figure 4-11. Decrease of metal species complexation in multiple-element system without Mg and Ca when 2 g/L of kaolin was used as complexation medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. $C_0$ was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO$_3$. 
Figure 4-12. Decrease of metal species complexation in multiple-element system including Mg and Ca when 2 g/L of bentonite was used as exchange medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. C₀ was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO₃.
Figure 4-13. Decrease of metal species complexation in multiple-element system including Mg and Ca when 2 g/L of Amite soil was used as complexation medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. $C_0$ was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO₃.
Figure 4-14. Decrease of metal species complexation in multiple-element system including Mg and Ca when 2 g/L of kaolin was used as complexation medium. The decrease was calculated by the comparison of metal species binding in the multiple-element system to that in mono-element system. $C_0$ was initial metal species concentration. The ionic strength was kept constant at 0.01 NaNO$_3$. 
surface could become saturated with metal ions and the surface of the complex could act as new binding sites to complex more metal ions if the complexation follows Freundlich isotherm, whose basis assumes binding sites of different energies. A schematic representation of surface complexation for a multiple-energy isotherm (Freundlich Type) is illustrated in Figure 4-15. Since the value of $K_{\text{int}}^{\text{Me}^{2+}}$ is not necessarily equal to $K_{\text{Me}^{2+}}^\text{'}$, which is the constant of surface complexation between metal and metal-clay complex, the application of SC model could lead to large error at high metal concentration if the values of $K_{\text{int}}^{\text{Me}^{2+}}$ and $K_{\text{Me}^{2+}}^\text{'}$ are significantly different.

![Figure 4-15. Schematic representation of surface species of multiple-layer complexation. Me$^{2+}$ and A$^{n-}$ are divalent metal cations and anions, respectively. $K_{\text{Me}^{2+}}^\text{int}$, $K_{\text{Me}^{2+}}^{'}$ and $K_{\text{Me}^{2+}}^{''}$ are intrinsic complexation constants of metal-adsorbent complex, metal- metal-adsorbent complex and metal-anion-adsorbent complex.](image)

**CONCLUSIONS**

Surface complexation model (diffuse-layer model) has been utilized to model the complexation process of Cu, Zn, Cd and Pb on bentonite, Amite soil and kaolin. It was found that modeling of utilizing the DL model could fit the experimental data well under different
experimental conditions, including: mono-element systems where only one of the four metal species (Cu, Zn, Cd and Pb) existed, multiple-element system where all four metals were presented and multiple-element system where all metal species, Cu, Zn, Cd, Pb, Mg and Ca were presented. Results confirmed that the intrinsic surface complexation constants showed little variations between mono-element and multiple-element systems with and without the presence of Mg and Ca. Based on the analysis of $K_{Me^{2+}}^{\text{int}}$ values, results indicated that the binding affinities of the clays for metal species increased in the order of kaolin < Amite soil < bentonite while the affinities of the metals for the clays increased in the order of Cd < Zn < Cu < Pb. It was concluded that the high affinities of bentonite for the metals originated from its high specific surface area and high values of $K_{Me^{2+}}^{\text{int}}$.

The presence of other metals could decrease the binding of other metal species and the effect of competitive interaction was very significant for the binding of metals on kaolin. Although kaolin had the highest binding site density (1.18 sites/nm$^2$), kaolin still had a low binding capacity due to low total surface area and low $K_{Me^{2+}}^{\text{int}}$. Results indicate that binding of metal species with a low value of $K_{Me^{2+}}^{\text{int}}$ would be reduced significantly in the multiple-element system where competitive binding occurred.

Metal species speciation, both in aqueous phase and solid phase, were strongly pH dependent. However, metal species concentrations both in solid phase and aqueous phase changed slowly when kaolin was complexation medium.

The three-dimensional plots depicting the binding decrease as functions of pH and initial metal concentration were developed using the intrinsic surface complexation constants obtained by experimentation. Results indicate that the effect of competitive binding was not significant at
high pH and low initial metal concentration for the binding of the four metals on bentonite. However, competitive binding could reduce metal binding in multiple-element system when pH was low or initial metal concentration was high. The presence of Mg and Ca could alter the binding behavior of Cu, Zn, Cd and Pb. The binding of these metal species on the clays was decreased with the introduction of Mg and Ca. It can also be inferred from the results that binding decrease was very sensitive to the change of initial concentration at low pH value.

REFERENCES


Herbelin, A. L. and Westall, J. (1999) “A computer program for the determination of chemical equilibrium constants from experimental data.” Report 99-01, Department of Chemistry, Oregon State University, Corvallis, USA.


NOMENCLATURE

The following symbols are used in this paper:

- **Bentonite** = \{\text{Na, Ca}_{0.5}\}_0.7(\text{Mg, Fe, Al})_4(\text{Al, Si})_8\text{O}_{20}(\text{OH})_4
- **C_s** = adsorbent concentration (g/L)
- **C_0** = initial metal species concentration (mg/L)
- **CC** = constant capacitance model
- **CEC** = cation exchange capacity (meq/100g)
- **DL** = diffuse-layer model
- **E(x_i)** = the expected value
- **F** = Faraday constant (96500 C/mol)
- **Goethite** = FeOOH
- **Hematite** = Fe_2O_3
- **H_s^+** = hydrogen at the complexation surface
- **\{H^+\}** = H^+ activities in bulk solution
- **I** = ionic strength (N)
- **Kaolin** = Al_2Si_2O_5(OH)_4
- **K^{\text{int}}_{Me^{2+}}** = intrinsic surface complexation constant
- **K^{\text{SC}}_{Me^{2+}}** = constant of surface complexation between metal and metal-clay complex
- **Magnetite** = Fe_3O_4
- **M_s^{2+}** = metal ion at the complexation surface
- **\{M^{2+}\}** = metal activities in bulk solution
- **n** = the number of data points
- **N_A** = Avogadro’s number (6.02 × 10^{23})
- **N_s** = sorbing site density (sites/nm^2)
- **O(x_i)** = the observation data (modeled data)
- **pH_{50}** = pH value at which 50% of binding of metal species occurs
- **R** = ideal gas constant (8.314 J/mol•K)
- **R^2** = determination coefficient
- **SC** = surface complexation model
- **SOH** = neutral functional groups on adsorbent surface
- **SOM^+** = metal-complexation site complex
- **SSA** = specific surface area (m^2/g)
- **T** = absolute temperature (K)
- **TL** = triple layer model
- **Z** = electrolyte valence
- **\psi_0** = potential at the adsorbent surface (V)
- **\psi** = potential at complexation plane (V)
- **\sigma** = charge density (C/m^2)
- **\sigma_0** = charge density at clay surface (C/m^2)
- **\gamma** = activity (M)
- **\chi^2** = chi-squared result for computed goodness of the fit
- **\Gamma_{SOH}** = concentration of sorbing surface sites (mol sites/L)

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SUMMARY

Rainfall-runoff impacted by transportation and urban activities and infrastructure transports a wide gradation of particulates ranging from colloidal to gravel size material that are entrained with constituents such as metal species. The ubiquitous existence of clay-size and clay minerals in transportation land use rainfall-runoff was confirmed by the examinations of SEM, EDS and XRD. The XRD diffractogram revealed that montmorillonite, kaolinite and anorthite were the main clay minerals with minor fraction of illite and quartz present. On a number basis the clay-size fraction represented 97% of the total particle number distribution while on a mass basis represented 1.5% of the total particulate mass. The clay fraction can generate more than 16% of the total surface area in the urban transportation land use runoff solids with the specific surface area of the clay fraction as high as 130 m$^2$/g. The clay fraction aggregates had 1- and 2-dimensional fractal dimensions of 1.07 ± 0.03 and 1.92 ± 0.04, respectively at confidence interval of 95%. The adsorption isotherms of the clay fraction were investigated and the results indicated the clay fraction had significant heavy metal adsorption capacities. The existence of Mg or Ca in rainfall-runoff alters the adsorption performance of Cu, Zn, Cd and Pb. The introduction of Mg or Ca decreased the heavy metal adsorption capacities by as high as 50%. It seemed that the high concentration of Ca with typical range of 10 to 20 mg/L in storm water had a greater effect than Mg with typical concentration of 2 to 10 mg/L on the heavy metal adsorption. Both the adsorption isotherms and adsorption edges demonstrated that the relative adsorption affinities for the four common metal species in rainfall-runoff followed the order of Pb > Cd > Cu > Zn. While the mass of the clay-size fraction and the associated metal are small,
the number of clay-size particles is large as is the metal concentration leading to concerns of bioavailability for this fraction

**INTRODUCTION**

Specific urban land uses such as transportation have specific impacts both on the quantity and quality of the rainfall-runoff process due to the anthropogenic activities in our modern urban societies. Conventional pavement surfaces are designed to allow the effective conveyance of vehicular traffic and rainfall runoff. An unintended consequence of such effective conveyance is the enhanced transport of particulate and dissolved constituents from the pavement surface. As a result, transportation land use runoff is recognized as a substantial source of particulates and metal species to receiving waters (Davis et al. 2001).

Metal species are an important group of anthropogenic constituents that exhibit persistence, bioaccumulation, toxicity and non-degradability in the environment. Of the various metal species commonly detected in runoff from transportation land uses, Cu, Zn, Cd and Pb are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA). The transportation sources of metal species include brake linings, tire abrasion, vehicular parts abrasion, and infrastructure degradation and leaching (Sansalone and Buchberger 1997 and David et al. 2001). Particulates are also generated from traffic activities, pavement and infrastructure degradation and maintenance, and littering (Sansalone et al. 1998). These particulate materials can be in a wide gradation ranging in size from smaller than 1 µm (colloidal material) to greater than 10,000 µm (sand to gravel).

In response to the Clean Water Act (CWA), the USEPA developed the National Pollutant Discharge Elimination System (NPDES) Storm Water Program. As a goal of this program, sources of storm water runoff that had the greatest potential to negatively impact water quality...
were to be permitted and controlled. During the past 20 years, extensive research has been conducted to characterize both the quality and quantity of urban storm water (Smith et al. 2001, Wu et al. 1998, Line et al. 1996, Tsihrintzis and Hamid. 1997, Lee and Bang 2000 and Thomson et al. 1997, Tomanovic and Maksimovic 1996, Sansalone and Buchberger 1997, and Sansalone et al. (1998). For example, a hydraulic model considering the flow hydrograph was used to estimate the loads of Cu, Zn and Pb to the river by Smith et al. 2000. Wu et al. (1998) monitored three highway segments typical of urban, semiurban and rural settings in North Carolina. They found that runoff from both of the sites generated significant TSS loading associated with nitrogen and phosphorous. Similarly, COD, SS, T-N and T-P, in storm water were also evaluated for both combined and separate type sewer systems by Uchimura et al (1997) and Lee and Bang (2000). It was found that there were high concentrations of T-N and T-P in the storm water. The water quality of storm water runoff from the industrial sites was also studied by Line et al. (1996). A wide range of pollutants, such as metal species (Cu and Zn), organic compounds and pesticides were detected. Some models such Soil Conservation Service hydrology method and empirical equations developed by USEPA were used to perform urban storm water quantity and quality modeling (Tsihrintzis and Hamid 1997). Bertrand-Krajewski et al. (1998) used a dimensionless curve of the cumulative pollutant mass vs the cumulative discharged volume to compare pollutant discharge from different rainfall event. It was found that the curves were variable and dependent on the pollutant, the site, the rainfall event and the functioning of the sewer system. Tomanovic and Maksimovic (1996) measured the rainfall intensity, suspended solids, pH, conductivity and temperature in two urban areas in Sweden and Yugoslavia, respectively. A mathematical model was developed to describe suspended solids wash-off. Sansalone and Buchberger (1997) and Sansalone et al. (1998) studied the partition and first flush
of metals and the physical characteristics of urban rainfall-runoff solids. They found that Zn, Cd, Cu were mainly in dissolved form while Pb, Fe and Al were mainly particulate-bound.

**BACKGROUND**

Clays are fine-grained hydrous silicate solids with layer structures and are defined based on size to be smaller than 2 µm (Brown 1984, Grim 1968, Gier 1998). The clay size fraction is commonly entrained in rainfall-runoff and can have a significant impact on the physical and chemical properties of the gradation while only constituting a small fraction of the gradation on a mass basis. In the turbulent mixing regime typical of most urban flows, mass transfer from the aqueous phase to the clayey particulate fraction can be significant as a function of hydrodynamics, pH, alkalinity, residence time and physico-chemical particulate characteristics (Sansalone 1998). In the aqueous environment, entrained clayey particle surface is very active in reacting with metal species and organics and their reaction with different components in natural waters are also rapid (Langmuir 1997). As a result, higher concentrations of metals and organic mass are associated with the clay-size fraction of the particle gradation due to the higher specific surface area (Gibbs 1973, Schroth and Sposito 1998, Cells et al. 2000, Schroth and Sposito 1998, Papini et al. 2001 and Singh 2001). On the other hand, it is also quite possible that the clayey particles are highly amorphous, porous and fractal (Li and Yuan 2002). During settling process, the fractal aggregates can have higher collision frequencies between the aggregates and other particles than those between the impermeable spherical particles (Li and Logan 1997). Therefore, the size requirements of some water treatment facilities such as sedimentation tank can be overestimated.

In urban conveyance systems, whether as sheet flow or as more concentrated gutter or pipe flow, clay-size material can be readily mobilized, entrained and carried across the urban
environment. While large particles (silt and sand size) dominate the storm water particulate gradation on a mass basis and can be effectively separated from storm water through primary treatment, the clay fraction dominates the gradation on a number basis and can be recalcitrant to separation from storm water without advanced treatment such as coagulation / flocculation. Sansalone et al. (1998) confirmed that the storm water solids in the 1 to 5 µm range generated the largest particle numbers across the gradation.

The occurrence of clay minerals in the urban environment can be attributed to anthropogenic activities, vehicular and infrastructure paints released due to degradation, vibration, collision and abrasion. Some of the clays, such as kaolinite, sepiolite and palygorskite (attapulgite) are commonly found their application in paint since they improve the covering, thickening and thixotropic properties (Murray 1995). Besides these applications, sepiolite and palygorskite are also components in asphalts (Murray 1995). The existence of clay minerals in the soils of transportation land use is another source of these clay materials. Clay is ubiquitous in soils and can be transported to the pavement as a result of traffic turbulence and rainfall-runoff. The potential and ability of the syntheses of clays from the mixture of oxides and hydroxides at ordinary temperature and pressure comprises another potential source of clay occurrence in transportation land use runoff. It was reported that the product which was very similar to smectite based on XRD patterns could be synthesized by mixing sodium silicate, sodium aluminate and MgCl₂ at a pH of 5.6 and laboratory temperature for 4 years (Sedletsky 1937). In a similar way, kaolinite could also be synthesized by mixing very dilute solutions of silicate, or silicate and aluminate, with dilute solution of magnesium and aluminum salts (Henin 1956).

Physical and chemical characteristics of the particles are primary variables controlling factors such as partitioning and the removal efficiency in storm water treatment in primary
clarifiers, sedimentation basins and filters. The importance of the solid or colloid phase of storm water has been highlighted recently. Grout et al. (1999) investigated the composition of morphology of colloidal materials entering an urban waterway during a storm event. They found that carbon prevailed in the initial stage while silica dominated when the storm water flow reached the maximum. Physical and chemical characteristics, including particle size, water content and heavy metal contents, of bottom sediment from an on-stream pond were described by Marsalek and Marsalek (1997). They found that the sediments contained elevated levels of metal species, such as Cr, Cu and Pb. Krishnappan et al. (1999) investigated the seasonal variation of particle size and floc density of suspended solids in the same pond. They concluded that the naturally formed flocs with size of 5 to 15 µm had higher settling velocity than both smaller particles of high density and large flocs of low density.

Fractal geometry has been used extensively to describe fractal dimensions of aggregates, such as fluvial sediments (De Boer and Stone 1999, Billiones et al. 1999) and coagulated particles (Logan and Kilps 1995, Chakrabortl et al. 2000). De Bore and Stone (1999) studied the particle morphology of river sediment using two contrasting methods. In the first method, the river sediment particles settled on a microscope slide and were observed using an inverted microscope. The second method involved filtration and the particles were deposited on the filter and were observed with a microscope. They evaluated the effect of the two sample method on the fractal dimensions of the particles. It was found that fractal dimensions obtained with the settling method were less sensitive to the sampling site characteristics and conditions. The particulate materials isolated from water samples collected from the estuary were investigated by Billiones et al. (1999). Measurements of fractal dimensions were made and it was found that one-dimensional fractal dimensions were measurable for monocotyle with a value ranging from
1.04 to 1.37 with a mean value of 1.17, for dicotyles with values ranging from 1.25 to 1.86 with a mean of 1.46. Logan and Kilps (1995) studied the effects of different fluid mechanical environments on the fractal properties of aggregates. It was found that the rolling cylinder and paddle mixer could generate aggregates that had 2-dimensional fractal dimensions of 1.68 and 1.89, respectively. The fractal dimensions of aggregates formed by the addition of alum to lake water and a montmorillonite clay suspension were investigated by Chakrabortl et al. (2000). They found that charge-neutralization and sweep-floc mechanisms produced different fractal dimensions of the aggregates. Typically, fractal dimension was lower for sweep-floc coagulation which produced larger and more irregular flocs. For example, 2-dimensional fractal dimensions of the aggregates were 1.96 and 1.65 in charge-neutralization and sweep-floc stages, respectively for the lake water sample and were 1.89 and 1.77 for the clay suspension.

In the similar way, the fractal properties and methods can also be employed to describe fractal dimensions of the clayey particulates collected from rainfall-runoff of transportation land. Typically, the geometrical theory used to analyze fractal aggregates includes fractal dimensions which can be expressed as the following power functions (Logan 1995):

For 1-dimensional fractal dimension $D_1$

$$P \propto l^{D_1}$$ (1)

where $P$ is the aggregate perimeter ($\mu$m), $l$ is the maximum aggregate diameter ($\mu$m).

For 2-dimensional fractal dimension $D_2$

$$A \propto l^{D_2}$$ (2)

In this expression $A$ is the projected aggregate area ($\mu$m$^2$).

For Euclidean particles $D_1 = 1$ and $D_2 = 2$. A value of $D_1 > 1$ indicates that as particle size increases the perimeter increases faster than the particle length scale (De Bore and Stone 1999).
This implies that the particle outline will become more complex therefore the shape of the particle will become more irregular for larger particle. In a similar way, a value of $D_2 < 2$ indicates that as particle size increases the projected area increases slower than the square of the length scale. This means that the projected area of a larger particle, which surrounds or partially surrounds regions that are not part of the particle, is less than that of the Euclidean particle of the same scale. Therefore, fractal dimensions can be used to characterize particle shape and morphology.

**OBJECTIVES**

The geochemistry of the clay-size fraction influences the chemistry of natural waters through precipitation, dissolution and ion exchange reactions (Langmuir 1997). Transportation land use rainfall runoff is not an exception. In early investigations several investigators realized the importance of the presence of suspended solids in rainfall runoff and a strong relationship has been established between the chemical characteristics of storm water runoff and the concentration of suspended solids in storm water runoff (Lopes et al. 1995). However, the characteristics of the clay fraction in storm water runoff solids and significance of clays in mediating storm water chemistry have been overlooked or even ignored due to the minor mass percentage of clay fraction in storm water runoff particles. Consequently, there still remain some uncertainties about the contributions of clay fraction to transportation land use rainfall runoff geochemistry and the removal efficiency of clayey particles in the treatment of transportation land use rainfall-runoff. Under some circumstance, the clay fraction can generate very large particle number and comparable surface area with larger suspended solids. Therefore, ignoring the clay fraction could lead to the failure of infiltration or sedimentation process in the treatment of storm water runoff. In natural aqueous environment, the clays are typically negatively charged
and the repulsions between the clay particles will keep them in stable state which will impair filtration or sedimentation. In this paper, an effort to characterize physical and chemical properties of clay fraction in transportation land use rainfall runoff particles has been made. The first objective of this study is to investigate clay evidence in storm runoff solids and some basic physicochemical characterizations of the clays will be evaluated. The second objective is to identify clay composition with the aid of X-ray Diffraction (XRD) patterns. The third objective is to study the fractal dimensions of the clays recovered from rainfall-runoff of transportation land and pavement. The last objective is to study heavy metal adsorption capacity of the clays extracted from highway runoff. The effects of Mg and Ca, which can always be detected in high concentrations in highway runoff, on the clay adsorption performance will be evaluated.

