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Evaluation of Industrial CaF_2 Sludge Waste as Heavy Metal Sorption Material

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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Summary

Heavy metals (HM) immobilization materials developed from waste materials not only allow waste reuse but also is economical compared to synthetic sorbents. This project characterized the CaF_2 sludge and assessed its sorption capacity for aqueous Lead (Pb), Zinc (Zn) and Cadmium (Cd). The important parameters controlling aqueous metals removal, i.e., initial metal ion concentrations, solution pH, ionic strength, and HM removal kinetics were evaluated using batch experiments. Sequential extraction (SE) technique was also applied to assess the fractionation of the sorbed HM in the sludge material.

The presence of background ionic strength (0.05M KNO_3) reduces the sorption efficiency of HM. However, the effect is negligible for lower concentrations. It was concluded that the Pb and Cd sorption followed the Freundlich isotherm model and Zn sorption followed the Langmuir isotherm model. The HM sorption kinetics followed a biphasic characteristic model, with a rapid HM uptake rate followed by a decrease rate in the later stage. The HM uptake by the sludge for Cd and Zn decreased and Pb increased under extremely acidic condition (pH 2). The pH variance (from pH 3-7) did not have any significant effect on the HM uptake. It was observed that HM sorption efficiency increased when the pH was greater than 7. SSE results confirmed the effectiveness of the sludge in retaining Pb for remediation. The non-residual fractions of Zn and Cd in the sorbed materials would need further stabilization treatment prior to landfill disposal.

Chapter 1

Introduction

1.1 Background

As the world advances in technology and manufacturing processes, it is inevitable that massive amount of industrial waste, regardless of toxic or non-toxic, will be produced.

In Singapore, it was reported that approximately 180 to 230 tonnes of industrial sludge, are disposed of at the offshore Pulau Semakau landfill daily. Waste recycling is one viable alternative option to dumping the waste into landfills directly. By doing so, the objective of 60% recycling rate spell out in the Singapore Green Plan 2012 can be met and eventually towards “zero landfills” in the near future. As land is scarce in Singapore, it is crucial for us to work on the feasibility of waste recycling to pursue the vision of “zero landfills” in the Singapore Green Plan 2012.

Today, we are living in high-technology society where Flat Panel Display (FPD) products are commonly used; they include flat screened televisions, Liquid Crystal Display (LCD) monitors, laptops, pocket PC and mobile phones. The demands for such products are still on the rise. However, more industrial wastes will be produced along with the production of FPD and this bring along the problem of waste disposal. In general, the cost of proper waste disposal, especially in the case of metal sludge, is often quite costly, which in turn increase the manufacturing cost of the companies.

Calcium Fluoride (CaF_2) is a major raw material used in the production of FPD. The waste associated with the FPD production consists primarily of CaF_2 , phosphates and some heavy metals. Thus, this kind of industrial sludge is commonly termed as ‘ CaF_2 sludge’. Generally, the industrial metal sludge resulting

from the waste treatment was dewatered and then treated with Ordinary Portland Cement (OPC) before dumping into landfills.

CaF₂ industrial sludge used in this project was obtained from a local flat panel display manufacturer, AFPD Pte Ltd. AFPD Pte Ltd, which produces a substantial amount of CaF₂ sludge, have an estimated production rate of 10,000 kg of dewatered sludge per day.

Analysis using X-ray diffraction (XRD) revealed that the CaF₂ sludge has a characteristically high content of apatites, especially hydroxyapatite Ca₁₀(OH)₂(PO₄)₆ and fluorapatite Ca₅(PO₄)₃F. The presence of apatites, neutral pH of sludge (pH=7.2 after method 9045D) and high cation exchange capacity (CEC) are favorable characteristics suggesting that CaF₂ sludge may be a effective sorbent for the removal of aqueous heavy metals from contaminated water and soils.

Metals contamination is a persistent problem at many contaminated water and soil sites. The leachates from the contaminated sites also pose a threat to groundwater supplies if the metals are not properly contained or removed. Heavy metals may persist for long period of time creating long-term hazards to the environment or human health. The most commonly occurring metals at contaminated sites are lead(Pb), chromium(Cr), arsenic(As), zinc(Zn), cadmium(Cd), copper(Cu), and mercury(Hg).

A range of technologies is available for remediation of metal-contaminated soils. Since metals cannot be destroyed, remediation of metal contaminated soil primary consists of manipulating (i.e. exploiting, increasing, decreasing or maintaining) the mobility of metal contaminants to produce a treated site that has an acceptable total or leachable metal content.

One of the common methods of remediation is by adsorption with a medium. The technology mechanically concentrates the contaminants into a much smaller mass for subsequent treatment. This includes adsorption by apatites, which has been

largely researched and demonstrated to have significant potential of adsorbing heavy metals.