MATERIALS AND METHODS

Sample Collection and Preparation

The transportation land use rainfall runoff was collected in urban Baton Rouge, Louisiana. The sampling site is located in an elevated section of Inter-State 10 eastbound span over the City Park Lake and the map of the site is shown in Figure 1. The site receives 1460 mm of rainfall annually and the average daily traffic load is about 70,400 vehicles. The drainage area was completely paved and rainfall that became runoff only contacted the pavement and not surrounding soils adjacent to the pavement. A section of the bridge deck with Portland cement concrete pavement drainage area of 544 m² was chosen and runoff flows were drained to a 0.2-m cast iron storm effluent pipe, which was used to channel to flow directly to an 80-L debris separator that removed the coarse fraction of transported particles (> 10,000 µm). A summary of hydrology, traffic loading, rainfall-runoff quality, aqueous and particulate metal concentrations are shown in Table 5-1.
Table 5-1. Summary of hydrology, traffic, rainfall-runoff water quality of the experimental site. The number of events for hydrologic, traffic and water quality analysis (event mean concentrations) is 12.

<table>
<thead>
<tr>
<th></th>
<th>VDS (vehicles)</th>
<th>Rainfall Duration (min)</th>
<th>Runoff Duration (min)</th>
<th>Total Precipitation (mm)</th>
<th>Total Flow (L)</th>
<th>Q_p (L/min)</th>
<th>t_p (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ</td>
<td>3891</td>
<td>67</td>
<td>71</td>
<td>12</td>
<td>2484</td>
<td>110</td>
<td>32</td>
</tr>
<tr>
<td>σ</td>
<td>3685</td>
<td>79</td>
<td>59</td>
<td>16</td>
<td>3485</td>
<td>127</td>
<td>41</td>
</tr>
</tbody>
</table>

VDS: Vehicles Duration Storm, the total number of vehicles passing the transportation land during the rainfall-runoff event.

Rainfall Duration: The time spanning between the start and stop of effective rainfall for each event.

Runoff Duration: The time spanning between the start and stop of effective runoff for each event.

Total Precipitation: The total amount of precipitation recorded on the site for each event.

Total Flow: The total amount of runoff generated from the experimental section for each event.

Q_p: The measured peak flow of runoff for each event.

t_p: The time spanning between start of effective runoff and the peak flow for each event.

<table>
<thead>
<tr>
<th></th>
<th>SSC [mg/L]</th>
<th>VSSC [mg/L]</th>
<th>COD [mg/L]</th>
<th>Alk. [mg/L]</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
<th>ORP [mV]</th>
<th>D.O. [mg/L]</th>
<th>Conductivity (µs/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ</td>
<td>275</td>
<td>88</td>
<td>430</td>
<td>31</td>
<td>253</td>
<td>7.1</td>
<td>+404</td>
<td>6.2</td>
<td>303</td>
</tr>
<tr>
<td>σ</td>
<td>138</td>
<td>58</td>
<td>280</td>
<td>20</td>
<td>157</td>
<td>0.3</td>
<td>55</td>
<td>1.5</td>
<td>299</td>
</tr>
</tbody>
</table>

SSC: Suspended solid concentration.

VSSC: Volatile suspended solid concentration.

COD: Chemical oxygen demand.

Alk.: Alkalinity.

ORP: Oxidation-reduction potential

D.O.: Dissolved oxygen

<table>
<thead>
<tr>
<th></th>
<th>Cu [mg/L]</th>
<th>Zn [mg/L]</th>
<th>Cd [µg/L]</th>
<th>Pb [µg/L]</th>
<th>Mg [µg/L]</th>
<th>Ca [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Fraction µ [mg/L]</td>
<td>48.9</td>
<td>185.6</td>
<td>6.7</td>
<td>11.0</td>
<td>3600</td>
<td>74000</td>
</tr>
<tr>
<td>Dissolved Fraction σ [mg/L]</td>
<td>59.5</td>
<td>270.4</td>
<td>10.5</td>
<td>17.0</td>
<td>4000</td>
<td>93000</td>
</tr>
<tr>
<td>Particulate-Bound Fraction µ [µg/L]</td>
<td>82.4</td>
<td>353.5</td>
<td>11.9</td>
<td>567.4</td>
<td>4800</td>
<td>16000</td>
</tr>
<tr>
<td>Particulate-Bound Fraction σ [µg/L]</td>
<td>74.2</td>
<td>284.8</td>
<td>13.6</td>
<td>1200</td>
<td>4900</td>
<td>15000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>f_d µ</th>
<th>f_d σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>σ</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

f_d: Dissolved metal fraction = dissolved metal mass / total metal mass.
Sampling was carried out for the storm event on 2002 April 10 with a precipitation of 109 mm. The sample of transportation land use rainfall runoff was taken from the debris separator. The clays were extracted by normal settling procedure which was based on an application of Newton's Law (Aparicio and Ferrell 2001). It was calculated that a 2-µm spherical quartz particle with a density of 2.65 g/cm³ would travel 5 cm after 3.5 h of settling time at laboratory temperature. The stormwater was allowed to settle and the upper 5 cm of supernatant with a volume of 500 liter was collected after sedimentation time of 3.5 h.
The upper 5-cm supernatant volume containing clay particles was placed in a 35°C hot room and the solid residuals were collected after the water had been evaporated. The particles were re-suspended in 20% H\textsubscript{2}O\textsubscript{2} solution and put on a hot plate overnight so that any storm water organic matters was oxidized (Henderson et al. 1997). The suspensions were centrifuged for 20 minutes at a speed of 12,000 rpm and decanted. The clayey residuals were re-suspended in water overnight and then centrifuged. This process was repeated 3 times so that the impurities, such as organic matters in the clays could be removed.

**Scanning Electron Microscopy**

Samples for Scanning Electron Microscopy (SEM) were collected from different particle size ranges to provide the evidence of extensive existence of clay fraction in highway runoff solids. All samples had been rinsed with D. I. water and dried before they were mounted on the slides. The samples on the slides were coated with carbon or gold before SEM examination. Qualitative information on the element composition of a particular site on the solid surface was obtained with the aid of Energy Dispersive Spectroscopy (EDS).

**Elemental Analysis of Clay**

Approximately 0.2 gram of the clay was digested in a mixture of 9 mL of 70% HNO\textsubscript{3} and 3 mL of 37% HCl for ten minutes using a hot plate as outlined in SW-486 Method 3051 (USEPA 1990). Once cool, the samples were diluted to 100 mL with D. I. water and a 10-mL sample was withdrawn for metal analysis. Quality control was conducted by digesting a standard soil (CLP Inorganic Soils, supplied by Environmental Resource Associates, CO) and the results were accepted if the metal concentrations of the standard fell in the specified limits. Metal analysis was performed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, ELAN 6000) instrument. The following metals were examined: Ca, Mg, Cu, Zn, Cd and Pb.
**Specific Surface Area**

The EGME (Ethylene Glycol Monoethyl Ether) method (Sansalone et al. 1998) is a gravimetric method utilized for the determination of clay specific surface area (SSA). This method determines the amount of EGME adsorbed at a constant vapor pressure, by measuring the increase in clay weight due to the adsorbed monolayer of EGME. A dry representative sample of 0.5 g was first saturated with EGME, by completely wetting all particle surface area in a glass desiccators over 600 grams of EGME-CaCl$_2$ solvate. A constant vapor pressure was produced from this solvate. The EGME to CaCl$_2$ ratio was 1.5:1. Samples were weighed at 2 to 4-hour intervals after 24 hours in the desiccators until a constant weight (less than 1 mg across 4 hours) for each sample was obtained. Based on the assumption of a monolayer surface coverage of EGME, molecular weight and molecular diameter of EGME, specific surface area (SSA) of clay was calculated according to:

$$\text{SSA} = \frac{W_a}{0.000286(W_s)} \quad (3)$$

where $W_a$ is the weight of EGME adsorbed by clay while $W_s$ is the weight of clay. Granular activated carbon (GAC) with a SSA of 1100 m$^2$/g (Calgon Carbon Corporation 1995) was used as quality control.

**Particle Density**

The particle density of clay was measured using a pycnometer (Quanta Chrome Corporation, FL). The methodology followed ASTM D5550-94 (ASTM 1994). The pycnometer is an instrument specially designed to measure the volume of solid sample. It determines the volume of solid by measuring the pressure difference when a known quantity of inert gas (UHP helium in this case) is allowed to flow under pressure from a precisely known reference volume
(VR) into a sample cell containing clay material. The true solid volume can be calculated using Eqs. (4).

\[ V_S = V_C - V_R \left( \frac{P_1}{P_2} - 1 \right) \]  \hspace{1cm} (4)

In this expression, \( V_S \) is true sample volume, \( V_C \) is cell volume, \( V_R \) is reference volume, \( P_1 \) is initial pressure and \( P_2 \) is final pressure. Particle density can be obtained by dividing weight of sample (\( M_S \)) by the true volume of sample (\( V_S \)). Triplicates were analyzed for each sample.

**Particle Size Gradation**

Particle size distribution of clay fraction was analyzed using a laser diffraction particle analyzer with triplicate samples for each. Since particle size distribution of the clay was analyzed on a number basis, Eq. (5) was used to make the conversion of from number basis to mass basis.

\[ \text{Mass} \% = \frac{N_i d_i^3}{\Sigma (N_i d_i^3)} \]  \hspace{1cm} (5)

In the above expression \( N_i \) is the number of particles with diameter of \( d_i \).

**X-Ray Diffraction**

The sample had been pre-treated with 20 % \( \text{H}_2\text{O}_2 \) so that the organic matter could be removed before being subjected to XRD analysis (Henderson et al. 1997). The comparison of XRD patterns of four states of the sample was conducted. The four states included: air-dried, treated with ethylene glycol, heated to 350 °C and heated to 550 °C at 1 hour, respectively. To eliminate the contribution of the reflections other than \( 00l \), the sample was prepared by smearing on the slide. The patterns of the oriented clay-aggregate sample were recorded.

The XRD patterns were collected with Cu-K\( \alpha \) radiation in a Siemens D5000 diffractometer at 40 kV, 30 mA, in the 2-36° 2θ range. MacDiff software was employed to locate the peak position and measure peak height. The identification of the clays was made using this
A semi-quantitative estimate of the percentage of each clay component could be made if it was assumed that the clay content was proportional to its peak height (Atteia et al. 1997). The mass percentage of each clay can be estimated using the following equation:

\[ P_i = \frac{H_i}{\Sigma H_i} \times 100 \]  

(6)

In this expression, \( P_i \) is mass percentage of clay \( i \) (\%) and \( H_i \) is the peak height of clay \( i \).

**Surface Charge**

Surface charge was analyzed using a potentiometric titration method described by Van Raij and Peech (1972). Approximately 0.2 g of clay was suspended in 20 mL of 0.001, 0.01 and 0.1 M NaNO\(_3\), respectively. The suspension was purged with nitrogen gas, sealed and kept mixed using a reciprocating shaker at room temperature for 24 hours after which the pH values of the supernatant were recorded. During the titration process, the suspension was continuously bubbled with N\(_2\) to eliminate the effect of CO\(_2\). Surface charge values were calculated by the amounts of H\(^+\) or OH\(^-\) required to bring the samples to the final equilibrium pH, minus the amount necessary to bring 20 mL of a blank solution to the same pH. Triplicate analyses were conducted for each sample.

**Fractal Dimensions**

The clay fraction was first re-suspended and diluted with D.I. water to produce a solution with concentration of roughly 50 mg clay/L. A drop of this clay suspension was smeared on a slide and discrete aggregates were obtained after the sample was air-dried in a closed chamber to prevent the contamination of dust. The images for fractal analysis were acquired using SEM and viewing fields were selected at random on the slides. One hundred clayey particulates were randomly chosen from the SEM images and these particles were traced using Image-Pro Plus software. The images were processed and some parameters, such as the maximum aggregate...
diameter, average aggregate diameter, projected aggregate area and aggregate perimeter, were obtained using the software. The fractal dimensions of aggregates were calculated by linear regression analysis of the logarithm of the maximum aggregate diameter versus the logarithm of the aggregate perimeter and projected area as suggested by Eqs. (1) and (2), respectively.

**Adsorption Isotherm**

Adsorption isotherms were constructed based on the data obtained in batch-mode experiment using 50-ml polypropylene centrifuge tubes. The 100 ± 1 mg of the clay collected from highway runoff was equilibrated with 40 ml of heavy metal solutions with different compositions and concentrations for 24 hours at room temperature on a reciprocating shaker. Four metal species, including Cu, Zn, Cd and Pb were tested. In order to evaluate different heavy metal affinities with the clays with and without the presence of Mg and Ca, two commonly detected metals with relatively high concentrations in highway runoff, and the adsorption performance of clay for different metals in a simulated stormwater runoff environment, two sets of adsorption isotherm were developed by two different approaches: one with the same initial heavy metal concentrations and other with different initial heavy metal concentrations which were proportional to the typical values of stormwater event mean concentration (EMC). For the first case, the initial heavy metal concentrations were set at 0.015, 0.03, 0.06, 0.09, 0.12 and 0.15 mM for each heavy metal, respectively, while for the second case, the initial heavy metal concentrations of Cu, Zn, Cd and Pb were in proportion to 1:10:0.06:0.15 (in mM). The isotherm experiments were conducted at pH 6 and ionic strength of 0.001, 0.01 and 0.1 N NaNO₃, respectively. The test was run in duplicate so that the error bars could be presented in the isotherms. Freundlich isotherm, which is shown in Eq. (7), was employed to model the experimental data.
\[ q = kC^n \]  

In this expression, \( q \) is heavy metal adsorbed per unit mass of adsorbent (mmol/g), \( k \) and \( n \) are constants and \( C \) is equilibrium heavy metal concentration (mM). The Freundlich isotherm assumed an exponential distribution of adsorption energy (Sheindorf et al. 1981) and was used extensively by numerous researchers (Yong and MacDonald 1998, Wang et al. 1998, Zehetner and Wenzel, 2000, Manning and Goldberg 1997 and Roy et al. 1991).

**Adsorption Edge**

The adsorption edges for the four metal species were constructed in a similar way as those in the development of adsorption isotherms. The 100 ± 1 mg of the clay was equilibrated with 40-ml mixture of 0.0015 mM Cu, 0.154 mM Zn, \( 8.9 \times 10^{-5} \) mM Cd and \( 2.4 \times 10^{-4} \) mM Pb, 0.083 mM Mg and 0.5 mM Ca. The solution was adjusted using HCl or NaOH so that the equilibrium pH values varied from 1.8 to 6.9. The heavy metal concentrations in aqueous solution were analyzed after 24-hour equilibrium on the reciprocating shaker.

**Metal Concentration Analysis**

The concentrations of metals, including Cu, Zn, Cd, Pb, Ca and Mg were measured using Inductively Coupled Plasma – Mass Spectroscopy (ICP - MS). Five-point calibration was employed to construct the standard curve. The concentrations of the standard solution used included 0, 10, 20, 100 and 500 µg/L. The measuring conditions were 100 ms dwell time, 50 sweeps/reading and 3 replicates for each sample to check reproducibility. The internal standards including Sc, Ge and Rh which were introduced into the plasma with the sample, giving a concentration of 10 µg/L. The elements were measured at m/z values of 63 for Cu, 64 for Zn, 114 for Cd and 208 for Pb. QA/QC included checking a standard solution with concentration of
50 μg/L for each metal. The amount of adsorbed heavy metal was calculated as the difference between the amount added initially and that remaining in solutions.

RESULTS

Ubiquitous Existence of Clay in Transportation Land Use Rainfall Runoff

SEM together with EDS was used to provide information on morphology, as well as qualitative composition of transportation land use rainfall-runoff particles. The SEM analysis of the runoff particles of different size is shown in Figure 5-2 from which it can be seen that there were many fine particulate materials coated or attached on the surface of larger particulate materials via electrostatic attraction or chemical bond. Figure 5-3 is an illustration of one particulate material which was covered completely by a mixture of quartz, calcite (CaCO₃) or anorthite (CaAl₂Si₂O₈) and clays. The occurrence of Na on the particle surface may be the result of ionic exchange reaction in which metal species in the storm water could replace Na⁺ which was present in the interlayers of some of clays, such as smectite. Further investigation using EDS shown in Figure 5-4 revealed that they were matrix of Si- and Al-rich crystals with different levels of Ca, Fe, Na, K and Mg. The high contents of Si and Al are reflections of the existence of clays which contain continuous two-dimensional tetrahedral sheets of composition T₂O₅ (T = Si, Al, Fe, …) (Brown 1984). Webster et al. (2000) also observed that there were different contents of Si, Al, Fe and Ca in the <1 μm fraction of suspended particulate matter collected from fresh waters receiving storm water runoff.

The SEM images of some of non-flocculated and discrete clay particles collected from storm water are presented in Figure 5-5 in which the EDS spectra were the quantitative compositional information of the clay particles. It was found that all these clay particles
contained Si, Al and Ca and some of them contained Mg and Na, two common interlayer ions in some of clays such as smectite.

Figure 5-2. Ubiquitous existence of clay particles in urban transportation land use rainfall-runoff. Various sized runoff particles were coated with clays and the crystals encompassed by circles were indicative of clays.
Figure 5-3. A sand-size particulate substrate covered with clay minerals.

Characteristics of Clay Fraction

Table 5-2 is a summary of the physical and chemical characteristics of the clay fraction of transportation land use rainfall-runoff particles. It can be seen from the table that the clay-size fraction had a very high specific surface area. In this experiment, only the suspended clay fraction was collected from runoff particles and this portion accounted for 1.5 % mass percentage of the total suspended solids in the transportation land use rainfall-runoff. The total suspended solid measured in this storm event was 330 mg/L and the specific surface area was only 12 m²/g. Based on the above information, it can be calculated that clay-size fraction could contribute 16.25 % of the total surface area in the runoff particles. Considering the clay coated on large particle surfaces, this contribution should be greater. Although Pb typically has low concentration in stormwater (the typical EMC value for Pb is 0.05 mg/L), Pb showed high content in the clay-size fraction. This was attributed to the preferential affinity of Pb for clay minerals. On the other hand, the high contents of Zn, Mg and Ca in the clay were believed to be
Figure 5-4. Energy dispersive spectroscopy (EDS) of the circled areas in Figure 5-1.
Figure 5-5. SEM and EDS of non-flocculated and discrete clay particles
the result of their high concentrations in highway runoff. Another explanation of the high Ca content is that there exist some minerals, such as calcite (CaCO$_3$) or anorthite (CaAl$_2$Si$_2$O$_8$), in the solids.

Table 5-2. Characteristics of clay fraction of rainfall-runoff particulates at experimental site in Baton Rouge, LA. n = 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean ($\mu$, $\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.68 (0.03)</td>
</tr>
<tr>
<td>SSA (m$^2$/g)</td>
<td>130 (0.6)</td>
</tr>
<tr>
<td>$d_{50}$ ($\mu$m)$^1$</td>
<td>1.7 (0.02)</td>
</tr>
<tr>
<td>$d_{50}$ ($\mu$m)$^2$</td>
<td>3.5 (0.02)</td>
</tr>
<tr>
<td>Cu [µg/g]</td>
<td>210 (19)</td>
</tr>
<tr>
<td>Zn [µg/g]</td>
<td>2160 (142)</td>
</tr>
<tr>
<td>Cd [µg/g]</td>
<td>8.8 (9.6×10$^{-1}$)</td>
</tr>
<tr>
<td>Pb [µg/g]</td>
<td>728 (36)</td>
</tr>
<tr>
<td>Mg [µg/g]</td>
<td>1511 (98)</td>
</tr>
<tr>
<td>Ca [µg/g]</td>
<td>7612 (67)</td>
</tr>
</tbody>
</table>

$^1$Number-based
$^2$Mass-based

Figure 5-6 depicts the concentrations of the four metal species, including Cu, Zn, Cd and Pb which may cause great concerns in the transportation land use rainfall-runoff particles of different size. It is obvious that of the wide gradation of the rainfall-runoff particulates, clay-size fraction had the highest heavy metal contents. The contents of Zn, Cd and Pb in clay fraction were much higher than those in the silt and gravel fractions, suggesting that Zn, Cd and Pb had much stronger affinities for the clay fraction than for other fractions.

Figure 5-7 illustrates the particle size gradation of the transportation land use rainfall-runoff particles of different gradation. At the same time, the gradation of clay-size fraction was also plotted. It can be seen from the figure that clay fraction had a very small particle size. Although clay fraction had a small mass percentage which was only 1.5%, it generated huge numbers which accounted for 97% of the total numbers in the runoff particulates.
Figure 5-6. Typical heavy metal contents for the transportation land use rainfall particulates in a wide range of gradation. The calculation was based on 1000 g of particles. The volume of sample was 500-liter and 165 g of particle was recovered.

Figure 5-8 illustrates the surface charges of the clay fraction at different ionic strengths as a function of pH. It can be seen that the point of zero charge (PZC) was 5.9, indicating that clay fraction was positively charged when pH was less than 5.9 while it was negatively charged when pH was greater than 5.9. Since the PZC value of quartz, the dominant component of grit in transportation rainfall-runoff particles is 2 - 3 (McBride 1992) and the typical pH value of stormwater runoff is between 5.6 and 7.1 (Sansalone and Buchberger 1997), the sign of surface charge of quartz and the clays fraction could be different under some circumstances. In the transportation land use rainfall-runoff environment, quartz is typically negatively charged while the clay fraction is probably positively charged. Therefore, it is reasonable to postulate that the
electrostatic attraction could play an important role in promoting the initial attachment of fine clay particles on the large grit surface.

Figure 5-7. Representative mass and number gradation for non-flocculated particles in storm water runoff ($V = 500$-Liter) from $544$-m$^2$ pavement drainage area. (a) Clay-size fraction, and (b) Clay-size fraction to gravel fraction.
Identification of the Clay

The identification of the clay is often very difficult and painstaking because of the very small particle size, the poor crystallinity and the co-existence of organic matter. Usually, XRD provides the only trustworthy method of identifying the new phase (Grim 1968).

Characteristic XRD patterns of the clay-size fraction of transportation land use rainfall-runoff treated with different methods are shown in Figure 5-9. It can be seen from the figure that there is a broad peak at the lower diffraction angle position for air-dried pattern. This broad peak was probably a reflection of smectite. To verify this conclusion, the sample was further treated with ethylene glycol (EG) and heated to 350 °C and 550 °C. It is a common practice that smectite can be usually identified by its ability to incorporate two sheets of ethylene glycol molecules in the interlayer during solvation, thereby expanding the basal spacing to 17 Å when it is treated with ethylene glycol. On heating smectite to 350 °C, the water is removed from the
interlayer, but the mineral quickly rehydrates on exposure to moisture at room temperature. As a result, the peak collapses to 10 Å with a very weak 5 Å-peak, which is equivalent to two water layer thickness. However, if the mineral is heated to 550 °C, there is no expansion again. As a result, the 14-Å peak and higher order of it disappear and a new peak at 10.0 Å shows up on the XRD pattern. Illite could be excluded from the fitting since illite is a nonexpandable phase and the associated elementary peaks must not shift with ethylene glycol solvation. The comparison of the different patterns in Figure 5-6 indicates that the broad peak expanded to 17 Å with EG treatment and collapsed to 10 Å at 350 ºC and there was a slight additional collapse at 550 °C. Based on the XRD patterns of different treatments, it was concluded that the broad peak at the lower diffraction angle position for air-dried pattern was associated with smectite. Based on the

Figure 5-9. XRD patterns of the clay fraction. The d-values are in units of Å. The abbreviations S, I, K, Q and A represent for smectite, illite, kaolinite, quartz and anorthite, respectively.
determination of d-values, it was concluded that the clay fraction of the transportation land use rainfall-runoff particles collected was an assemblage of smectite, kaolinite, anorthite, with trace amount of illite and quartz.

Table 5-3 summarizes the percentage of the total phase. It was found that smectite was the dominant species in the clay fraction.

Table 5-3. The composition of clay-size fraction of transportation land use rainfall-runoff particulates (n = 2).

<table>
<thead>
<tr>
<th></th>
<th>Clay</th>
<th>Smectite</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Quartz</th>
<th>Anorthite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>51.4 (0.3)</td>
<td>7.6 (0.2)</td>
<td>6.3 (0.2)</td>
<td>6.8 (0.1)</td>
<td>27.8 (0.2)</td>
<td></td>
</tr>
</tbody>
</table>

Fractal Dimensions

Figure 5-10 was used to determine fractal dimensions of the clay fraction aggregates. Based on the values of the maximum aggregate diameter, aggregate perimeter and projected aggregate area obtained from image analysis, it was found that 1-dimensional and 2-dimensional fractal dimensions were $1.07 \pm 0.03$ and $1.92 \pm 0.04$, respectively. It should be noted that $D_1$ and $D_2$ obtained using this approach does not measure the fractal dimensions for single particles. Instead, they are reflections of the average fractal dimensions across the whole population of aggregates in the clay fraction. Although the value of 1.07 and 1.92 are very close to 1 and 2, respectively, however, since the errors are so small, t-statistics indicates that 1.07 and 1.92 are still different from 1 and 2, respectively at a confidence interval of 95% ($p = 95\%$). The 1- and 2-dimensional fractal dimensions calculated from power law equations indicate that clay fraction particulates were slightly fractal. It is believed that aggregates with highly irregular perimeters have $D_1$ values of greater than unity. The $D_2$ value obtained in this study seems higher than those of such as lake water aggregates ($D_2 = 1.65 -1.96$, Chakrabortl et al. 2000), marine snow ($D_2 =$
1.28 -1.86, Logan and Wilkinson 1990) and coagulation floc (D2 = 1.89, Logan and Kilps 1995) reported in the literatures.

Figure 5-10. The determination of fractal dimensions of the clay fraction particulates. The slopes of the regression lines are equal to the fractal dimensions D1 and D2 based on perimeter and area, respectively. P, A and l are particle perimeter, projected particle area and the maximum particle diameter, respectively.
The clay particle size distribution obtained from image analysis is plotted in Figure 5-11. An exponential distribution was employed to fit the relative distribution of the clay aggregates and the result is plotted in Figure 5-11. It can be seen from the figure that an exponential function described the data well. At the same time, the cumulative distribution of the aggregate size was also shown in Figure 5-11 (b). The comparison between Figure 5-11 (b) and Figure 5-7 (a) shows that there existed similarity between the two figures, indicating that image analysis and particle counter technique could generate very close results.

Figure 5-11. Particle number distribution of the clay fraction. (a) Histogram and (b) Cumulative distribution. Exponential distribution was used to model the relative particle size distribution.
Adsorption Isotherms

The adsorption isotherms of metal species with and without the presence of Mg and Ca are shown in Figures 5-12 and 5-13. The adsorption isotherms indicated that heavy metal adsorption on the clay fraction of stormwater solids follows the Freundlich isotherm. Two sets of isotherms were obtained: Figure 5-12 can be used to evaluate and compare the adsorption capacities of the four metal species (Cu, Zn, Cd and Pb) with the clay fraction of transportation land use rainfall-runoff particles while Figure 5-13 is a reflection of heavy metal affinities with the clay fraction in transportation land use rainfall-runoff environment. Figure 5-12 was developed with the same initial heavy metal concentrations for each heavy metal without and with the presence of 0.083 mM of Mg and 0.5 mM of Ca, which are typical EMC values of Mg and Ca in transportation land use rainfall-runoff. Figure 5-13 was constructed with different initial heavy metal concentrations which were in proportion to the typical EMC values of metal species in urban rainfall-runoff both without and with the existence of 0.083 mM of Mg and 0.5 mM of Ca. The comparison of Figures 12 and 13 showed that the two sets of adsorption isotherm were basically different. This was not surprising since it was reported that the adsorption isotherm was dependent on initial concentration (Yussa et al. 1996 and Matsui et al. 1998). The comparison of the isotherms without and with the presence of Mg and Ca also confirmed that the existence of either Mg or Ca could also alter heavy metal adsorption performances which were reflected in the isotherms.

In the case of adsorption isotherms with the same initial concentrations, it could be found from Figure 5-12 that heavy metal affinities with the clay without the presence of Mg or Ca follows the following relation: Cu > Pb > Cd > Zn. This conclusion could also be made based on the values of k, which was believed to be an indication of adsorption affinity. The higher value
of k, the greater adsorption capacity. However, the introduction of either Mg or Ca could reduce the heavy metal affinities for the clay and the order of heavy metal adsorption affinities could also be changed. When 0.083 mM of Mg was added, the relative adsorption affinities followed Pb > Cd > Cu > Zn. Although the introduction of 0.083 mM of Mg could decrease the adsorptions of the four metal species significantly, Cu suffered the highest decrease in adsorption affinity. This can be verified from the decrease of k values. It was postulated that the competitive adsorption of Mg had so great influence on Cu adsorption that Cu showed second lowest adsorption affinity among the four metal species. However, when 0.5 mM of Ca was introduced into the system, either with or without the existence of Mg, the observed heavy metal affinities were changed back to the order of Cu > Pb > Cd > Zn. It could be concluded at this stage that the competition of Ca had a comparable effect on the adsorptions of the four metal species.

Figure 5-13 illustrated that in the case of transportation land use rainfall-runoff environment with a pH value of 6, the adsorption affinities of the four metal species always followed the order of Pb > Cd > Cu > Zn, either with or without the introduction of Mg or Ca.

Metal species are usually associated with various solid phases in aqueous environment. For example, they are usually adsorbed onto mineral surface (Lee et al. 1996). It was found that Pb showed the highest affinity with the clay fraction in storm runoff. This observation is in consistent with that of Webster et al. (2000). They concluded that among Cu, Pb, Zn, Cr and As, Pb had the strongest association with suspended particulate matter. Therefore, Pb presents the greatest potential for accumulation in aqueous environment.

It was believed that there existed competitive adsorptions between Mg or Ca and the four metal species. Although the introduction of 0.083 mM of Mg and 0.5 mM of Ca could decrease
heavy metal adsorption significantly, the influence of 0.5 mM of Ca was greater than 0.083 mM of Mg.

Figure 5-12. Adsorption isotherms developed with the same initial concentrations for Cu and Zn. The initial metal concentration were set at 0.015, 0.03, 0.06, 0.09, 0.12 and 0.15 mM. The pH and ionic strength were kept at 6.0 and 0.01 NaNO₃, respectively. The Mg and Ca concentrations were 0.083 and 0.5 mM, respectively.
Figure 5-13. Adsorption isotherms developed with the same initial concentrations for Cd and Pb. The initial metal concentrations were set at 0.015, 0.03, 0.06, 0.09, 0.12 and 0.15 mM. The pH and ionic strength were kept at 6.0 and 0.01 NaNO₃, respectively. The Mg and Ca concentrations were 0.083 and 0.5 mM, respectively.
Figure 5-14. Adsorption isotherms developed with different initial concentrations for Cu and Zn. The initial metal concentrations were set in proportion to 1:10:0.06:0.15 (in mM). The pH and ionic strength were kept at 6.0 and 0.01 NaNO₃, respectively. The Mg and Ca concentrations were 0.083 and 0.5 mM, respectively.
Figure 5-15. Adsorption isotherms developed with different initial concentrations for Cd and Pb. The initial metal concentrations were set in proportion to 1:10:0.06:0.15 (in mM). The pH and ionic strength were kept at 6.0 and 0.01 NaNO₃, respectively. The Mg and Ca concentrations were 0.083 and 0.5 mM, respectively.
**Adsorption Edge**

Metal species adsorption by particulates is typically a function of pH and a small variation in pH can have a significant influence on the heavy metal adsorption process. The transportation land use rainfall-runoff is of stochastic nature and the pH of runoff can be variable. Therefore it is important to investigate how the clays react with the metal species at different pH conditions in transportation land use rainfall-runoff environment. Figure 5-16 is a depiction of adsorption edge, the relationship between heavy metal adsorptions and pH. It can be seen from the figure that heavy metal adsorption increased with pH. This is not surprising since the negative surface charges of the clay fraction increased with pH. The higher negative surface charge, the higher electrostatic interaction between the clay and heavy metal cations which were positively charged.

![Figure 5-16](image_url)

Figure 5-16. Metal species adsorption as a function of pH. Ionic strength was 0.01 NaNO₃. The initial metal concentrations were 0.0015 mM Cu, 0.154 mM Zn, $8.9 \times 10^{-5}$ mM Cd and $2.4 \times 10^{-4}$ mM Pb, 0.083 mM Mg and 0.5 mM Ca.
Figure 5-16 also indicated that the adsorption for the four metal species followed the order of Pb > Cd > Cu > Zn, which was in consistent with the result obtained from the adsorption isotherm (Figure 5-13).

Either the adsorption isotherm or adsorption edge confirmed that Pb has a high affinity with the clay. Although Pb concentration in stormwater is relatively low compared with Cu and Zn concentrations, it can still be expected to detect high Pb content in the solids. This has been confirmed by the digestion results of clay fraction of the runoff particles (Table 5-1).

**IMPLICATIONS**

Clays are ubiquitous in transportation land use rainfall-runoff and the clayey coating on the quartz surface can change the surface charge of quartz and make the quartz reactive in aqueous environment. As a result, heavy metal adsorption can take place on the surface of quartz particles or other inert particles such as calcite.

It is quite possible that the deposits on the large particle surface have a long residence time before a sufficiently large storm event sweeps the transportation land and transports the clay fraction to aqueous environment. These clays have very good opportunities to catch metal species or other pollutants during their residence on the highway in storm events. Therefore, there is a great potential and tendency for accumulation of metal species and other pollutants in the clay-size fraction. When there is a heavy storm event, these large particles can be readily flushed from the transportation land and metal species or other pollutants can be released into receiving environments thereafter. This creates a more tough issue than aqueous phase of stormwater does to environmental scientists and engineers (Parker et al. 2000).

The suspended aggregates in the clay fraction are only slightly fractal based on the fractal dimension values. Therefore, the curvilinear models can be employed without underestimating
much the coagulation rates for large particles in storm water treatment facilities. Clay particulates can almost be regarded as spherical in developing mathematical models to predict the removal rate of clay aggregates.

CONCLUSIONS

The characteristics of clay fraction of transportation land use rainfall-runoff were investigated in this study. It was confirmed that clay was in extensive existence in the transportation land use rainfall-runoff. Although the clay fraction (< 2 µm) was a minor component in the runoff particles, it could contribute more than 16% of the total particle surface area and 97% of particle numbers. The clay fraction was very reactive with the four metal species, including Cu, Zn, Cd and Pb. Based on the results of image analysis, 1- and 2-dimensional fractal dimensions of the clay fraction particulates were determined by plotting logarithm of the maximum diameter vs logarithm of the perimeter and 1 project area of the particles, respectively. The clayey aggregates had D₁ value of 1.07 ± 0.03 and D₂ value of 1.92 ± 0.04, respectively. Results from the adsorption isotherms and adsorption edge indicated that heavy metal adsorption affinities followed the order of Pb > Cd > Cu > Zn in the stormwater environment. However, for the adsorption isotherm constructed with the same initial concentrations of the four metal species the relative adsorption affinities of the four metal species could be expressed as Cu > Pb > Cd > Zn. The introduction of Mg could change this sequence and the new order of heavy metal adsorption followed the trend of Pb > Cd > Cu > Zn. However, upon the introduction of Ca, this sequence restored to Cu > Pb > Cd > Zn. Freundlich isotherm could be used to describe the adsorption of the four metal species on the clay fraction. The existence of Mg or Ca could lead to a decrease in heavy metal adsorption on the clay and it seemed that 0.5 mM of Ca had a greater influence compared to 0.083 mM Mg in stormwater.
environment. Metal species could be accumulated in the transportation land use rainfall-runoff particles and this could cause environmental concerns.

REFERENCES


**Nomenclature**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>projected aggregate area ($\mu$m²)</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td>C</td>
<td>equilibrium heavy metal concentration (mM)</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>d_i</td>
<td>diameter of particle ($\mu$m)</td>
</tr>
<tr>
<td>D_1</td>
<td>1-dimensional fractal dimension</td>
</tr>
<tr>
<td>D_2</td>
<td>2-dimensional fractal dimension</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EGME</td>
<td>Ethylene Glycol Monoethyl Ether</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>H_i</td>
<td>peak height of clay i</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma – Mass Spectroscopy</td>
</tr>
<tr>
<td>k</td>
<td>constant in Freundlich isotherm</td>
</tr>
<tr>
<td>l</td>
<td>the maximum aggregate diameter ($\mu$m)</td>
</tr>
<tr>
<td>n</td>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
<td>P_2</td>
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<tr>
<td>P_i</td>
<td>mass percentage of clay i (%)</td>
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<tr>
<td>q</td>
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<td>Scanning Electron Microscopy</td>
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<tr>
<td>SS</td>
<td>Suspended Solid</td>
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<td>X-Ray Diffraction</td>
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Chapter 6. Kinetic Modeling of Metal Species Transport in Clay Liner Materials

SUMMARY

Knowledge of the reaction kinetics is very important to the prediction of the fate of metal species in the subsurface environment of landfill facilities where there are accumulations of metal species coming from rainfall-runoff treatment sludge. The kinetics models of metal species binding onto clays and compacted clay liner materials were applied in this research to describe the concentration decay in the batch model experiments. First order reaction, second order reaction and Elovich equation were used initially to describe metal species binding onto dispersed clays. It was found that first order reaction was the best of the three models investigated. The highest values of the binding rate constant were obtained for Pb followed by Cu and Zn while Cd had the smallest value of reaction constant. Metal species binding onto uncompacted clays followed the order: bentonite > Amite soil > kaolin. Unlike dispersed clays, metal species binding onto compacted clays was a very slow process. Although the order of metal species in the binding process did not change, the order of clays followed: bentonite > kaolin > Amite soil. Shrinking-core model and pore and surface diffusion model were tested to model the binding processes onto compacted clays. The models indicated the pore water diffusivities of the four metal species within the compacted bentonite, kaolin and Amite soil were in the order of magnitudes of $10^{-10}$, $10^{-10}$ and $10^{-11}$ cm$^2$/s, respectively. It was also found that both of the shrinking-core model and pore and surface diffusion model could well simulate heterogeneous metal species binding onto compacted clay liner materials. The analysis of the relative importance of pore and surface diffusions in the effective diffusivity indicated that pore diffusion and surface diffusion were dominant within compacted bentonite and kaolin, respectively, while both pore and surface diffusions were equally important within compacted
Amite soil. A simple linear regression between metal species adsorbed per unite mass of compacted clays and square root of time was made and the results indicated that this simple relationship was valid during the time interval investigated.

**INTRODUCTION**

A variety of metals, such as Cu, Zn, Cd, Pb, Mg and Ca are ubiquitous in urban rainfall-runoff and snowmelt sludge separated by Best Management practices (BMPs) (Sansalone and Buchberger 1997, Thomson et al. 1996 and Wu et al. 1998). It has been recognized that the untreated discharge of rainfall-runoff or snowmelt into waterways is responsible for much of the degradation of US water bodies (Dennison 1996). Therefore, the significance of rainfall-runoff and snowmelt control in improving water quality has become increasingly recognized. Several control practices have been proposed and all these techniques, such as detention ponds (Hares and Ward 1999), infiltration system (Sansalone 1999) and coagulation and flocculation (Heinzmann 1994, De Cock et al. 1999 and Droppo et al. 2002) followed by filtration or sedimentation can effectively reduce a broadest range of runoff pollutants including metal species and suspended solids. Typically, solids concentration in rainfall-runoff ranges from 76 to 36200 mg/L (Makepeace et al. 1995) and these particulate materials play an important role in mediating rainfall-runoff and snowmelt chemistry since these solids often have high binding capacity for metal species. The sludge generated from rainfall-runoff and snowmelt BMP facilities can be high in various metals. During the last couple of decades landfilling has been found its application in urban solid waste disposal actions all over the world and is becoming an important strategy to treat sludge from BMPs. As a result, metals such as Cu, Zn, Cd and Pb are commonly detected in such landfills receiving a mixture of rainfall-runoff and snowmelt sludge. Under anaerobic processes common in many landfills metal species will be released from the
sludge residuals and become mobile under acidic and anaerobic (low redox potential) conditions. Predicting the rate at which these metals will bind to the landfill liner is an important topic along with knowing the binding capacity of the clay landfill liner materials. Since equilibrium studies do not convey information on reaction rates or reaction mechanisms, the kinetics and mechanisms of the binding reaction on clay liner materials must be fully understood to accurately predict the fate and mobility of metal species.

In the past two decades, numerous studies have been conducted on the kinetics of metal species surface reactions on natural materials and some of the results indicated that the chemical reactions of metal species on soil are rapid (Sparks and Jardine 1984, Roy et al. 1991, Juang and Chen 1997 and Raven et al. 1998). Numerous models have been developed to describe the relationship between the amount of metal species adsorbed and reaction time. Traditionally, the kinetics has been described by either first order reaction or second order reaction. Wu et al. (2001) investigated the binding of reactive dyes and Cu from water using chitosan. First order and second order models were tested with respect to the data. They found that the surface reactions for Cu could be best represented by the pseudo-second-order model. Ho and McKay (2001) developed a second order rate equation describing the surface reaction kinetics of Cu, Ni and Pb onto sphagnum moss peat. They correlated the equilibrium binding capacity with rate constant and initial binding rate. While ordered kinetics models have been used extensively to describe surface reactions onto natural materials, some other kinetic models also have been employed. For example, Schmitt et al. (2001) investigated the surface reaction kinetics of six metal ions, including Al, Zn, Hg, Pb, Cu and Cd onto living microalgae. They concluded that in most case the surface reaction rate could be described by using the equations of a Langmuir rate expression. The Elovich equation was another tool which has been used extensively to describe
the kinetics of surface reactions for various inorganic materials on soil (Chien and Clayton 1980) and resins (Juang and Chen 1997). These researchers found that the Elovich equation fit the experimental data well. Aside from these kinetic models, other successfully-applied models include parabolic diffusion model, power function and fraction-order model (Sposito 2000).