The CaF_2 sludge used in this study has a high content of apatites, and could be a cost effective sorbent material for treating contaminated water and soil sites.

1.2 Objectives

The primary objective of this project was to evaluate the heavy metal immobilization potential of the CaF_2 sludge. The main tasks were to investigate quantitatively the effects of concentrations, pH, and ionic strength on the aqueous Pb, Cd and Zn removal efficiency of the sludge, and as well as to investigate in detail its removal kinetics. Sequential extraction techniques were also applied to assess the fractionation of the heavy metals species in the sludge material.

1.3 Scope

The scope of this project includes:

- (i) Sludge characterization
- (ii) Spiking of the solutions with Lead (Pb), Cadmium (Cd), and Zinc (Zn) nitrate salts in laboratory.
- (iii) Sorption experiments using spiked Pb, Cd and/or Zn solutions with dried sludge fines ($<250\mu\text{m}$), including kinetics studies
- (iv) Sequential extraction of carbonate, reducible, organic and the residual fractions of the heavy metals retained by the sludge.

Chapter 2

Literature Review

2.1 Overview

Heavy metals are toxic to human as well as to other organisms. Unlike organic compounds that can biodegrade with time, or can be incinerated, heavy metals are robust and remain a potential threat to the environment or human health for a very long time.

The promising method for immobilization of most heavy metals from contaminated environments by using apatites has been widely researched. Since the CaF_2 sludge in this study has a high content of apatites (such as Hydroxyapatites and Fluoroapatites), it could be a cost effective sorbent media for the removal of most heavy metals from contaminated water and in situ immobilization of heavy metals in contaminated ground sites.

2.2 Background of Hydroxyapatite

Apatite is a general name for different minerals, usually referring to hydroxyapatite, fluorapatite and chlorapatite with the formula $\text{X}_5(\text{Y}\text{O}_4)_3(\text{OH},\text{F},\text{Cl})$, where X can be any of several metal cations such as calcium, barium, sodium, lead and strontium, etc. and Y can be phosphorus, vanadium or arsenic. Apatite minerals which form naturally as the components of all rock types are stable across a wide range of geologic conditions. Apatite can be also produced synthetically by the precipitation reaction or temperature solid state processes obtained from apatite ore (Tanaka et al., 2005). For example, calcium hydroxyapatite (Ca-HAP) or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a sparingly soluble, stable and inexpensive salt can be produced through precipitation from calcium phosphate solution (Sheha, 2007).

In the market, commercially available hydroxyapatite (HAP) powders exhibit a high degree of chemical variability. The crystal lattice quite readily undergoes substitutions, with ions such as CO_3^{2-} , HPO_4^{2-} and F^- often found in place of stoichiometric hydroxyapatite components. Also, calcium to phosphorus molar ratios often vary in various species of hydroxyapatites from the stoichiometric ratio of $\text{Ca/P} = 1.67$. For this reason, it is not uncommon for companies to synthesize their own powders for various uses, such as in reconstruction of human bones and teeth (Wang et al., 2006).

Substitutions within the hydroxyapatite lattice can also induce changes in properties. For instance, fluoride substituting for hydroxide, producing fluorapatite, which result in a more chemically stable compound. Property changes have inspired researchers to deliberately substitute ions to try and modify the properties and behaviour of apatites, such as bone bonding.

Hydroxyapatite powders can be synthesized via numerous production routes, using a range of different reactants. Some processing techniques (Gross, 2006) include:

- Wet chemical methods (precipitation)
- Hydrothermal techniques
- Hydrolysis of other calcium phosphates
- Sol-gel

Of these methods the first two are the most commonly used techniques.

HAP has a great importance for environment processes such as water purification. It has been considered as an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, lower water solubility, high stability under reducing and oxidizing conditions, availability and low cost. HAP has been studied, and found to be good sorption for metal ions such as Zn^{2+} , Cd^{2+} , Pb^{2+} , Fe^{2+} , etc.

The characteristic property of HAP is its ability to undergo isomorphous substitution which may be defined as a replacement of one ion by another in a

crystal lattice without disrupting its crystal structure. This means that it is common for non-stoichiometric structure HAP to exist. The most common substitution involves carbonate, fluoride and chloride substitution for OH⁻ groups. Ca²⁺ can be substituted to some extent by monovalent (Na⁺, K⁺), divalent (Sr²⁺, Ba²⁺, Pb²⁺) and trivalent (Y³⁺) cations. Anion PO₄³⁻ can be replaced by CO₃²⁻, AsO₄³⁻ and VO₄³⁻ (Riberio et al. 2006). These substitutions affect the crystallinity, morphology and lattice parameter of the HAP, which may alter its stability.