The applications of these kinetics models were valid only when the solid-phase medium (such as powder activated carbon, soil, clay or small resin particles) were small in particle size and thereafter the diffusion inside the solid-phase medium could be neglected. However, although these models were simple these models could not be used directly to model the reaction process onto granular activated carbon, large ion exchange resin, compacted clay or other large size solid-phase materials due to the existence of intra-particle mass transport. The kinetics of ion exchange resins has drawn the attention of researchers and the mechanisms of ion exchange kinetics have been investigated. Chiarle et al. (2000) presented the experimental and theoretical analysis of the binding of mercury onto ion exchange resins with the consideration of a diffusion resistance inside the solid resin. They concluded that the change in kinetics with the initial mercury concentration was a reflection of diffusion phenomena taking place inside the particles. Fernandez and Diaz (1995) studied the cationic and chelating ion exchange using the pore diffusion model and unreacted core model and fitted the experimental data obtained from K⁺ and Na⁺ exchange resins and metal and Na⁺ chelating resin systems. It was concluded that only the pore diffusion model was adequate to describe the K⁺ and Na⁺ ion exchange process while the chelating process could be represented by both the pore diffusion model and unreacted core model. Arevalo et al. (1998) concluded that experimental results obtained in an exchange system of Cu and Co with chelating resins at different concentrations for various Cu/Co ratios could be reasonably predicted by the shrinking-core model. In a similar way, the pore diffusion model was
also employed to predict the breakthrough of fix-bed reactor to remove Cu and Cd using bone char as adsorbent (Ko et al. 2001).

So far the kinetics study on the transport of metal species within compacted clay liner materials is relatively limited compared to those on the kinetics of metal species reactions onto uncompacted clays. Although there are researchers who applied mathematical models such as shrinking-core model to study the binding of contaminants onto activated carbon (Spahn and Schlunder 1975), bone char (Cheung et al. 2001) and ion exchange resins (Fernandez et al. 1995), little data on the diffusivities of metal species in the compacted clay liners is available. Such studies are important in the prediction of the fate of metal species in the landfill environment. As in the case of resin or granular activated carbon systems, the heterogeneous system of compacted landfill clay liner is also complicated by the simultaneous occurrence of molecular diffusion, complexation and exchange reaction. However, modeling of transport of metal species coupled with reactions within the compacted clay liner material is similar to that of the removal of contaminants using ion exchange resin or activated carbon. The compacted clay liner materials can also be described by the “homogeneous diffusion model” (Fernandez and Diaz 1995) and the mass balance will lead to a partial differential equation for the solid phase concentration. Knowledge of equilibrium reaction isotherm and kinetics is required so that the contaminant concentration profile in aqueous phase can be developed.

OBJECTIVES

The first objective of this research is to quantify the reaction of Cu, Zn, Cd and Pb, in the presence of Ca and Mg onto bentonite, kaolin or Amite soil. Isotherms will be developed for each material. Binding capacity of the solid phase is an important parameter in the expression of metal species reaction kinetics. The second objective is to test the applicability of several
The commonly used kinetic models such as first order reaction, second order reaction and Elovich equation to model the metal species binding onto clay liner materials. The best model to describe metal species binding onto clays will be decided based on the evaluation of goodness of fit. These results are useful in evaluating metal species fate and transport within compacted clay liners. The third objective is to investigate metal species binding onto compacted clay liner materials. Two different models, shrinking-core model and pore and surface diffusion model will be employed to model the reaction process. Metal species transport within the compacted clay liners will be evaluated and the diffusivities of the metal species within the compacted clay liners will be calculated.

**BACKGROUND**

**Kinetic Study on Uncompacted Clays**

While equilibrium models describe the attainment of equilibrium, they give no information regarding the time the reaction takes to reach the equilibrium. Typically, rate laws are first established and the experimental data was fitted so that the reaction order and date constants can be determined.

**First Order Reaction**

A simple kinetic analysis of binding is first order reaction equation which can be expressed as (Ho and McKay 1999):

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

where \(k_1\) is first order reaction constant (min \(^{-1}\)) and \(q_t\) and \(q_e\) are the amount of sorbate per unit mass of sorbent at time \(t\) and equilibrium (mg/g), respectively.

The integration of Eq. (1) yields:
\[
\ln(1 - \frac{q_t}{q_e}) = -k_1 t
\]  
(2)

**Second Order Reaction**

If binding rate is proportional to the square of the difference of \(q_e\) and \(q_t\), second order reaction is straightforward (Ho and Mckay 1999).

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]  
(3)

where \(k_2\) is second order reaction constant (g/min·mg). Upon rearrangement and integration,

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t
\]  
(4)

**Elovich Equation**

The Elovich equation was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surface (Low 1960). The Elovich equation is generally expressed as (Chien and Clayton 1980):

\[
\frac{dq_t}{dt} = \alpha_1 e^{-\beta t}
\]  
(5)

where \(\alpha_1\) and \(\beta\) are constants in a given experiment. To simply the Elovich equation, we assume \(\alpha_1 \beta t \gg 1\), Eq. (5) can be simplified to as:

\[
q_t = \frac{1}{\beta} \ln(\alpha_1 \beta) + \frac{1}{\beta} \ln t
\]  
(6)

**Kinetic Study on Compacted Clay Liners**

**Shrinking-core Model**

Metal species binding will be changed significantly if the solid phase such as the clay is compacted to form compacted clay liner materials. There exist simultaneous mass transfer and binding of metal species and these two processes have to be considered at the same time.
Therefore different models are needed to describe the binding of metal species in the compacted clay liner. The shrinking-core model is one of these models considering both mass transfer and species binding (Levenspiel 1972, Missen et al. 1999). Figure 6-1 is an illustration of an isothermal compacted clay liner cube illustrating the basis for the analysis using the shrinking-core model in this study. The essence of the shrinking-core model is that it is assumed that there is a sharp boundary (concentration front) between the reacted and unreacted regions (Missen et al. 1999). This assumption implies that within the compacted matrix when the metal species concentration in the pore fluid is greater than zero, the metal species bound per unit mass of solid phase is equal to that which is in equilibrium with the bulk concentration (Ruthven 1984). As time increases, the reaction concentration front moves progressively toward the center of the cube. The zone bound with metal species then moves into inwards, leaving behind completely reacted material. Consequently, the unreacted region shrinks. In addition to the assumption of the existence of a sharp concentration front, in this study the following approximations were also made. (1) No chemical precipitation occurs during the process of metal species transport within the compacted clay liner so that the decrease of metal ions in the pore water is due completely to reaction within the clay. (2) Clay particles and pores are homogeneously distributed and the structure of the compacted clay is assumed to be uniform. Therefore the internal surface area of the compacted clay was uniformly distributed throughout the compacted clay. (3) The external mass transfer resistance is damped greatly and became negligible when the size of the compacted clay liner cube is large, the pore dimensions of the liner are small and the solution is well-mixed. (4) The diffusion of metal species in the pore water within the compacted clay liner followed Fick’s law and the diffusivities for the metals in the compacted clay liner are constants.
Figure 6-1. The shrinking-core model for the experimental compacted clay liner cube. The adsorbed region is the area which is bound with metal species, unadsorbed region is the area where there is no metal species, control volume is used for the development of diffusion equation and concentration front is the boundary of adsorbed region and unadsorbed region. The volume of the beaker is 2 Liter and compacted clay cubes were used in the experiment.

The basis for the analysis using the shrinking-core model is shown in Figure 6-1. The diffusion of metal species ions in the pore water within the compacted clay liner cube is based on Fick’s law and can be expressed as the following equation (Cheung et al. 2001 and Spahn and Schlunder 1995).

\[
\frac{dN}{dt} = \frac{4DC_i}{\left(\frac{1}{x} - \frac{1}{a}\right)}
\]

(7)
In this expression \( \frac{dN}{dt} \) is metal species diffusion flux in the pore water (mg/s), \( D \) is diffusivity of metal species ion in the pore water within compacted clay liner (cm\(^2\)/s), \( C_t \) is metal species concentration in the bulk solution at time \( t \) (mg/L), \( x \) is one-half of the unadsorbed region dimension (cm) and “\( a \)” is one-half of the compacted clay liner cube dimension (cm).

At the same time, the velocity of the concentration front is obtained from the mass balance on the control volume (Spahn and Schlunder 1975).

\[
\frac{dN}{dt} = \frac{d[\rho_b q_e (8a^3 - 8x^3)]}{dt} = -24x^2 \rho_b q_e \frac{dx}{dt}
\]  

(8)

In this expression \( \rho_b \) is bulk density of compacted clay liner (g/cm\(^3\)).

The even amount of metal species bound per unit mass of compacted clay liner (\( q_t \)) can be equated with the following equation.

\[
q_t = q_e [1 - (\frac{x}{a})^3]
\]  

(9)

From a batch mode reaction experiment, \( q_t \) can also be calculated directly based on the following definition.

\[
q_t = \frac{V(C_0 - C_t)}{M}
\]  

(10)

In this expression \( V \) is the volume of metal species solution (L), \( C_0 \) is initial metal species concentration (mg/L) and \( M \) is the mass of compacted clay liner material (g).

Combining Eqs. (7), (8), (9) and (10), the following equation can be generated.

\[
\frac{DC_t}{C_0 - C_t} \frac{dt}{\frac{dC_t}{dt}} = -6\rho_b \frac{V}{M} \cdot \frac{a^2 x}{x^2 + ax + a^2} dx
\]  

(11)

Integration and rearrangement of Eq. (11) gives the following equation.
\[ D = 6\rho_b \frac{V}{M} \left[ \int_0^x \frac{a^2 x}{x^2 + ax + a^2} dx \right] \]

From Eq. (12) D is the slope of the straight line of \[ \frac{C_t}{C_t - C_0} \] against \[ \int_0^t \frac{C_t}{C_t - C_0} dt \]. Since \( C_t \) is a function of \( t \), \[ \int_0^t \frac{C_t}{C_t - C_0} dt \] can be calculated using numerical integration at different time. The values of \[ 6\rho_b \frac{V}{M} \int_0^x \frac{a^2 x}{x^2 + ax + a^2} dx \] at different time can also be determined by introducing the relationship between \( t \) and \( x \). To find this relationship, the relationship between \( C_t \) and \( x \) has to be established by inclusion of isotherm. Eq. (13) can be generated by combination of Eqs. (9) and (10).

\[ \frac{V(C_0 - C_v)}{M} = q_e \left[ 1 - \left( \frac{x}{a} \right)^3 \right] \]

The rearrangement of Eq. (13) yields the following equation.

\[ x = a \left( \frac{C_t - C_v}{C_0 - C_v} \right)^{\frac{1}{3}} \]

Therefore, the relationship between \( x \) and \( t \) can be developed by introducing the relationship between \( C_t \) and \( t \). In the above calculation, the integration must be carried out numerically. This was done through the discrete summation of differential areas.

**Pore and Surface Diffusion Model**

In order to develop the pore and surface diffusion model, the shrinking-core model assumptions and the assumption of Fickian diffusion of metal species from the compacted clay surface were employed. However, the hypothesis of sharp concentration front was excluded.
Based on Fick’s law the mass fluxes of pore water diffusion and surface diffusion can be expressed as the following equation.

\[ J_p = -D_p \frac{\partial c_{x,t}}{\partial x} \]  
(15)

\[ J_s = -D_s \frac{\partial q_{x,t}}{\partial x} \]  
(16)

In this equation \( J_p \) and \( J_s \) are mass fluxes of pore water diffusion and surface diffusion (mg/cm\(^2\)-s), respectively, \( c_{x,t} \) is metal species concentration in the pore water phase (mg/L), \( D_s \) and \( D_p \) are diffusivities of metal species ion on the adsorbent surface (g/s-cm) and in the pore water (cm\(^2\)/s) within compacted clay liner and \( q_{x,t} \) is the amount of metal species adsorbed per unit mass of adsorbent inside the compacted clay liner at location \( x \) and time \( t \) (mg/g).

Mass balance across a thin cubic shell at position \( x \) and thickness \( dx \) with the considerations of both the metal species diffusion in the pore water and on the clay surface can be written as the following equation.

\[ \rho_s dv \frac{\partial q_{x,t}}{\partial t} = -\frac{\partial (J_s S)}{\partial x} dx - \frac{\partial (J_p S)}{\partial x} dx \]  
(17)

In this expression, \( dv \) and \( S \) are volume (cm\(^3\)) and surface area (cm\(^2\)) of differential cubic shell of compacted clay liner. The volume and surface area of the differential cubic shell of the compacted clay can be written as \( 24x^2 \) and \( 24x \), respectively. Substitutions of these expressions together with Eqs. (15) and (16) into Eq. (17) yield the follow equation.

\[ \frac{\partial q_{x,t}}{\partial t} = D_{eff} \left( \frac{\partial^2 q_{x,t}}{\partial x^2} + \frac{2}{x} \frac{\partial q_{x,t}}{\partial x} \right) \]  
(18)

The boundary conditions are expressed in the following equations.

\[ q_{x,0} = 0 \quad \text{for all } x \]  
(19)
\[ \frac{\partial q_{b,t}}{\partial x} = 0 \text{ for all } t \]  \hspace{1cm} (20)

In this expression $D_{\text{eff}}$ is the effective overall diffusivity of metal species within the compacted clay liner (cm$^2$/s) and it can be defined as follows.

\[
D_{\text{eff}} = \frac{D_s}{\rho_b} + \frac{D_p}{\rho_b (dq_{x,t} / dc_{x,t})} \hspace{1cm} (21)
\]

It is convenient to define the following equation.

\[ D'_{s} = \frac{D_s}{\rho_b} \hspace{1cm} (22) \]

Therefore $D'_{s}$ has the dimension of cm$^2$/s which is comparable with $D_p$. $D_{\text{eff}}$ is composed of two components: surface diffusion and pore diffusion and the relative contributions of the surface diffusion and pore diffusion to the overall transport can be evaluated by calculating the ratio of $D'_{s}$ to $D_{\text{eff}}$ and $\frac{D_p}{\rho_b (dq_{x,t} / dc_{x,t})}$ to $D_{\text{eff}}$. From Eq. (21) $D_{\text{eff}}$ is constant only if the isotherm is a linear type. In most case, $D_{\text{eff}}$ is dependent on the metal species concentration which is a function of both the position and time throughout the compacted clay liner. If a Freundlich isotherm can be used to characterize binding equilibrium, Eq. (21) can be written as the following equation.

\[
D_{\text{eff}} = D'_{s} + \frac{D_p}{\rho_b n k^n q_{x,t}^n} \hspace{1cm} (23)
\]

In this expression $k$ and $n$ are Freundlich constants, respectively. Typically, numerical solutions have to be employed to solve Eq. (18). The numerical solution includes the iteration calculation with the initial input of estimate.

An approximation solution to Eq. (18) can be obtained by assuming that $D_{\text{eff}}$ is a constant. This simplification is equivalent to setting an average value of $D_{\text{eff}}$ as a best fit of the
experimental data. This simplification can be valid when the isotherm is reasonably linear since the slope of the isotherm is relatively constant. Ruthven (1976) suggested that the value of effective diffusivity is a constant as long as the binding experiment was carried out over a small concentration step. An average effective diffusivity over the concentration range $0 < q < q_0$ was proposed to replace $D_{eff}$ in Eq. (18) so that the solution of this equation could be simplified. The average diffusivity is defined as the following equation (Yoshida et al. 1994).

$$\overline{D}_{eff} = \frac{1}{q_0} \int_0^{q_0} D_{eff} dq$$  \hspace{1cm} (24)

In this expression $\overline{D}_{eff}$ is average effective diffusivity (cm$^2$/s) and $q_0$ is metal species adsorbed per unit mass of clay at equilibrium with initial metal species concentration (mg/g). The substitution of Eq. (23) into Eq. (24) yields the following equation.

$$\overline{D}_{eff} = D_s \cdot \frac{D_p}{\rho_v k} C_0^{1-n}$$  \hspace{1cm} (25)

Crank (1975) presented a solution to Eq. (18) when $D_{eff}$ is constant and the binding was conducted in a well-stirred solution of volume of $V$, assuming the initial solute concentration was $C_0$. The result is shown in Eq. (26).

$$\frac{q_t}{q_c} = 1 - \sum_{n=1}^{\infty} \frac{\alpha}{6}(\alpha + 1) \exp(-\overline{D}_{eff} q_n^2 t / a^2)$$  \hspace{1cm} (26)

In this expression $\alpha$ is obtained by the ratio which is expressed in Eq. (27) (Guibal et al. 1998).

$$\alpha = \frac{C_c}{C_0 - C_c}$$  \hspace{1cm} (27)

In this expression $C_c$ is bulk equilibrium concentration of metal species (mg/L) and $q_n$ is the non-zero root of Eq. (28).
\[ \tan q_n = \frac{3q_n}{3 + \alpha a q_n - \frac{1}{2}} \]  

(28)

The metal species concentration in the pore water phase within compacted clay liners is given by the following equation.

\[ c_{x,t} = C_e \left[ 1 + \sum_{n=1}^{\infty} \frac{6(1 + \alpha) \exp(-\overline{D_{\text{eff}}} q_n^2 t / a^2) \cdot a \cdot \sin(q_n x / a) \cdot x \cdot \sin q_n}{9 + 9\alpha + q_n^2 \alpha^2} \right] \]  

(29)

Eq. (26) was used to determine \( D_{\text{eff}} \) which was best fit to the experimental data by minimizing the sum of the square of the differences between the experimental and calculated data. Therefore, \( D_{\text{eff}} \) was adjustable in this procedure applied by other researchers (Cheung et al. 2001, Guibal et al. 1998). The values of \( D_s \) and \( D_p \) in Eq. (25) can be obtained by evaluation of the different species metal concentrations.

**METHODOLOGY**

**Isotherm Study**

Isotherms were obtained in batch-type experiments using 50-mL polypropylene centrifuge tubes. 200 mg of bentonite, 400 mg of kaolin or 400 mg of Amite soil were equilibrated with 40 mL of metal solutions with different concentrations for 24 h at room temperature using a reciprocating shaker. The metal solutions were obtained by diluting 1000 mg/L metal species stock solutions of Cu(NO₃)₂, Zn(NO₃)₂, Cd(NO₃)₂ and Pb(NO₃)₂. The initial concentrations were 5, 10, 15, 20, 25, 30 and 35 mg/L for each metal species including Cu, Zn, Cd and Pb. In order to evaluate the effects of Mg and Ca, two commonly detected metals in leachate, on the binding performance, Mg(NO₃)₂ and Ca(NO₃)₂ were also added so that Mg and Ca concentrations were kept at 10 and 200 mg/L in the experiment. NaNO₃ was used as background electrolyte and the ionic strength was kept at 0.01 M throughout the experiment (Lee
et al. 1996, Sansalone et al. 1998). The initial pH values were adjusted to 3.5 so that the equilibrium pH values were maintained at 5.5. After equilibration, the solution was separated from the clay by a syringe membrane filter (cellulose, 0.45 μm) and 0.1 or 0.2 mL of the filtered solution was removed and acidified with 10 % trace metal HNO₃ for ICP-MS analysis. The amount of adsorbed metal species was calculated as the difference between the amount added initially and that remaining in solutions. The experiments were run in duplicates.

**Compaction of the Clay**

The optimum moisture contents of the three clay liner materials were determined elsewhere and the three clay liner materials were compacted with the optimal moisture contents: 41%, 31% and 16% for bentonite, kaolin and Amite soil, respectively.

The mold for the fabrication of compacted clay liner was 19 cm in diameter, 31 cm in height and 2.43 L in volume. The moist clay with the optimum water content was poured into the mold in 8 equal layers. Each layer had been compacted uniformly by the Standard Proctor hammer 112 times before the next layer of loose clay was poured into the mold. The compaction energy (593 kJ/cm³) was kept the same as that in the standard proctor (ASTM D698).

After the compaction of clay material was finished, small clay pieces were cut carefully and these small clay pieces were used in the kinetic study.

**Kinetic Study**

The kinetic study consisted of two parts, the binding of metal species onto uncompacted and compacted clay liner materials. Batch mode experiments were chosen to characterize the binding kinetics for both parts since batch studies were convenient for the determination of the binding kinetic parameters such as diffusion coefficient (Robinson et al. 1994). Batch tests also simplify the mathematical models because the external film mass transfer resistance was
negligible at high mixing speeds. In the first experimental part, 5 g of bentonite or 10 g of kaolin or Amite soil was added into a 2-liter beaker containing 1000 ml of metal species solutions. In the second experimental part, 5 g of compacted bentonite liner materials, and 10 g of compacted kaolin and Amite soil liner materials were netted in a small nylon mesh and soaked in D.I. water for 5 days, to ensure the degree of saturation with water was 100%. The water-saturated compacted clay cubes were then transferred to and suspended in 1000 ml of a well-mixed aqueous solution containing a metal species in the beaker. The dimensions of the three types of compacted clay liner cubes were 1.7 cm × 1.7 cm × 1.7 cm for bentonite, 1.0 cm × 1.0 cm × 1.0 cm for kaolin and 1.9 cm × 1.9 cm × 1.9 cm for Amite soil. The masses of the three cubes were equivalent to those of the clays applied in the first experimental part that consisted of uncompacted clay. By doing this, the behavior of metal species bound onto uncompacted and compacted clays could be compared and evaluated on an equal mass basis. Two different initial concentrations were tested. In the first experimental part, the initial concentration was 10 mg/L for each metal Cu, Zn, Cd and Pb. In the second experimental part, the initial concentrations consisted of 5 and 10 mg/L for Cu, Zn, Cd and Pb, respectively. Mg and Ca concentrations were kept at 10 and 200 mg/L in the two experimental parts. The solution was stirred with a magnetic stirring bar and the solution was well mixed. Time zero began upon the introduction of clay liner materials into the solution. At different time intervals, approximately 5 mL of sample was taken and fractionated using a syringe membrane filter (cellulose, 0.45 µm) to separate clay materials from metal species solution so that the reaction can be stopped quickly. The first experimental run lasted 500 minutes (uncompacted clay) while the experiments of metal species binding for compacted clays continued for up to 15 days. The beakers were sealed with parafilm during the experiments to prevent the evaporation of water. The values of pH of the solutions were kept at
5.5 by adding NaOH or HCl throughout the experiment. Each experiment was duplicated under identical experimental conditions.

**Elemental Analysis**

The concentrations of metal species were analyzed using ICP-MS. Five-point calibration was employed to construct the standard curve. The concentrations of the standard solution used included 0, 10, 20, 100 and 500 µg/L. The measuring conditions were 100 ms dwell time, 50 sweeps/reading and 3 replicates for each sample. The internal standard was Rh which was pumped into the plasma with the sample, giving a concentration of 10 mg/L. The elements were measured at m/z values of 63 for Cu, 64 for Zn, 114 for Cd and 208 for Pb. QA/QC included checking a standard solution with concentration of 50 µg/L for each metal every 10 samples. Check samples (50 µg/L) were evaluated to ensure that the measured value was within 45 to 55 µg/L for each metal.

**Numerical Technique**

The integrations in the shrinking-core model were performed numerically. In the pore and surface diffusion model, Eq. (26) which is an approximate solution to Eq. (18) was solved numerically. Eq. (28) was first solved to obtain values of q_n before Eq. (26) can be solved. Eq. (28) had infinite numbers of solution and it was solved by assuming the existence of period for q_n series when q_n was large enough. q_1, q_2, \ldots, q_n were obtained and these q_n values were utilized to calculate the expression \[
\sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + q_n^2\alpha^2}.
\] The calculation of q_n was stopped when the summation of \[
\sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + q_n^2\alpha^2}
\] was greater than 0.998. The values of q_n obtained were
substituted into Eq. (26) to solve $D_{\text{eff}}$. $D_{\text{eff}}$ was adjusted until the minimum value of the sum of the squares of the errors was obtained. The calculation of SE is calculated using Eq. (30).

$$SE = \sqrt{\frac{\sum(q_{t,\text{exp}} - q_{t,\text{mod}})^2}{m-1}}$$  (30)

In this expression SE stands for standard error of estimate, $q_{t,\text{exp}}$ and $q_{t,\text{mod}}$ are experimental binding capacity and theoretical binding capacity based on different kinetic models and $m$ is the number of experimental data. This technique of parameter estimation was employed extensively by Guibal et al. (1998) and Cheung et al. (2002).

The estimations of $D_p$ and $D_s$ were carried out in a similar way by minimizing the sum of the squares of the errors between the experimental and theoretical binding data and Eq. (30) was used to evaluate the discrepancies between the experimental and modeling data.

RESULTS AND DISCUSSION

Isotherm

Equilibrium study of metal species binding onto the uncompacted clay liner materials with the presences of Mg and Ca had been previously investigated before the kinetic study was carried out. The equilibrium study provided information on the binding reaction limits. Figure 6-2 is an illustration of isotherms of metal species binding onto the clay liner materials. Figure 6-2 reveals that Freundlich isotherm was a good model to represent the binding process. The Freundlich can be expressed as Eq. (31).

$$q_e = kC_e^n$$  (31)

In this equation, $q_e$ is binding density defined as mass of metal species bound per unit mass of clay, $C_e$ is equilibrium concentration of metal species and $k$ and $n$ are constants which can be determined experimentally.
Figure 6-2. Isotherms of metal species onto uncompacted clay liner materials with the presence of 10 mg/L of Mg and 200 mg/L of Ca in solution. pH was kept at 5.5 and the dosage for bentonite, kaolin and Amite soil were 4 g/L, 8 g/L and 8 g/L, respectively.
Kinetics of Metal Species Binding on Uncompacted Clays

Figure 6-3 illustrates that metal species concentration decreases as the results of binding onto uncompacted clays as a function of time. It can be seen from the figure that typically, the binding processes were initially rapid; and further reduction in metal species concentrations continue at a decreasing rate and eventually approach a constant equilibrium concentration. Metal species bound onto the clays could take place and approach equilibrium state within short period of time scale. For example, the binding of the four metal species Cu, Zn, Cd and Pb onto uncompacted bentonite was so rapid that the equilibrium could be reached within 25 minutes. The binding of Pb onto uncompacted Amite soil was also very fast, requiring about 20 minutes to reach 97% of equilibrium. Although the binding of the four metal species onto uncompacted kaolin and Cu, Zn and Cd onto Amite soil were slower compared to those onto bentonite, 500 minutes was sufficient to equilibrate the metal species with the dispersed uncompacted clays.

Past studies have indicated that binding reaction on some clay materials could even occur on time scale of seconds or even milliseconds (Sparks 1999). The rapid rates of metal species binding onto clay materials may in large part be due to the availability of binding sites (Sparks 1998).

Several kinetics models, including first order reaction, second order reaction and Elovich equation, were employed to model the metal species binding onto bentonite, kaolin and Amite soil. The validities of the different models were tested by plotting ln(1-q_t/q_e) vs t, 1/(q_e-q_t) vs t and q_t vs ln(t), respectively. The goodness of fitting was evaluated based on R^2 of simple linear regression and the standard error of estimate (SE) which is expressed as Eq. (30) (Chen and Clayton 1979). The values of q_e used in the kinetic modeling were obtained from the previous isotherm study.
Figure 6-3. Metal species binding onto uncompacted clay liner materials as a function of time. The initial metal concentrations were 10 mg/L for Cu, Zn, Cd and Pb with the presence of 10 mg/L of Mg and 200 mg/L of Ca. pH value was kept at 5.5.
Table 6-1. Kinetic parameters, coefficients of determination ($R^2$) for fit of listed models with metal species data on uncompacted clays.

<table>
<thead>
<tr>
<th></th>
<th>First Order Reaction</th>
<th></th>
<th>Second Order Reaction</th>
<th></th>
<th>Elovich Equation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (h$^{-1}$)</td>
<td>$R^2$</td>
<td>SE (mg/g)</td>
<td>$k_2$ [g/(mg⋅h)]</td>
<td>$R^2$</td>
<td>SE (mg/g)</td>
</tr>
<tr>
<td>Bentonite</td>
<td>30.66</td>
<td>0.944</td>
<td>$9.58 \times 10^{-2}$</td>
<td>3346.2</td>
<td>0.617</td>
<td>$7.38 \times 10^{-1}$</td>
</tr>
<tr>
<td>Kaolin</td>
<td>0.39</td>
<td>0.984</td>
<td>$5.63 \times 10^{-3}$</td>
<td>21.46</td>
<td>0.899</td>
<td>$2.95 \times 10^{-2}$</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>0.834</td>
<td>0.983</td>
<td>$2.32 \times 10^{-2}$</td>
<td>175.2</td>
<td>0.807</td>
<td>$2.99 \times 10^{-1}$</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
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<td>Zn</td>
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<td>Pb</td>
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</table>

First order reaction: \( \ln(1 - \frac{q_t}{q_e}) = -k_1t \)

Second order reaction: \( \frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \)

Elovich equation: \( q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \)

\( k_1 \): first order reaction constant (min$^{-1}$)
\( q_t \): the amount of metal species per unit mass of clay at time t (mg/g)
\( q_e \): the amount of metal species per unit mass of clay at equilibrium (mg/g)
\( k_2 \): second order reaction constant (g/mg⋅h)
\( t \): reaction time (min)
\( \alpha \) and \( \beta \): constants in a given experiment in Elovich equation

The modeling results are summarized in Table 6-1. It can be seen from Table 6-1 that first order reaction model is the best of the various equations to represent the metal species binding onto clay materials since this model typically generated the smallest values of SE and the highest values of $R^2$. At the same time, it seems that Elovich equation can also describe the binding of Cu on Amite soil and the binding of Pb on kaolin and Amite soil given the high values of $R^2$ or low values of SE. However, it should be realized that Elovich equation is only applicable within
a range of experimental condition since when $t$ tends to infinite, $q_t$ is also infinite. This is impossible because thermodynamically when $t \to \infty$, $q_t$ approaches $q_e$. Therefore, special caution must be taken when modeling metal species transport within compacted clay liner since this process can take longer period of time. Table 6-1 also indicates that second order reaction model is not a suitable model to predict metal species binding onto uncompacted clay liner materials since the modeling results were low in $R^2$ and high in SE. The modeling results of the first order reaction are presented in Figure 6-4. Based on the kinetic parameters determined, it is concluded that the metal species binding rate follows the order of $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$ and bentonite $> \text{Amite soil} > \text{kaolin}$. It also seems that the binding of Pb onto clays and the binding of metal species onto bentonite have much higher rates than other clays.

**Kinetics of Metal Species Binding onto Compacted Clays**

Figure 6-5 illustrates metal species concentration decrease in aqueous solution as a function of time when the compacted clay cubes were in contact with the well-mixed aqueous of metal species. Metal species concentrations in the leachate decreased steadily as a function of time over a much larger period of time (days as opposed to hours as compared to the uncompacted clays) when compacted clays were used as binding medium. Results indicate that adsorption rate differences between metal species were less pronounced for compacted clays (with the exception of Pb) than for the uncompacted clays. For example, although aqueous Pb concentrations decreased much faster than Cu, Zn and Cd when uncompacted Amite soil was used as a binding medium, these differences were small when compacted Amite soil cubes were employed in the binding tests. It also appears that the intrinsic binding rate constants had a minor effect on the rate of binding onto compacted clay. Since the uncompacted dispersed clays were very small in size (individual clay particle), there was likely little mass transfer resistance and
Figure 6-4. First order reaction model fit of measured data for the binding of metal species on uncompacted clays. The initial metal concentrations were 10 mg/L for Cu, Zn, Cd and Pb with the presence of 10 mg/L of Mg and 200 mg/L of Ca. pH value was kept at 5.5.
Figure 6-5. Metal species binding onto compacted clay liner materials as a function of time. The initial metal concentrations were 5 and 10 mg/L, respectively for Cu, Zn, Cd and Pb with the presence of 10 mg/L of Mg and 200 mg/L of Ca. pH value was kept at 5.5. Ionic strength was 0.01 N NaNO₃. The dry densities of the compacted bentonite, kaolinite and Amite soil were 1.71, 1.39 and 1.94 g/cm³, respectively.
metal species had access to the binding sites. Therefore, binding process was very fast if metal species were adsorbed by uncompacted clays. On the other hand, the binding of metal species on compacted clay materials could be slow, tortuous and mass transfer controlled. The finding that slower reactions at the clay-water interface can be examined by diffusion models indicates that the kinetics of metal species binding onto compacted clays cannot be considered separately from transport phenomena. Although the same mass of clay was used as adsorbents in both compacted and uncompacted experiments, metal species binding rates were significantly decreased when compacted clays were involved. When metal ion transport is the rate-controlling step of binding onto compacted clay, it could be regarded that the binding reaction occurred virtually instantaneously as compared to the transport of metal ions from the bulk of the solution phase to the location where binding occurs (Yiacoumi and Tien 1995).

To better understand the processes of metal species binding onto compacted clay liners and to predict metal species transports through engineered landfill clay liners, two different models, including shrinking-core model and pore and surface diffusion model, were tested to model the experimental data and to determine kinetic parameters. The mathematical modeling could be simplified by ignoring external film diffusion which could be eliminated or diminished significantly since the metal species solution was well-mixed in the presence of the clay materials (Ogwada and Sparks 1986). In a well-mixed system, the binding reaction rate coefficient obtained is considered as approximating the reaction-controlled rate constant (Sparks 1988).

The shrinking-core model diffusivities of Cu, Zn, Cd and Pb within the compacted clay liner materials were calculated through Eq. (12) and approximating the slope of the data using a best fit regression. Figure 6-6 illustrates the determination of the diffusivities (as slopes) and the
resulting diffusivities are tabulated in Table 6-2. Figure 6-6 indicates that typically there were only small changes in the diffusivities at different initial metal species concentrations. In this study, these small changes were ignored and the data obtained at two different initial concentrations were pooled and one single linear regression of the slope was applied for each metal species and clay liner material. It can be seen from the table that individually, Cu, Zn, Cd and Pb had different values of diffusivity and application of different solid phase resulted in different diffusivity values. The diffusivities within Amite soil could be an order of magnitude lower than those within bentonite and kaolin. Although bentonite and kaolin had comparable values of diffusivities, bentonite had slightly higher values of diffusivity than kaolin.

The ratios of effective diffusivities within compacted clay liner obtained in this research were on the order of 10^{-5}-10^{-4} times of that of diffusivities in the bulk solution. Other studies documented similar values. For example, diffusivities as low as 10^{-7} – 10^{-10} cm²/s were reported by Findon et al. (1993) and Guibal et al. (1998). These values were 1 to 4 orders of magnitude lower than diffusivities in pure water which are in the order of 10^{-6} cm²/s (Lide 1996). D can be regarded as a function of the free water diffusion coefficients and the physical properties of the solid matrix (Choy and Deible 2000). It was suggested that D could be expressed as the following equation (Cheung et al. 2001).

\[ D = D_f \frac{\varepsilon}{\tau} \]  

In this expression, \( D_f \) is the free water diffusivity (cm²/s), \( \varepsilon \) is the porosity of the adsorbent and \( \tau \) is the factor representing the tortuosities of the flow path. If the porosity of 0.5 is assumed (Li and Wu 1999), the value of \( \tau \) should be in the range of 10¹ – 10⁴.

Intraparticle diffusivities, \( D_{eff} \), at two different initial concentrations in the pore and surface diffusion model were also estimated by matching the predictions of the models to the
Figure 6-6. Determination of diffusivities in the shrinking-core model (1). A stands for the expression \[ 6\rho_b V \int_a^x \frac{a^2 x}{x^2 + ax + a^2} dx \] while B represents \[ \int_0^t \frac{C_t}{C_t - C_0} dt. \] \( \rho_b \) is bulk density of compacted clay liner (g/cm\(^3\)), \( V \) is volume of metal species solution (L), \( M \) is mass of compacted clay (g). \( a \) is half of the size of the compacted clay liner cube (cm), \( C_t \) and \( C_0 \) are metal concentrations (mg/L) at time zero and \( t \) (d), respectively. pH value was kept at 5.5. Ionic strength was 0.01 N NaNO\(_3\). The dry densities of the compacted bentonite, kaolin and Amite soil were 1.71, 1.39 and 1.94 g/cm\(^3\), respectively.
Figure 6-7. Determination of diffusivities in the shrinking-core model (2). A stands for the expression $6 \rho_b \frac{V}{M} \int \frac{a^2}{x^2 + ax + a^2} dx$ while B stands for $\int C_t - C_0 \frac{t}{C_t - C_0} dt$. $\rho_b$ is bulk density of compacted clay liner (g/cm$^3$), V is volume of metal species solution (L), M is mass of compacted clay (g). a is half of the size of the compacted clay liner cube (cm), $C_t$ and $C_0$ are metal concentrations (mg/L) at time zero and t (d), respectively. pH value was kept at 5.5. Ionic strength was 0.01 N NaNO$_3$. The dry densities of the compacted bentonite, kaolin and Amite soil were 1.71, 1.39 and 1.94 g/cm$^3$, respectively.
experimental data. The values of $D_p$ and $D_s$ were determined by solving two Eqs. (25) simultaneously which were obtained at two different initial concentrations. The calculated values of diffusivities are tabulated in Table 6-2. The relative contribution of surface diffusion and pore diffusion are summarized in Figure 6-8. There are two different diffusivities in this model and it was found that the diffusivities in the pore water phase ($D$ and $D_p$) were in the same order of magnitude as those in the shrinking-core model. These similarities were not surprising since both $D$ and $D_p$ were reflections of metal species transport in pore water within the compacted clay cubes. However the values of $D_s$ or $D_s'$ were significant different from those of $D_p$. Results were one order of magnitude lower while the others were one or two orders of magnitude higher than those of $D_p$. The relative importance of pore and surface diffusion for the metal species within the compacted clays can be assessed by comparing their contributions to $\bar{D}_{\text{eff}}$.

The degrees of the contribution of the pore and surface diffusion are summarized in Figure 6-8 and the calculations were based on Eq. (25). In the calculation, the relative importance of surface and pore diffusion were defined as the ratio of the first and second terms of the right side of Eq. (25) to $\bar{D}_{\text{eff}}$, respectively. Figure 6-8 indicates that the pore and surface diffusion contributed differently to the transport of metal species within the different compacted clays. For bentonite, pore diffusion was the dominant mechanism while for kaolin surface diffusion was more important than pore diffusion. Amite soil behaved differently from both bentonite and kaolin since pore and surface diffusion were equally important for metal species transport.

The fittings of the theoretical results to the experimental data using the two different models are shown in Figures 6-9. It can be seen from the figure that the two models resulted in very similar curves and both of these two models could describe the binding process for the
Table 6-2. Diffusivities of metal species within compacted clays and standard error of estimate based on the different models.

<table>
<thead>
<tr>
<th></th>
<th>Shrinking-core Model</th>
<th>Pore and Surface Diffusion Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D (cm²/s)</td>
<td>SE (mg/g)</td>
</tr>
<tr>
<td>Bentonite Cu</td>
<td>9.48x10⁻¹⁰</td>
<td>4.45x10⁻²</td>
</tr>
<tr>
<td>Kaolin</td>
<td>4.73x10⁻¹⁰</td>
<td>4.92x10⁻³</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>5.49x10⁻¹¹</td>
<td>2.55x10⁻³</td>
</tr>
<tr>
<td>Bentonite Zn</td>
<td>6.02x10⁻¹⁰</td>
<td>1.30x10⁻²</td>
</tr>
<tr>
<td>Kaolin</td>
<td>4.80x10⁻¹⁰</td>
<td>1.51x10⁻³</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>5.68x10⁻¹¹</td>
<td>2.31x10⁻³</td>
</tr>
<tr>
<td>Bentonite Cd</td>
<td>5.35x10⁻¹⁰</td>
<td>9.69x10⁻³</td>
</tr>
<tr>
<td>Kaolin</td>
<td>3.31x10⁻¹⁰</td>
<td>2.21x10⁻¹⁰</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>3.18x10⁻¹¹</td>
<td>1.95x10⁻³</td>
</tr>
<tr>
<td>Bentonite Pb</td>
<td>12.87x10⁻¹⁰</td>
<td>6.72x10⁻²</td>
</tr>
<tr>
<td>Kaolin</td>
<td>9.62x10⁻¹⁰</td>
<td>4.84x10⁻¹⁰</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>8.22x10⁻¹¹</td>
<td>3.06x10⁻³</td>
</tr>
</tbody>
</table>

Shrinking-core model: \( D = 6 \rho_b \frac{V}{M} \int_a^b \frac{a^2 x}{x^2 + ax + a^2} dx \int_0^t \frac{C_t - C_0}{C_t - C_0} dt \)

Pore and surface diffusion model: \( \frac{\partial q_{x,t}}{\partial t} = D_{eff} \left( \frac{\partial^2 q_{x,t}}{\partial x^2} + \frac{2}{x} \frac{\partial q_{x,t}}{\partial x} \right), \quad D_{eff} = \frac{D_s}{\rho_b} + \frac{D_p}{\rho_b \left( dq_{x,t} / dc_{x,t} \right)} \)

\( D_s' = D_s, \quad D_{eff} = D_s' + \frac{D_p}{\rho_b n k^{1/2} q_{x,t}^{n-1/2}} \)

\( x = a\left( \frac{C_t - C_e}{C_0 - C_e} \right)^{1/3} \)

D: diffusivity of metal species ions in the pore water within compacted clay liner in the shrinking-pore model (cm²/s)

\( D_{eff} \): effective overall diffusivity of metal species within the compacted clay liner (cm²/s)

\( D_s \): diffusivity of metal species ion on the adsorbent surface within compacted clay liner (g/s·cm)

\( D_p \): diffusivity of metal species ion in the pore water within compacted clay liner (cm²/s)

\( q_{x,t} \): the amount of metal species per unit mass of clay at time t and position x (mg/g)

Even if the effective overall diffusivity in Eq. (18) is concentration dependent, the assumption of a constant diffusivity was still an acceptable approximation during the concentration range.
investigated in this research. Douglas (1984) found that this assumption was valid provided that the solid-phase uptake curve was measured over a small change in adsorbed phase concentration.