In other studies (Singh et al. 2001 & 2006, Sandrine et al., 2007, and Chen et al., 1997), HAP displayed excellent capacity in the removal of lead of up to 0.729 mmol of Pb/g of HAP, representing a removal of 99.9% for that study. HAP was found to be able to remove Zn²⁺ from aqueous solution with an efficiency higher than 98% at initial pH 6 to 8. The initial uptake was rapid and equilibrium was established in 20 min (Sheha, 2007). Siobhan et al. (2001) studied the interaction of cadmium ions in aqueous solution with HAP and conducted a study on eliminating cadmium from polluted water by using HAP. The concentration of Cd²⁺ sorbed on the HAP as a function of initial Cd²⁺ concentration in the solution peaked at 0.82 mol/mol for a concentration of 0.015 mol/l and then decreased subsequently. This is an unusual isotherm because the sorption equilibrium is not achieved within the contact time. In addition, the sorption is limited by the diffusion in solid. Other factors like pH and ionic strength are responsible for the behavior of Cd²⁺ sorption process.

Many studies (Sandrine et al., 2007, Singh et al., 2001 & 2006, and Chen et al., 1997, Ma et al, 1993, and Xu et al., 1994) observed a similar trend in the kinetics studies of sorption rate of the heavy metal by various phosphatic materials. They concluded that there are at least two distinct stages: a rapid decrease in the first 30 min followed by a slow and decreasing rate which is a function of the logarithm of reaction time.

2.3 Lead Contamination

Lead (Pb) is a bluish-white, silvery, or gray metal that is highly lustrous when freshly cut but tarnishes when exposed to air. Lead is an extremely stable element categorized as a heavy metal. It is very toxic to humans and animals. Lead is a neurotoxin and lead poisoning is one of the most common pediatric health problems. (USEPA, 1997).

Lead has been associated with toxic effects in numerous systems in the body. As summarized by the USEPA (1997), the major low level effects of concern include (1) heme biosynthesis and related functions; (2) neurological development and function, (3) reproduction and physical development, (4) kidney function, and (5) cardiovascular function. (Ross, 1996).

Anthropogenic activities of lead contamination include mining and ferrous/non-ferrous smelting operations, Pb-acid battery breaking and manufacturing, combustion of leaded gasoline, salvage yards, urban and Pb-industrial wastes disposal, continuous use of fertilizers, pesticides and use of Pb bullets. (Singh et al., 2006; USEPA, 1997)

2.4 Zinc Contamination

Zinc (Zn) is a trace element needed for peoples' health but too much zinc accumulation can cause adverse effects in human health. Its extensive use and widespread disposal in the environment have resulted in numerous cases of contaminated water and soil. Industries discharging wastewater streams that contain significant concentration of zinc includes steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscous rayon yarn and fiber production, ground wood pulp production, newsprint paper production and rubber thread manufacturing. Zinc is also employed for various applications in metallurgical, textile, electroplating, metal finishing chemical industries. Zinc salts are also used in the inorganic pigments industry (e.g. zinc chromate) and high zinc

levels have been reported in acid mine drainage. Concentrations of zinc can range from less than 1 to more than 48,000 mg/L in various waste streams. (Deliyanni et al., 2007)

2.5 Cadmium Contamination

Cadmium (Cd) is a frequent toxic heavy element pollutant in the water, which can be introduced into surface waters in amounts significant to human health by improper disposal of industrial wastewater. The health effects of cadmium on human health can be either acute (exposure to high concentration), or chronic (by accumulation in liver and renal cortex) (Hammer, 1986). Environmental contamination by cadmium ions is increasingly important for public health and environment protection.

Its contamination to the environment is especially severe in the vicinity of smelters and urban industrialized areas. Cadmium is found with high concentration in the plating effluent and residue, runoff from waste of batteries and paints industries and from the mining activities.

Sub-lethal effects to marine animals recorded at cadmium concentrations of 0.5 to 10 ppb included decreased growth, respiratory disruption, altered enzyme levels and abnormal muscular contractions. Also, sub-lethal effects of cadmium in birds, which were similar to those in other animals, included growth retardation, anemia and testicular damage.

Strict regulations of cadmium composition in wastewater have to be imposed by the government, hence ensuring that the wastewater has to be treated before releasing to the open waters. The US Environmental Protection Agency (EPA)'s Maximum Contaminant Level Goals (MCLG) for Cd has been set at 5 ppb. The pollution is caused by the emission of liquid effluents with harmful cadmium concentrations without any previous treatment, reaching values higher than 10 000 times the legal limit (5 ppb) imposed to this contaminant.

The common method to treat cadmium in wastewater is via hydrogen peroxide oxidation precipitation system at pH 10-11 (Eckenfelder, 1989).