Figure 6-8. The relative importance of pore and surface diffusion for the metal species transport within the compacted clays. $D_{\text{eff}} = D_s' + \frac{D_p}{\rho_b k} C_0^{1-n}$. $D_s'$ and $\frac{D_p}{\rho_b k} C_0^{1-n}$ represent surface and pore diffusion, respectively. $D_s'$ is $D_s/\rho_b$ (cm$^2$/s), $D_s$ is diffusivity of metal species ion on the adsorbent surface within compacted clay liner (g/s·cm), $\rho_b$ is bulk density of compacted clay (g/cm$^3$), $D_p$ is diffusivity of metal species ion in the pore water within compacted clay liner(cm$^2$/s), $C_0$ is initial metal concentration (mg/L), $k$ and $n$ are Freundlich constants.
Figure 6-9. Modeled and measured data of metal species adsorption for compacted bentonite. The shrinking-core model is represented by the dashed curves while solid curves represent the pore and surface diffusion model. The Mg and Ca concentrations were 10 and 200 mg/L, respectively, pH was kept at 5.5 and ionic strength was 0.01 N NaNO₃. The bulk density of compacted bentonite was 1.71 g/cm³.
Figure 6-10. Modeled and measured data of metal species adsorption for compacted kaolin. The shrinking-core model is represented by the dashed curves while solid curves represent the pore and surface diffusion model. The Mg and Ca concentrations were 10 and 200 mg/L, respectively, pH was kept at 5.5 and ionic strength was 0.01 N NaNO₃. The bulk density of compacted kaolin was 1.39 g/cm³.
An empirical equation to describe metal species binding with diffusional resistance is provided in Eq. (33) (Guibal et al. 1998).

\[ q_t = a_0 + b_0 \sqrt{t} \]  

In this expression, \( q_t \) is in unit of mg/g, \( a_0 \) is a constant which is a reflection of the boundary layer diffusion (external film resistance) and is proportional to the boundary layer thickness while \( b_0 \) is also a constant which is related to the intraparticle diffusion. Both \( a_0 \) and \( b_0 \) could be...
determined experimentally. When the external mass transfer resistance is negligible Eq. (33) is reduced to a straight line through origin.

Figures 6-12 to 6-14 are depiction of metal species binding varying as a function of $t^{0.5}$. Results demonstrate a good linearity between $q_t$ and $t^{0.5}$ during the time interval investigated (up to 15 days). Eq. (33) is an empirical expression and caution should be used when applying this equation to predict metal species transport. Eq. (33) can reasonably model the initial stages of metal species binding and results would begin to deviate from the model for large times. $q_t$ tends to be infinite when $t$ approaches infinity based on Eq. (33) and this is not correct.

Figure 6-12. Plots of $q_t = a_0 + b_0 \sqrt{t}$ (solid lines) with respect to measured data for compacted bentonite. $a_0$ and $b_0$ are empirical constants which can be determined experimentally. The Mg and Ca concentrations were 10 and 200 mg/L, respectively, pH was kept at 5.5 and ionic strength was 0.01 N NaNO$_3$. The bulk density of compacted bentonite was 1.71 g/cm$^3$. 

$$C_0 = 10 \text{ mg/L}, \quad q_t = 0.158t^{0.5}$$
$$R^2 = 0.897$$

$$C_0 = 5 \text{ mg/L}, \quad q_t = 0.143t^{0.5}$$
$$R^2 = 0.914$$

$$C_0 = 10 \text{ mg/L}, \quad q_t = 0.094t^{0.5}$$
$$R^2 = 0.964$$

$$C_0 = 5 \text{ mg/L}, \quad q_t = 0.039t^{0.5}$$
$$R^2 = 0.986$$

$$C_0 = 10 \text{ mg/L}, \quad q_t = 0.078t^{0.5}$$
$$R^2 = 0.989$$

$$C_0 = 5 \text{ mg/L}, \quad q_t = 0.031t^{0.5}$$
$$R^2 = 0.855$$

$$C_0 = 10 \text{ mg/L}, \quad q_t = 0.315t^{0.5}$$
$$R^2 = 0.966$$

$$C_0 = 5 \text{ mg/L}, \quad q_t = 0.282t^{0.5}$$
$$R^2 = 0.981$$
Figure 6-13. Plots of $q_t = a_0 + b_0 \sqrt{t}$ (solid lines) with respect to measured data for compacted kaolin. $a_0$ and $b_0$ are empirical constants which can be determined experimentally. The Mg and Ca concentrations were 10 and 200 mg/L, respectively, pH was kept at 5.5 and ionic strength was 0.01 N NaNO₃. The bulk density of compacted kaolin was 1.39 g/cm³.
Figure 6-14. Plots of $q_t = a_0 + b_0 \sqrt{t}$ (solid lines) with respect to measured data for compacted Amite soil. $a_0$ and $b_0$ are empirical constants which can be determined experimentally. The Mg and Ca concentrations were 10 and 200 mg/L, respectively, pH was kept at 5.5 and ionic strength was 0.01 N NaNO$_3$. The bulk density of compacted Amite soil was 1.94 g/cm$^3$.

CONCLUSIONS

Different kinetic models were employed to investigate metal species binding kinetics with the presences of Mg and Ca onto clay liner materials. These materials serve as reactive barriers to separate the underground environment from landfill receiving sludge produced from rainfall-runoff and snowmelt residuals. Results indicate that the behavior of metal species binding with uncompacted clays was completely different compared to compacted clays. The binding of metal species with uncompacted dispersed clay was a very fast process which could
be accomplished within several hours. Several kinetics models, including a first order reaction, second order reaction and Elovich equation, were tested to model the binding process. It was confirmed that the experimental data could be best approximated by a first order reaction. Based on the parameters determined, it was found that metal species binding rates follow the order of Pb > Cu > Zn > Cd and bentonite > Amite soil > kaolin. On the other hand, the binding of metal species with compacted clay was a very slow process due to the existence of internal mass transport limitation within the compacted clays. This process might take many days or even longer. Although the binding order of metal species did not change, the reaction rate order of clays followed bentonite > kaolin > Amite soil. Metal species binding with compacted Amite soil was a slower process compared to those with bentonite and kaolin. This phenomenon was caused by the smallest intraparticle diffusivities of metal species within compacted Amite soil. A shrinking-core model and pore and surface diffusion model were used to simulate metal species binding with compacted clays. The pore water diffusivities of Cu, Zn, Cd and Pb were on the order of $10^{-10}$ cm$^2$/s for bentonite and kaolin and $10^{-11}$ cm$^2$/s for Amite soil. Simplified mathematical models assuming the diffusivities in the pore water and adsorbent surface were independent of concentration could be used to model the experimental data reasonably well. The analysis of the relative importance of pore and surface diffusion indicated that pore diffusion was the dominant mechanism within compacted bentonite, surface diffusion was the principal mechanism within compacted kaolin and pore and surface diffusions were equally important within compacted Amite soil.

It is hypothesized that diffusivity differences for different clays were due in part to the different texture, tortuosity and different optimum moisture contents for compaction. The optimum moisture contents (ASTM D698) of the clays were 41%, 31% and 16% for bentonite,
kaolin and Amite soil, respectively. The dry density of each clay was 1.71, 1.39 and 1.94 g/cm$^3$ for compacted bentonite, kaolin and Amite soil, respectively. The tortuosity was regarded as a geometric factor which accounted for a longer diffusion path through randomly oriented pores that through a straight cylindrical pore (Robinson et al. 1994).

The shrinking-core model is an ideal model since the boundary between the adsorbed and unadsorbed regions would tend to be blurred in the real case. If this ambiguity is significant, a more general model may be required.

An empirical equation was also evaluated and the result indicated that there was a linear relationship between metal species binding and the square root of time during the time interval investigated.

REFERENCES


ASTM D698. (1988) “Standard test methods for moisture-density relations of soils and soil-aggregate mixture using 5.5 lb (2.49 kg) rammer and 12-in. (305-mm) drop.”


**NOMENCLATURE**

The following symbols are used in this paper:

- \( a \) = half of the size of the compacted clay liner cube (cm)
- \( A \) = \( 6 \rho_b \frac{V}{M} \int_{a}^{x} \frac{a^2 x}{x^2 + ax + a^2} \, dx \) (s)
- \( B \) = \( \int_{0}^{t} \frac{C_t}{C_t - C_0} \, dt \) (cm²)
- \( c_{x,t} \) = metal species concentration in the pore water phase (mg/L)
- \( C_0 \) = initial metal species concentration (mg/L)
- \( C_e \) = equilibrium metal species concentration (mg/L)
- \( C_t \) = metal species concentration in the bulk solution at time t (mg/L)
- \( dV \) = volume of differential cubic shell of compacted clay liner (cm³)
- \( dN/dt \) = metal species diffusion flux in the pore water (mg/s)
- \( D \) = diffusivity of metal species ions in the pore water within compacted clay liner in the shrinking-pore model (cm²/s)
- \( D_{eff} \) = effective overall diffusivity of metal species within the compacted clay liner (cm²/s)
- \( D_f \) = free water diffusivity (cm²/s)
\begin{align*}
D_s & = \text{diffusivity of metal species ion on the adsorbent surface within compacted clay liner (g/s-cm)} \\
D_s' & = \frac{D_s}{\rho_b} \text{ (cm}^2/\text{s)} \\
D_p & = \text{diffusivity of metal species ion in the pore water within compacted clay liner (cm}^2/\text{s)} \\
\bar{D}_{\text{eff}} & = \text{average effective diffusivity (cm}^2/\text{s)} \\
\text{ICP-MS} & = \text{Inductively coupled plasms-mass spectroscopy} \\
J_p & = \text{mass fluxes of pore water diffusion (mg/L-cm}^2\cdot\text{s)} \\
J_s & = \text{mass fluxes of surface diffusion (mg/L-cm}^2\cdot\text{s)} \\
k & = \text{Freundlich constant} \\
k_1 & = \text{first order reaction constant (min}^{-1}) \\
k_2 & = \text{second order reaction constant (g/min-mg)} \\
m & = \text{number of experimental data} \\
M & = \text{mass of compacted clay liner material (g)} \\
n & = \text{Freundlich constant} \\
q_0 & = \text{metal species adsorbed per unit mass of clay at equilibrium with initial heavy metal concentration (mg/g)} \\
q_t & = \text{the amount of sorbate per unit mass of sorbent at time t (mg/g)} \\
q_e & = \text{the amount of sorbate per unit mass of sorbent at equilibrium (mg/g)} \\
q_{\text{exp}} & = \text{experimental binding capacity (mg/g)} \\
q_{\text{t,mod}} & = \text{theoretical binding capacity based on different kinetic mode (mg/g)} \\
S & = \text{surface area of differential cubic shell of compacted clay liner (cm}^2) \\
SE & = \text{standard error, } \sqrt{\frac{\sum(q_{\text{t,exp}} - q_{\text{t,mod}})^2}{m-1}} \text{ (mg/g)} \\
t & = \text{reaction time (min or d)} \\
V & = \text{volume of metal species solution (L)} \\
x & = \text{half of the size of unadsorbed region (cm)} \\
\alpha & = \frac{C_e}{C_0 - C_e} \text{ (-)} \\
\alpha_1 & = \text{constant in Evolich equation} \\
\beta & = \text{constant in Evolich equation} \\
\gamma_d & = \text{compacted dry density of clay (ASTM D698) (g/cm}^3) \\
\rho_b & = \text{bulk density of compacted clay liner (g/cm}^3) \\
\varepsilon & = \text{porosity of the adsorbent} \\
\tau & = \text{factor representing the tortuosity of the flow path}
\end{align*}
Chapter 7. The Effects of Cyclic Interfacial Redox Potential and Coupled pH Changes on Structural Changes to Clay Liners and Leachate Metal Transport

SUMMARY

Three clays, including bentonite, kaolin and Amite soil, were used to fabricate the clay liners. The porosities of the clay liners were estimated from the clay-water characteristic curves. At the optimum moisture content, bentonite clay liner had the highest while Amite soil had the lowest porosity. However, bentonite showed the smallest while kaolin possessed the highest hydraulic conductivity. It was found that Darcy’s law no longer applied for the compacted clay liners and a modified Darcy’s law which was a power law function was developed instead to describe the relation between water flow rate and hydraulic gradient. Clay liners were exposed to cyclic redox potential (-200 mV, 0 mV and +300mV) and coupled pH (5, 6 and 7) changes in this study. The experimental results indicate that some parameters, such as pore size distribution and hydraulic conductivity were changed for bentonite and Amite soil clay liners. However, kaolin clay liner showed little changes either in porosity or hydraulic conductivity. The increase in hydraulic conductivity of the clay liner was attributed to the increase in the portion of larger pores, which could be reflected by the increase in the leachate metal transport rate after the clay liners were subjected to cyclic redox potential and coupled pH changes. The relative order of the metal migration rate within the clay liners followed Ca > Pb > Cu > Zn ≈ Cd > Mg while the order of the clay transporting capacity followed bentonite > kaolin > Amite soil.

INTRODUCTION

Although some of metal species are necessary trace elements for mammals (Forstner and Wittman 1981), these metal species can also be toxic at elevated levels and over extended times to mammals and aquatic life. The fate and transport of metal species in landfill leachate and groundwater have long been an interesting topic for numerous researchers (Christensen et al.
It is recognized that the migration of metal species in the subsurface environment is significantly affected by geochemical conditions. An understanding of these geochemical processes is required to predict and control the fate of metal species such as Cu, Zn, Cd and Pb.

Many geochemical processes are controlled by reduction and oxidation (redox) potential and coupled pH conditions in the subsurface environment. These processes are strongly influenced by transient changes in oxygen, microorganism activity, and trace element levels caused by seasonal variations of groundwater quality and level. For example, there exist a variable phreatic surface with relatively high organic content soil in the Gulf Coast regions of the USA. The variable phreatic surface can occur due to wet weather precipitation either on an event basis or seasonally. Temporal and spatial changes to the groundwater table provides opportunities to come into contact with the microorganism-mediated redox changes in surfacial soils along with degradation of organic matter alter redox potential of the groundwater. As a result, oxygen diffusion into soils and landfill clay liners is significantly curtailed. Gascoyne (1997) confirmed that the groundwater redox potential changed from oxidizing to reducing conditions due to rapid consumption of dissolved oxygen by organics in the upper soils in Canada. Organic acid can be generated by anaerobic fermentation and as a result pH is decreased. On the other hand, the redox potential of groundwater will return to aerobic conditions due to the decrease in the groundwater table in dry weather. Therefore, landfills constructed in such areas can be subject to cyclic redox potential and coupled pH changes.

Among all parameters that have an effect on the transport of metal species, pH and redox potential have long been recognized as important parameters controlling the fate of metal species in the environment (Masscheleyn et al. 1990, Masscheleyn et al. 1991, Sommers and Lindsay
1978 and Chuan et al. 1996). Chuan et al (1996) investigated the effects of redox potential and pH on metal solubility to assess the mobility of Pb, Cd and Zn in a contaminated soil. Results indicate that changes in metal speciation would change the fate of metal species in the subsurface environment. Masscheleyn et al. (1990) studied the influence of Eh and pH on Se solubility, speciation and volatilization in reservoir sediments contaminated with Se. Results indicate that Se solubility was low under reducing conditions (- 200 mV) while the solubility was high when redox potential was increased to + 200 mV and the solubility reached the maximum when redox potential was + 450 mV. They concluded that both redox potential and pH were key factors in the biogeochemistry of Se.

Aside from metal speciation, redox potential and pH may also alter the structure of clay liner and thus have an influence on the transport of leachate through the landfill liner. Clay materials are commonly used in constructing the impervious liners for landfills because of their low hydraulic conductivity. In many cases, the hydraulic conductivity of the clay liner is the controlling factor in subsurface migration of waste leachate (Finno and Schubert 1987). The structural change of clay liner, including a potential change in hydraulic conductivity of the clay liner, has the potential to significantly influence the transport of leachate.

Research has been conducted to study the effects of various geochemical parameters on the structure of clay liners and the results indicated that the structure of the clay liner could be altered in a number of ways. Calcite and gypsum mineral in natural clayey soil used for landfill liner have relatively high solubility. Therefore, the dissolution of these minerals or silica from the crystal lattice in acidic environment could lead to an increase in hydraulic conductivity (Brown and Anderson 1980 and Laguros and Robertson 1978). The influence of polysaccharides on kaolin structure and properties has been reported (Yong and Mourato 1990). In their study,
kaolin-polysaccharide soils were subjected to anaerobic and low redox potential conditions. It was found that the capability of polysaccharides to act as flocculants should be considered in evaluating soil structural change. Some other parameters, such as the geochemical solution composition, could also have effects on the clay structure. Finno and Schubert (1987) attributed the increase of hydraulic conductivity to the following interactions: (1) Ion exchange in which the soil was made more porous; (2) piping of clay particles with reduced double layers; (3) dissolution of soil minerals by acid and bases; (4) syneresis of highly polar molecules; and (5) dissolution of clay minerals by complexation. However, the experimental results obtained by different researchers are sometimes conflicting. Research by Fernandez and Quigley (1985) and Anderson et al. (1985) confirmed that soil could have an increase in hydraulic conductivity if the soil was permeated with concentrated organic liquids. However, Ganapragasam et al. (1995) observed that the application of aniline solution to the clay could result in a decrease in the hydraulic conductivity. The effect of pH on the surface area, pore size distribution, density and porosity of montmorillonite was investigated by Altin et al. (1999). They found that surface area and porosity at lower pH were lower than at higher pH. They concluded that this was caused by the release of Na\(^+\) ions from interlayer at lower pH which might be followed by the reduction of repulsive forces. Other researchers such as Yanful et al. (1990) found that the leachate did not have any impact on the clay liner and the hydraulic conductivity might not be expected to increase as a result of interaction with leachate.

Processes such as denitrification can occur when the soil is saturated and this phenomenon has been reported by many researchers (Killpack and Buchholz 1993 and Gibbs et al. 1994). When the soil is saturated, water fills in the spaces between soil particles, reducing oxygen transfer. Once oxygen is depleted selected soil microorganisms will use nitrite (NO\(_2^{-}\))
and nitrate (NO$_3^-$) forms as electron acceptors. When this happens, nitrogen (N$_2$) and nitrous oxide (N$_2$O) gas are formed in this reducing environment. Denitrification can become significant when the soil is waterlogged for 36 hours or more (Killpack and Buchholz 1993). Water logging causes anaerobic conditions in the soil and microorganisms use nitrate as a source of oxygen for growth. Methanogenesis can also occur if redox potential is decreased further (< -200 mV). During this process, methane will be produced. The production of nitrogenous gases and methane can generate pores in the soil or clay and this can increase hydraulic conductivity of clay liner.

Since the reactions at the leachate – clay liner – groundwater interface are critical in assessing the fate of metal species in landfill system, it is important to model this processes. Although numerous researchers have explored the importance of both redox potential and pH on the mobility of metal species with respect to adsorption in soils, clays or sediments, few studies have investigated the effects of cyclic interfacial redox potential and coupled pH changes on the structural change of landfill clay liner.

**OBJECTIVES**

Research is needed to delineate the effect of cyclic redox potential and pH changes on clay liner structure. Although some researchers explored the role of specific variables, such as pH, redox potential and leachate composition on the clay structure, further study concerning the engineering behavior of landfill clay liner is necessary. For example, the coupled effects of cyclic redox potential and pH changes on leachate metal species transport have not been investigated. There were three objectives in this study. The first objective was to develop a landfill – groundwater interaction system. The second objective was to examine the structural change caused by cyclic redox potential and coupled pH changes. The third objective was to
investigate the effects of redox potential and pH changes on metal species transport in the clay liner. The clay liner and groundwater systems developed in this study and the experiments were designed to provide information on the behavior of metal species transport through clay liners under different redox potential and pH conditions.

BACKGROUND

Hydraulic Conductivity

A critical parameter when evaluating the ability of a landfill liner to isolate leachate from the subsurface environment is hydraulic conductivity. Of all the landfill liner parameters investigated by researchers, hydraulic conductivity has been received the most attention when designing and analyzing the performance of a landfill (Yanful et al. 1990, Fernandez and Quigley 1985 and Quigley et al. 1987). Although Darcy’s law (a linearly proportional relationship between flow and hydraulic conductivity) is valid for a wide range of soil types, however, Darcy’s law is not valid for very small hydraulic gradients in clays (Bardet 1997). For example, Hansbo (1960) found a nonlinear relationship between discharge velocity and hydraulic gradient for a very small hydraulic gradient in Swedish clays. It was found that discharge velocity increased slowly initially and increased linearly with hydraulic gradient when hydraulic gradient increased. In the current study, a power law function (a non-linear Darcy’s law) was utilized to describe the relationship between flow rate and hydraulic gradient for compacted clay liners. This relation is expressed in the following equation.

\[ Q = kA_c \left( \frac{H}{L} \right)^N \]

having the general form of \( q = k_i^N \)  

(1)

In this expression, \( Q \) is volumetric flow rate (cm\(^3\)/s), \( k \) is hydraulic conductivity (cm/s), \( A_c \) is cross sectional area of specimen (cm\(^2\)), \( H \) is head loss across the specimen (cm), \( L \) is length of specimen (cm), \( q \) is flow rate (cm/s) and \( N \) is a constant that is a function of soil type, moisture
content, physical and chemical solution characteristics and compaction parameters. This equation can also be rearranged to yield the following equation.

\[
\ln \left( \frac{v}{t} \right) = \ln(kA_v) + N \ln \left( \frac{H}{L} \right) 
\] (2)

In this expression v is water volume collected at any time t (cm\(^3\)).

**Redox Potential and pH Changes**

Biogeochemical processes can lead to redox reactions and change redox potential in groundwater (Maier et al. 2000). Microorganisms in the soil can utilize the organic matter or other nutrients as carbon and nitrogen sources to drive redox reactions. Denitrification is a biological process and is encouraged by higher soil temperatures and occurs during and after flood irrigation and/or heavy rainfall sufficient to saturate the soil profile (Gibb et al. 1994). Denitrification is carried out by facultative bacteria under anoxic condition and the reaction for denitrification is

\[
3\text{CH}_2\text{O} + 4\text{NO}_3^- \rightarrow 2\text{N}_2 + 3\text{HCO}_3^- + \text{H}^+ + 2\text{H}_2\text{O} 
\] (3)

In this equation methyl alcohol (CH\(_2\)O), which is commonly used as electron acceptor in waste treatment, represents the organic matter. The denitrification pathway is very sensitive to oxygen and as little as 0.2 mg/L of dissolved oxygen or less can inhibit the activity of denitrification enzyme (Maier 2000). When redox potential is reduced further, anaerobic degradation of organic matter will take place and methanogenesis results in the production of methane. The following equation can be used to describe the transformation of organic matter into methane if glucose is used as substrate:

\[
\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 3\text{CH}_3\text{COO}^- + \text{H}^+ 
\] (4)

\[
\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{CH}_4 
\] (5)
Reduced or anaerobic conditions can be developed in saturated soils with high organic matter content (Maier 2000). Under these circumstances, oxygen will be depleted faster than it is supplied. When oxygen is depleted, the activities of anaerobic microorganisms are stimulated and pH will be decreased due to the generation of H\(^+\) which can be seen from Eq. (4). On the other hand, oxidized conditions can be found in the soil with small amount of organic matters since redox potential can be maintained high values due to the existence of sufficient oxygen.

**METHODOLOGY**

**Optimum Moisture Content and Compaction of the Clay Liner**

The compaction tests were used to determine the relation between water content and dry unit weight and to find the maximum dry density and optimum moisture content. Maximum dry density was determined utilizing ASTM D698.

Once optimum moisture content was determined clay material was mixed at optimum moisture content. The split mold utilized to fabricate the compacted clay liner was 19 cm in diameter, 31 cm in height and 2.43 L in volume. The moist clay (at 2% wet-of-optimum) was placed and compacted in the mold in 8 equal layers. Each layer had been compacted uniformly by the Standard Proctor hammer 112 times (this number was calculated based on the height and weight of the hammer) before the next layer of loose clay was placed in the mold. The compaction energy (593 kJ/cm\(^3\)) was kept the same as that in the standard proctor test.

After compaction of the clay cylinder was completed, a stainless steel tube was used to bore and extract a center annular volume with a diameter of 9 cm from the compacted clay. The compacted clay cylinder became a container for landfill leachate in the 9 cm annular area with a cylinder wall and bottom thickness of 5 cm.
Porosity and Pore Size Distribution

Considerable efforts have been expended trying to explain the water retentive characteristics of clay or soil by assuming that clay or soil was a complex system of capillary tubes. It was realized that the water retention function was primarily dependent upon the texture or particle-size distribution of the clay, the structure, and arrangement of the particles (Hanks and Asheroft 1980). The water retention curve can be used to estimate pore size distribution and the total porosity was equal to the saturated water content (Stephens et al. 1998).

The traditional method of determining the water retention function involves establishing a series of equilibrium between water in the clay samples and a volume of water at known potential. The compacted clays with optimum moisture content are first fully saturated with water before the experiment is started. The clay-water system is in hydraulic contact with the volume of water through a water-wetted porous plate or membrane. At each level of equilibrium, the volumetric water content of the clay was determined and paired with the corresponding value of the matric pressure head. The equipment for determining the water retention in the compacted clay liner was of two types: a suction cell apparatus and a pressure cell apparatus which are illustrated in Figure 7-1 (Luthin 1966). When the matric pressure was low (less than 150 cm of H₂O), suction cell apparatus was employed and when the matric pressure was high (greater than 150 cm of H₂O), pressure cell apparatus was used. The compacted clay was 6 cm in diameter and 2 cm in thickness and the suctions applied were 10, 20, 50, 80, 120 and 150 cm of H₂O and the pressures applied were 0.3, 0.5, 1, 2 and 5 bars (which were equivalent to 300, 500, 1000, 2000 and 5000 cm of H₂O).

If the suction force or pressure head h was changed, different volume of water were withdrawn and the volume of water withdrawn was equal to the volume of pores with diameter
The porosity of the compacted clay is equal to the volume of water retained by the clay when fully saturated when the matric potential is zero. The relation between h and d can be expressed as (Hanks and Asheroft 1992).

\[ d = \frac{4 \gamma \cos \theta}{\rho gh} = \frac{0.30}{h} \]  

In this expression, d is pore size (cm), h is head pressure (cm), \( \gamma \) is water surface tension (0.072 N/cm), \( \theta \) is water contact angle (zero for pure water), \( \rho \) is density of water (1 g/cm\(^3\)) and g is gravitational acceleration (9.8 m/s\(^2\)).

Figure 7-1. Water retention measurement apparatus: (a) suction cell apparatus and (b) pressure cell apparatus.

**Hydraulic Conductivity**

Clay samples compacted with the same compactive efforts as samples used in the measurement of porosity were utilized in the determination of hydraulic conductivity. Laboratory apparatus for measurement of hydraulic conductivity consisted of a plexiglas column with
diameter of 7 cm and height of 80 cm. The clay was compacted at the bottom of the column with the same compactive effort as other compacted specimens at optimum moisture content. Based on the methodology illustrated by Bardet (1997), the compacted clay specimen was 7 cm in diameter and 3 cm in thickness. The methodology consisted of a series of constant head tests. A range of gradient (H/L) values were set up by varying the water level above the specimen. Hydraulic conductivities were calculated at different H/L values (H/L = 2, 3, 5, 8, 10 and 15). From Eq. (2) a plot of ln(v/t) versus ln(H/L) would yield a line and the values of k and n were determined from the slope and the intercept of the line, respectively.

**Experimental Setup**

The experimental setup for the leachate and groundwater system is detailed in Figure 7-2. The reactor was made of plexiglas which has outer dimension of 38×38×50 cm. The landfill clay liner, which was 20 cm in outer diameter, 31 cm in height and 5 cm in wall thickness, was located in the middle of the reactor which was filled with synthetic groundwater. The clay liners were compacted at a water content of approximately 2 % wet-of-optimum. A groundwater reservoir located adjacent was varied in elevation so that the groundwater level in the reactor could be changed to model the fluctuation of groundwater table caused by precipitation and infiltration. The interior annular volume of the clay liner was filled with metal solution which acted as synthetic landfill leachate and the level of metal species solution was kept constant throughout the experiment. The leachate in the clay liner and groundwater in the reactor were each kept mixed using peristaltic pumps so that metal species concentration was uniformly distributed in the synthetic leachate and the groundwater quality was spatially constant. Inlets and outlets for circulation were connected at the top of one side of the reactor and at the bottom of the opposite side of the reactor, respectively. The synthetic groundwater was bubbled with N₂.
Figure 7-2. Experimental setup to model the influence of cyclic redox and pH changes on the structural changes of clay liners.
to purge oxygen or with air to oxygenate the reactor so that the groundwater redox potential could be varied. It was found that redox potential could be controlled successfully by microbial cultivation (Kamon et al. 2002), therefore glucose and the supernatant of anaerobically digested sludge were added as required to reduce redox potential in the groundwater. A pH cell and a redox potential cell were connected in parallel to the reactor and a peristaltic pump was employed to circulate synthetic groundwater through the cells. As a result the pH and redox potential values were monitored and recorded on line. The following experimental conditions were set for groundwater: -200, 0 and +300 mV for redox potential and 5, 6 and 7 for pH values. Metal concentrations in the clay liner were monitored daily.

In order to determine the speciation of metal species under different conditions, MINTEQ algorithms were employed. In this experiment, the metal species were: Cu, Zn, Cd and Pb. Beside these metal species, Ca and Mg were also included in the synthetic leachate since these two metals are commonly detected in rainfall-runoff and snowmelt leachate and these metals can influence on metal species adsorption and therefore the fate of metal species in the subsurface environment. For rainfall-runoff and snowmelt residual sludge organic contaminant concentrations are relatively low compared to metal species (Sansalone and Buchberger 1997, Sansalone et al. 1998). The synthetic solution with pH 5.5 was prepared to mimic leachate and the composition of the synthetic solution is listed Table 7-1. MINTEQ algorithms were used to ensure that there was no metal precipitation at pH 5.5.

Cations and anions such as Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and NO$_2^-$ are often found in groundwater as a result of the dissolution of minerals from the soil when infiltrating water passes through soil. Based on previous research (Scheytt 1997 and Mohseni-Bandpi et al.
1999), the groundwater species and their concentrations in the synthetic groundwater used in this research are summarized in Table 7-2.

Table 7-1. Characteristics of synthetic leachate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.5</td>
</tr>
<tr>
<td>Cu</td>
<td>10 [mg/L]</td>
</tr>
<tr>
<td>Zn</td>
<td>10 [mg/L]</td>
</tr>
<tr>
<td>Cd</td>
<td>10 [mg/L]</td>
</tr>
<tr>
<td>Pb</td>
<td>10 [mg/L]</td>
</tr>
<tr>
<td>Ca</td>
<td>200 [mg/L]</td>
</tr>
<tr>
<td>Mg</td>
<td>12 [mg/L]</td>
</tr>
</tbody>
</table>

Table 7-2. The composition of synthetic groundwater.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>20</td>
</tr>
<tr>
<td>K⁺</td>
<td>4</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>100</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>5</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>150</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>50</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>85</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>45</td>
</tr>
</tbody>
</table>

**Measurement of Redox Potential**

The redox potential in natural groundwater system is a mixed potential that represents the overall potential of several redox couples reacting simultaneously (Kamon et al. 2002). Generally, under a certain redox potential, only one important redox reaction dominates the system. The measurement of redox potential was conducted using the redox/ORP glass combination electrode (Model 97-98, Orion) with built-in Ag/AgCl as reference. The electrode had been calibrated using a standard solution with a redox potential of + 200 mV before the measurement.
RESULTS AND DISCUSSION

Understanding the pollutant transport in the clay liner requires knowledge of physical and chemical properties of the clay liners. Physical characteristics of the clay liners are listed in Table 7-3.

Table 7-3. Physical characteristics of compacted clay liners.

<table>
<thead>
<tr>
<th></th>
<th>Bentonite</th>
<th>Kaolin</th>
<th>Amite Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density (g/cm³)</td>
<td>1.71</td>
<td>1.39</td>
<td>1.94</td>
</tr>
<tr>
<td>Specific Surface Area (m²/g)</td>
<td>86</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>54.1</td>
<td>48.1</td>
<td>41.5</td>
</tr>
<tr>
<td>Optimum Moisture Content (%)</td>
<td>41</td>
<td>31</td>
<td>16</td>
</tr>
<tr>
<td>Tested Moisture Content (%)</td>
<td>43</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>Hydraulic Conductivity (cm/s)</td>
<td>2.62×10⁻¹⁰</td>
<td>1.42×10⁻⁷</td>
<td>9.59×10⁻⁸</td>
</tr>
<tr>
<td>Clay Composition</td>
<td>S</td>
<td>K</td>
<td>S, K, I, G, Q</td>
</tr>
<tr>
<td>Organic Matter (%)</td>
<td>0.23</td>
<td>0.18</td>
<td>0.34</td>
</tr>
</tbody>
</table>

S: Smectite K: Kaolinite I: Illite
G: Goethite Q: Quartz

Compaction Curve

The typical standard proctor compaction curves for the three clays are presented in Figure 7-3. It can be seen from the figure that of the three clay liners, Amite soil showed the smallest optimum moisture content and highest dry density, bentonite had the highest optimum moisture content and an intermediate dry density while kaolin possessed an intermediate value of optimum moisture content and the lowest dry density.

Pore Size Distribution of Compacted Clays

The pore size distributions of the three clay liners at 2% wet-of-optimum moisture content are plotted in Figure 7-4. Results indicate that bentonite had the smallest pore size while kaolin had the largest pore size. The values of d₅₀ of the pore size were 3, 9 and 12 µm for bentonite, kaolin and Amite soil, respectively. The large pores are most effective in conducting water and metal diffusion within the compacted clay liner. Therefore, although bentonite had the
Figure 7-3. Moisture-density relationship for the three clay materials. Each data point was replicated 3 times.

Figure 7-4. Initial pore size distribution of compacted clay liner materials.

highest porosity of the three compacted clays, bentonite still had the smallest hydraulic conductivity since it had much smaller pores than kaolin or Amite soil. A higher percentage of large pores will result in higher values of hydraulic conductivity and diffusivity. If pore size
distributions were the same for different clays than higher porosity may suggest potentially higher flow and metal transport.

**Hydraulic Conductivity**

The power law form of Darcy’s law (Eq. (1)) was used to model the flow of water within the compacted clays and determination of the proportionality between flow and gradient (hydraulic conductivity) are depicted in Figure 7-5. The application of the power law successfully described the relationship between flow rate and hydraulic gradient. It can be seen from the figure that the kaolin clay liner exhibited the highest hydraulic conductivity, bentonite showed the lowest, while Amite soil had intermediate hydraulic conductivity. Anderson et al. (1985) also found the similar result in their research: kaolin generated the highest hydraulic conductivity while smectite had the smallest hydraulic conductivity. They reported that the hydraulic conductivities of kaolin and smectite were in the range of $10^{-7}$ and $10^{-9}$ cm/s, respectively. The maximum dry densities were 1.6 and 1.5 g/cm$^3$, respectively.

Figure 7-6 compares application of Darcy’s law and the modified power law form of Darcy’s law. It can be seen from the figure that there existed large deviation between Darcy’s law and the experimental data when hydraulic gradient were greater than 5. This discrepancy was dominant for bentonite even when hydraulic gradient was greater than 3.

**Effect of Cyclic Redox Potential and pH Changes**

An Eh range of - 200 to + 300 mV and a pH range of 5 to 7 were modeled to reflect the consequence of cyclic redox potential change caused by the fluctuation of the groundwater table as driven by precipitation.
Figure 7-5. Determination of hydraulic conductivity for compacted clay liner. Power law form ($q = k i^N$) of Darcy’s law applied.
Figure 7-6. Deviation of flow-hydraulic gradient relationship from Darcy’s law for compacted clay liner materials. The dashed and solid lines represent the results obtained from Darcy’s law and power law while dots are experimental data.
The developments of cyclic redox potential and pH changes are shown in Figure 7-7. There were two cycles in the experiment and in each cycle the redox potentials were kept at – 200, 0 and +300 mV while pH levels were maintained at 5, 6 and 7, respectively.

Figure 7-7. Developments of cyclic redox potential and pH changes. The target redox potentials were –200, 0 and +300 mV and the corresponding pH values were 5, 6 and 7, respectively.

The clay liners were examined for changes in pore size distribution and hydraulic conductivity hypothesized to be a reflection of the structural changes of clay liner. Figures 7-8, 7-9 and 7-10 plot the pore size distributions of the clay liners under the cyclic redox potential and coupled pH conditions while Table 7-4 summarizes the changes in the porosity of the clay liners under different experimental conditions. Results indicate that the pore size distribution curves of the compacted clay specimens subject to cyclic redox potential and coupled pH changes were all of an exponential form. Cyclic redox potential and pH changes had significant
influences on the pore size distributions of bentonite and Amite soil clay liners while the pore size distribution of kaolin clay liner was not significantly changed.

Figure 7-8. Changes in relative distribution of pore sizes and cumulative distribution of pore sizes as a result of cyclic redox changes for compacted bentonite.
Figure 7-9. Changes in relative distribution of pore sizes and cumulative distribution of pore sizes as a result of cyclic redox changes for compacted kaolinite. The cyclic redox potential changes had little effect on the pore size distributions of the kaolin clay liner.
Figure 7-10. Changes in relative distribution of pore sizes and cumulative distribution of pore sizes as a result of cyclic redox changes for compacted Amite soil. The cyclic redox potential changes had effects on the pore size distributions of the Amite soil clay liner.
For example, in the case of compacted bentonite clay, the relative percentage of pores with diameter of about 100 µm was increased when redox potential was reduced to –200 mV while the percentage of large pores (with diameter greater than 200 µm) was not significantly changed. When redox potential was raised to 0 mV, there was still a slight change in the pore size distribution. In the second cycle, the same trends in the clay pore size distributions as those developed in the cycle 1 were observed but the increase was not as large as those observed in the first cycle. Although the redox potential and pH were switched back to the initial conditions (redox potential was –200 mV and pH was 5), the pore size distribution of the clay liner did not return to its original state.

Amite soil clay liner underwent similar changes in the pore size distribution when redox potential and pH were changed cyclically. This observation is not surprising since more than 50% of the clay fraction on Amite soil is composed of smectite. For both of bentonite and Amite soil compacted clays, the portions of small sized pores with diameter of less than 25 µm were decreased when the clay liners were subject to the cyclic redox potential and pH changes. However, compacted kaolin had little changes in the pore size distribution under the cyclic redox potential and coupled pH changes in this study. Since kaolin had much smaller specific area and surface charge compared to those of smectite, which was the dominant component in bentonite, the flocculation of kaolin particles may not have been as significant as for smectite particles which were very sensitive to flocculation. Smectite was also a very important component of Amite soil based on the X-ray diffraction (XRD), therefore, the structure of Amite soil clay liner was also influenced by metal solution changing the flocculation characteristics. Another explanation why kaolin clay was not influenced by the changes in redox potential and pH could be attributed to the large sized pores of the three clay liner materials.
studied. Although a small proportion of larger pores could be produced, this increase in the percentage of large sized pores was still negligible compared to the original percentage of large sized pores.

Alternatively, the dissolution and crystallization of metal species under different redox potential and pH conditions within the compacted clay liner could also produce changes in porosity. For example, some of metals including Cu, Zn, Cd, Pb, Mg and Ca were in the forms of Cu$_2$S (s), ZnS (s), CdS (s), PbS (s), Mg$^{2+}$ (aq) and CaSO$_4$ (s) under highly reducing (-200 mV) and low pH (5) conditions (Brookins 1988). When redox potential was switched to moderately reducing condition (0 mV) with pH 6, the dominant species of the above metals did not change. However, in the cases of highly oxidizing potential state (+300 mV) and high pH (7), the metals in the pore water within the compacted clay existed in the form of Cu$_2$(OH)$_2$CO$_3$ (s), Zn$^{2+}$ (aq), Cd$^{2+}$ (aq), PbCO$_3$ (s), Mg$^{2+}$ (aq) and CaCO$_3$ (s) as indicated by the Eh-pH diagram (Brookins 1988). It is hypothesized that any small pores generated by metal crystals are smaller than those generated by gases such as N$_2$ or CH$_4$ since the crystals of metal species was so small that the diameter of pores generated by crystallization was comparable to that of the original pore after compaction. The solubility of Cu, Pb, Mg and Ca did not change much under different redox potential and pH conditions in this study. Changes in redox potential had a small but significant effect on metal solubility of Zn and Cd and when the redox potential was changed from highly reducing state (-200 mV) to highly oxidizing state (+300 mV), Zn and Cd could be precipitated. According to the investigation of Maier et al. (2000), metal species became more soluble under oxidizing environment.
It was hypothesized that the compacted clay with some macro- and micro-pores that were produced from the cyclic redox potential and pH changes and as a result produced altered could have hydraulic conductivity compared to the original compacted clay.

Table 7-4 illustrates the overall porosity changes due to the effect of cyclic redox potential for compacted clays. Results indicate that the porosity of kaolin was not affected while those of bentonite and Amite soil were increased under cyclic redox potential conditions.

Table 7-4. The effect of cyclic redox potential on the porosity of compacted clay liners.

<table>
<thead>
<tr>
<th>Clay Liner</th>
<th>Original</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- 200 mV</td>
<td>0 mV</td>
<td>+ 300 mV</td>
</tr>
<tr>
<td>Bentonite</td>
<td>54.1</td>
<td>56.2</td>
<td>56.8</td>
</tr>
<tr>
<td>Kaolin</td>
<td>48.1</td>
<td>48.6</td>
<td>48.4</td>
</tr>
<tr>
<td>Amite Soil</td>
<td>41.5</td>
<td>44.4</td>
<td>45.7</td>
</tr>
</tbody>
</table>

Aside from redox potential, pH could also have an effect on the compacted clay structure. Altin et al (1999) found that a decrease in pH could reduce surface area while an increase in pH could increase surface area of montmorillonite, creating a more porous structure. It was hypothesized that lowering pH of montmorillonite could remove the repulsive forces due to the presence of hydrated ions, such as Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) and K\(^+\) while the interlayer forces became dominant when pH was high. Other studies (Pashley 1981) also hypothesized that the replacement of cations by H\(^+\) ions completely removed the repulsive forces. However, in contrast, this current study found that the decreases in pH and redox potential were accompanied by the increase in the porosity of compacted bentonite clay. Therefore, it was concluded that the effect of redox potential played a more important role than pH in changing the bentonite clay structure.

To verify the structural change caused by cyclic redox potential and pH changes, the following experiment was designed. The leachate inside the clay liners was removed completely after the clay liners had been subject to different redox potentials and the volume of groundwater
infiltrated into the compacted clay was measured at different time. If the power law form of the modified Darcy’s law is used to describe the infiltration, the following equation can be drawn to describe the water filtration through the compacted clay with a center annual volume described in this study.

\[
v = kt\left[\pi \frac{(D + 2\delta)}{\delta^N} \cdot \frac{l^{N+1}}{N+1} + \pi \frac{D^2}{4} \cdot \left(\frac{l}{\delta}\right)^N\right]
\]

(7)

In this expression \(D\) is the inner diameter of the clay liner (cm), \(\delta\) is the thickness of clay liner (cm) and \(l\) is the difference between groundwater table and the bottom of clay liner (cm). Let \(B = \pi \frac{(d + 2\delta)}{\delta^N} \cdot \frac{l^{N+1}}{N+1} + \pi \frac{d^2}{4} \cdot \left(\frac{l}{\delta}\right)^N\), plotting of \(v/B\) against \(t\) will generate a line with slope of \(k\).

Figure 7-11, which plots the changes of hydraulic conductivity of the clay liners at different redox potential conditions, confirmed that there did exist changes in hydraulic conductivities of bentonite and Amite soil if the clay liners were subject to cyclic redox potential and pH changes. The hydraulic conductivity of the compacted bentonite clay increased from \(2.6 \times 10^{-10}\) to \(3.15 \times 10^{-9}\) cm/s by a factor of 12 while Amite soil clay liner had a much smaller increase in hydraulic conductivity from \(0.95 \times 10^{-7}\) to \(1.3 \times 10^{-7}\) cm/s (a factor of 1.35) in cycle 1 in which redox potential increased from \(-200\) mV to \(+300\) mV. However, in cycle 2 in which redox potential still varied from \(-200\) mV to \(+300\) mV the hydraulic conductivities of compacted bentonite and Amite soil did not increase by the same magnitudes as those in cycle 1. For example, the hydraulic conductivity of compacted bentonite increased from \(3.15 \times 10^{-7}\) to \(6.12 \times 10^{-7}\) cm/s (a factor of 1.94) while that of compacted Amite soil increased from \(1.3 \times 10^{-7}\) to \(1.64 \times 10^{-7}\) cm/s (a factor of 1.26) in cycle 2. At the end of cycle 2, the redox potential of
Figure 7-11. The changes of hydraulic conductivities of the clay liners under cyclic redox potential and pH conditions. The dashed lines represent the initial hydraulic conductivity values, the dots are experimental data while solid lines illustrate liner regression of the experimental results. v = Bkt, and 
\[ B = \pi \left( \frac{D + 2\delta}{\delta^N} \right) \cdot \frac{I^{N+1}}{N + 1} + \pi \frac{D^2}{4} \cdot \left( \frac{I + \delta}{\delta} \right)^N. \]
I is the height of clay liner, D is the diameter of clay liner and \( \delta \) is the thickness of clay liner.
groundwater was returned to the original value. However, it seemed that the return of the groundwater redox potential to the original value did not return the compacted clay to their original hydraulic conductivities suggesting that the structural change of the compacted clay liner under cyclic redox and pH conditions was irreversible.

The metal species transport rates within the clay liners were hypothesized to change accordingly in response to the structural changes of the clay liners under cyclic redox potential and pH conditions. Figures 7-12 through 7-14 depict the decreases of leachate metal concentration as a function of time when the clay liners were exposed to cyclic redox potential and pH conditions. The solid lines and dashed lines are results obtained in the Cycles 1 and 2, respectively. The metal concentrations in the groundwater were also monitored at the same time. However, results indicate that the metal concentrations in the groundwater were very low which was less than 10 ppb and therefore, it was confirmed that there was no seepage in the clay liners and the decreases of metal in the leachate were completely due to the migration of metals within the clay liners.

Figures 7-12 through 7-14 indicate that metal concentrations changed at different rates under different experimental conditions. Metal migration rates were completely different for different groundwater table and redox potential conditions for all of the three clay liners. When the groundwater table was higher than the leachate level (redox potential was kept at – 200 mV), groundwater would be infiltrated through clay liner and come into the inside of clay liner. This is an advective transport process. Due to the difference in chemical potential between groundwater and leachate, metals would diffuse from leachate to groundwater through the clay liner at the same time. Therefore, metal diffusion and groundwater advection were in opposite directions and the transport of metal within the clay liner could be slowed down under this circumstance.
Figure 7-12. Leachate metal profiles in contact with a compacted bentonite clay liner under cyclic redox potentials. The first cycle started out at -200 mV, increased to 0 mV and was further increased to +300 mV. The +300 mV was dropped to -200 mV to start the second cycle.
<table>
<thead>
<tr>
<th>Time (d)</th>
<th>Concentration [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 7-13. Leachate metal profiles in contact with a compacted kaolin clay liner under cyclic redox potentials. The first cycle started out at -200 mV, increased to 0 mV and was further increased to +300 mV. The +300 mV was dropped to -200 mV to start the second cycle.
Figure 7-14. Leachate metal profiles in contact with a compacted Amite soil clay liner under cyclic redox potentials. The first cycle started out at -200 mV, increased to 0 mV and was further increased to +300 mV. The +300 mV was dropped to -200 mV to start the second cycle.
However, when groundwater table was lowered to the level which was comparable to that of leachate (redox potential was maintained at 0 mV), there was no water flow between leachate and groundwater and molecular diffusion of metal was the dominant process responsible for the metal migration within the clay liners. As a result, metal transport rate should be higher than that in previous case. When groundwater table was decreased further while redox potential was increased to +300 mV, groundwater table is below leachate level and leachate would be potentially transported as a function of both hydraulic gradient and diffusion. Therefore, metal transport would be potentially greater in this case as compared to the previous two cases.

For compacted bentonite and Amite soil, the metal transport rates under different redox potentials in the Cycle 2 were higher than the counterparts in the Cycle 1. In other words, metal transport rates did not return to original rates even when the groundwater table and redox potential were returned to the original states. Instead, metals migrated at faster rates due to the irreversible structural changes of the clay liners, which increased the porosity of the clay liners. However, the metal transport rates illustrated little change in Cycles 1 and 2 for compacted kaolin clay. This is not surprising since the porosity of kaolin did not show much variation under the cyclic redox potential and pH conditions.

The comparison of Figures 7-12 through 7-14 indicates that the relative order of the metal migration rate within the clay liners followed Ca > Pb > Cu > Zn ≈ Cd > Mg while the order of the clay transporting capacity followed bentonite > kaolin > Amite soil. It was found that the order of the clay transporting capacity was in accordance with that of clay porosity.

CONCLUSIONS

Compacted clay liners composed of three clay materials, bentonite, kaolin and Amite soil (a native clayey soil in South Louisiana) were examined in this research. The porosities of the
clay liners were estimated from the clay-water characteristic curves. At the optimum moisture content, bentonite clay liner had the highest porosity while Amite soil had the lowest porosity. However, since bentonite had the highest percentage of fine pores, the hydraulic conductivity of compacted bentonite liner was the smallest of the three liners. Kaolin clay liner had the highest while Amite soil clay liner had the intermediate hydraulic conductivity.

Darcy’s law was not applicable to the compacted clay liners and a modified Darcy’s law which was a power law function was employed to model the water infiltration through the compacted clay liners. The result indicated that the experimental data could be modeled by this power law function.

The influences of cyclic interfacial redox potential and coupled pH changes on the structural changes of clay liner and metal transport within clay liner was investigated. It was found that clay structures changed in response to the cyclic redox potential and coupled pH changes. Two redox cycles were modeled and the redox potentials and pH were set at – 200 mV (pH 5), 0 mV (pH 6) and + 300 mV (pH 7) in each cycle. The cyclic redox potential and pH changes produced measurable changes in the bentonite and Amite soil clay liner structures. The experimental results obtained suggested that cyclic redox potential and pH changes influenced the clay structure through the formation of larger pores possibly generated by flocculation and the formation of some gases, such as CH₄ and N₂. The structural changes of clay liners were irreversible and the restoration of the original experimental conditions could not bring the clay liners to their original state.

The clay liner, such as bentonite and Amite soil, had greater proportions of large pores after the exposure to highly reducing condition (- 200 mV). As a result, the clay liner underwent an increase in porosity and hydraulic conductivity. In contrast, the kaolin clay liner remained
almost intact after exposure to cyclic redox potential and pH changes. The increases of porosity and hydraulic conductivity of bentonite and Amite soil clay liners led to the increase of metal transport rates within the clay liners. Based on the previous research, metal species diffusivities in the three clay liners followed the order of bentonite > kaolin > Amite soil. Although the smaller pores in the bentonite clays were still effective with respect to diffusion of metal species, these small pores were not effective for water flow (advection). Therefore, it was concluded that the total porosity seemed to outweigh the percentage of large pores in determining the diffusion of pollutant within clay liner while the pore size distribution was more important in controlling advection of metal species within the clay liner.

The ability of cyclic redox potential and coupled pH changes to produce large pores in the compacted clay may be a potential mechanism for metal species migration through landfill liner since the pollutants such as metal species could migrate faster in the compacted clay liners.

The structural change of landfill clay liner caused by seasonal fluctuation in groundwater table has some implications for the performance of the landfill clay liner. The cyclic redox and pH changes did have a significant influence of the structure change of clay liner. This result suggests that metal migration rates could be increased due to the cyclic redox potential coupled with pH change if smectite is principal component in the clay liner material. In this study, bentonite and Amite soil which was smectite-dominated clayey soil showed irreversible structural change while compacted kaolin clay did not exhibit similar changes. Therefore, kaolin or kaolin-dominated clayey soil might be a more suitable material to construct landfill liner in the costal area which is subject to cyclic redox potential and coupled pH changes in groundwater.

REFERENCES


ASTM D698. (1988) “Standard test methods for moisture-density relations of soils and soil-aggregate mixture using 5.5 lb (2.49 kg) rammer and 12-in. (305-mm) drop.”


Laguros, J. G. and Robertson, J. M. (1978) “Problems of interaction between industrial residues and clays.” 3rd Annual Conference on Treatment and Disposal of Industrial Wastes, Wastewater, and Residues, Houston, TX.


**NOMENCLATURE**

The following symbols are used in this paper:
\( A_c \) = cross sectional area of specimen \( (cm^2) \)

\( B = \pi \frac{(d + 2\delta) \cdot l^{N+1}}{\delta^N} + \pi \frac{d^2 \cdot (l + \delta)^N}{4 \delta} \) (cm)

\( d \) = diameter of pore in compacted clay liner \( (cm) \)

\( D \) = inner diameter of the clay liner \( (cm) \)

\( g \) = gravitational acceleration \( (9.8 \text{ m/s}^2) \).

\( h \) = suction force or pressure head \( (cm) \)

\( H \) = head loss across the specimen \( (cm) \)

\( k \) = hydraulic conductivity \( (cm/s) \)

\( l \) = difference between groundwater table and the bottom of clay liner \( (cm) \)

\( L \) = length of specimen \( (cm) \)

\( N \) = constant in modified Darcy’s law

\( Q \) = flow rate \( (cm/s) \)

\( Q \) = volumetric flow rate \( (cm^3/s) \)

\( t \) = time \( (s) \)

\( v \) = water volume collected at time \( t \) \( (cm^3) \)

\( \delta \) = the thickness of clay liner \( (cm) \)

\( \gamma \) = water surface tension \( (0.072 \text{ N/cm}) \)

\( \theta \) = water contact angle \( (zero \text{ for pure water}) \)

\( \rho \) = density of water \( (1 \text{ g/cm}^3) \)
Chapter 8. Conclusions

Urban storm water and snowmelt residual leachate typically contains high levels of heavy metals. These heavy metals can be released from the storm water residuals or sludge and become dissolved into leachate under the acidic conditions commonly encountered in the landfill facility. Four heavy metals, including Cu, Zn, Cd and Pb, which are typically detected in storm water or snowmelt and three liner materials, bentonite, kaolinite and Amite soil, were investigated.

The physical and chemical characteristics of bentonite, kaolinite and Amite soil were firstly investigated since these characteristics have a significant effect on their adsorption behavior in the presence of heavy metal leachate. It was found that of the three clay materials investigated, bentonite has the highest specific surface area and surface charge while Amite soil has the smallest specific surface area and surface charge. The surface complexation models were used to calculate the acidity constants of the three clay liners.

Results from mono-element and multiple-element adsorption systems indicate that the adsorption of the heavy metals on the clay materials can be represented by Freundlich isotherms. Under the experimental conditions in this study the adsorption capacities of the three clay materials decrease in the order bentonite > Amite Soil > kaolinite and the relative affinities of the four metals for the 3 clay materials were Pb > Cu > Zn > Cd. The high affinity of heavy metals for bentonite is attributed to its high surface charge and high specific surface area. The comparisons of heavy metal adsorptions in mono-element systems and those in multiple-element systems show that competitive adsorption must be considered, since competition can significantly decrease heavy metal adsorption.

The adsorption process of Cu, Zn, Cd and Pb on the three clay liner materials was also studied from point view of surface complexation model. It was found that the mathematical
modeling of diffuse-layer model (DLM) could fit the experimental data well under different experimental conditions, including: mono-element system where only one of the four heavy metals existed and multiple-element system where the four metals and Mg and Ca were presented. It was confirmed that the intrinsic surface complexation constants showed little variations both in mono-element and multiple-element systems with and without the presence of Mg and Ca. Based on the analysis of $K_{Me^{2+}}^{int}$ values, it was found that the affinities of the clays for heavy metals increased in the order kaolinite < Amite soil < bentonite while the affinities of the metals for the clays increased in the order Cd < Zn < Cu < Pb. These results were in consistent with those obtained from adsorption isotherm study.

The presence of other metals could decrease the adsorption of certain heavy metal and the effect of competitive adsorption was very significant on the adsorption of metals on kaolinite. Although kaolinite had the highest site density, it still had a low adsorption capacity due to its low specific surface area and low $K_{Me^{2+}}^{int}$. It seems that adsorption of heavy metal with a low value of $K_{Me^{2+}}^{int}$ would be reduced significantly in the multiple-element system where the competitive adsorption occurred.

Different kinetic models were employed to investigate heavy metal adsorption kinetics onto the clay liner materials. It was found that the performance of heavy metal adsorption onto uncompacted clays were completely different from those onto compacted clays. The adsorption of heavy metal by dispersed clay was a very fast process which could be accomplished within several hours. Several commonly used kinetics models, including first order reaction, second order reaction and Elovich equation, were tested to model the adsorption process. It was confirmed that the experimental data could be best approximated by first order reaction. Based
on the parameters determined, it was found that heavy metal adsorption rates follow the order of Pb > Cu > Zn > Cd and bentonite > Amite soil > kaolinite. As a contrast, the adsorption of heavy metal onto compacted clay was a very slow process due to the existence of internal mass transport within the compacted clays. Heavy metal adsorption onto compacted Amite soil was a slower process compared to those onto bentonite and kaolinite. This phenomenon was caused by the smallest intraparticle diffusivities of heavy metals within compacted Amite soil. Shrinking-core model and pore and surface diffusion model were used to simulate heavy metal adsorption onto compacted clays. The pore water diffusivities of the four heavy metals were in the order of $10^{-10}$ cm$^2$/s for bentonite and kaolinite and $10^{-11}$ cm$^2$/s for Amite soil. The analysis of the relative importance of pore and surface diffusion indicated that pore diffusion was the dominant mechanism within compacted bentonite, surface diffusion was the principal mechanism within compacted kaolinite and pore and surface diffusions were equally important within compacted Amite soil.

The characteristics of compacted clay liners were also investigated. At the optimum moisture content, bentonite clay liner had the highest while Amite soil had the lowest porosity. However, since bentonite had the highest percentage of fine pores, compacted bentonite liner exhibited the smallest hydraulic conductivity of the three liners. Kaolinite clay liner had the highest while Amite soil clay liner had the intermediate hydraulic conductivity. Darcy’s law was not applicable to the compacted clay liners and a modified Darcy’s law which was a power law function was employed to model the water infiltration through the compacted clay liners. The result indicated that the experimental data could be well described by this power law function.

The influences of cyclic interfacial redox potential and coupled pH changes on the structural changes of clay liner and metal transport within clay liner have also been investigated.
It was found that clay structures changed in response to the cyclic redox potential and coupled pH changes. Two interfacial redox potential cycles were modeled and the redox potentials and pH were set at –200 mv (pH 5), 0 mv (pH 6) and +300 mv (pH 7) in each cycle. The cyclic redox potential and pH changes produced measurable changes in the bentonite and Amite soil clay liner structures. The experimental results obtained suggested that cyclic redox potential and pH changes influenced the clay structure through the formation of larger pores generated by flocculation and the formation of some gases, such as CH$_4$ and N$_2$. The structural changes of clay liners were irreversible and the restoration of the experimental condition could not bring the clay liners to the original states.

The clay liner, such as bentonite and Amite soil, had greater proportions of large pores after the exposure to highly reducing condition (-200 mV). As a result, they underwent increase in porosity and hydraulic conductivity. In contrast, kaolinite clay liner remained almost intact after exposure to cyclic redox potential and pH changes.
VITA

Ping Zhou received his Bachelor of Science degree in environmental engineering from Southeast University, Nanjing, China, in July 1989. He got his Master of Science degree in environmental engineering from the same university in February 1992. He joined the Department of Civil and Environmental Engineering, University of Pittsburgh, and started his graduate study in August 1999 and transferred to the Department of Civil and Environmental Engineering, Louisiana State University, in July 2000. His graduate research was focused on heavy metal transport in landfill clay liner for stormwater residual treatment and disposal and the interaction between groundwater redox potential and clay liner. He worked under the guidance of Dr. John J. Sansalone in the Department of Civil and Environmental Engineering, Louisiana State University. He will receive the degree of Doctor of Philosophy at the May 2003 Commencement.