2.6 Different Treatment of CaF_2 Sludge

Different methods have been used to prepare the sludge for solidification and stabilization process. One method is by melting the sludge by feeding the sludge at the top of the furnace with temperatures between 1350 and 1500°C (Huang et al., 2004). This technique involved dropping the sludge into the coke-bed, where the melted material flowed through and it was cooled in air to form slag. The slag is then crushed into finer particles. Huang et al. (2004) mixed 60% (w/w) calcium fluoride (CaF_2) sludge with 40% (w/w) waterworks sludge prior to sludge melting. In this way, the concentration heavy metals within the CaF_2 sludge were diluted. In this study, the sludge was dried in an oven at approximately 40°C to remove moisture, and then ground to fine particles (Lo et al., 2000).

2.7 Apatite and Phosphatic Material as Heavy Metals Adsorption Media

In the past, several studies had been made to explore the feasibility of using pure apatite as a potential reactive media to remediate heavy metal contaminated soils, sediments, mining wastes and contaminated surface and groundwater. Qi et al. (1993) studied the feasibility of using apatite as a potential reactive media for in situ Pb immobilization. However, Pb sorption onto unpure material, such as phosphatic clay, is a more complex process compared to other minerals.

In case of phosphatic clay (Singh et al., 2001 & 2006), precipitation and surface sorption reactions may occur simultaneously due to presence of both apatite and clay minerals. This could be the same case for the CaF_2 sludge used in this study. Pb adsorption on calcium fluoride sludge may be a much more complex process

because it is not a pure natural mineral but it contains many kinds of other minerals and compounds.

Phosphatic clay is a major waste by-product of phosphate strip mining, particularly in Florida, USA. Normally, for each tonnes of phosphate produced, one tonne each of sand and phosphatic clay is also produced. Phosphatic clay has a characteristically high content of natural apatite (about 24–32% of dry weight), which is too fine-grained to recover during processing. Phosphatic clay's favorable characteristics, such as neutral pH, high CEC, presence of natural apatite and smectite suggests that it could be a cost effective sorbent for the removal of aqueous heavy metals from contaminated water as well as for in situ stabilization of heavy metal contaminated soils and sediments (Singh et. al., 2001 & 2006). Application of phosphatic clay could also have the secondary benefits of improving soil fertility, soil structure and moisture-holding capacity particularly when added to sandy soils (Gonzalez et. al., 2006).

2.8 Mechanisms of Aqueous Heavy Metals Removal

The removal of heavy metals could be explained by the theory of sorption. Sorption is by definition a general term describing the attachment of species from a solution to its coexisting solid surfaces. Three types of processes are identified for the sorption phenomenon: surface adsorption, absorption or diffusion into the solid, cation exchange and precipitation or co-precipitation.

Adsorption involves accumulation of substances at an interface, which can either be liquid-liquid, gas-liquid, gas-solid or liquid-solid. The material being adsorbed is termed the adsorbate and the adsorbing phase the adsorbent.

A solid surface in contact with a solution has the tendency to accumulate a surface layer of solute molecules, because of the imbalance of surface forces – an adsorption takes place. The adsorption results in the formation of a molecular layer of the adsorbate on the surface. Often an equilibrium concentration is rapidly

formed at the surface and is generally followed by a slow diffusion onto the particles of the adsorbent.

The rate of adsorption is generally controlled by the rate of diffusion of the solute molecules. The rate varies reciprocally with the square of the diameter of the particles and increases with increasing temperature (Morris & Weber, 1964). For practical application either Freundlich's isotherm or Langmuir's isotherm provide a satisfactory relationship between the concentration of the solute and the amount of adsorbed material.

A second common type of reaction that occurs in an aqueous solution is precipitation reaction, which results in the formation of an insoluble product, or precipitate an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds in the solution.

For example, adding zinc ions can precipitate soluble phosphate ions and results in the formation of insoluble zinc phosphate (Singh et al., 2001):

The extent of precipitation is generally influenced by the concentration of aqueous zinc and the pH values.

In soil science, CEC is the capacity of a soil for ion exchange of positively charged ions between the soil and the soil solution. The concentrations of cations are expressed in centimoles of positive charge per kilogram of soil (cmol(+)/kg). Soil with high levels of swelling clay and organic matter have a CEC of 30 cmol (+)/kg or more. Soil pH is important for CEC because as pH increases (becomes less acidic), the number of negative charges on the colloids increase, thereby increasing CEC.

Studies conducted by Cameron et al. (1997) show that the Temuka soil, which has a high clay content and high CEC, sorbed more than 90% of added Zn^{2+} at all the initial added Zn^{2+} concentrations. In contrast, the Lismore soil, which has a low clay content and a low CEC value, was able to sorb only 43% to 55% of the Zn^{2+} .

2.9 Langmuir Adsorption Isotherm Model

Langmuir adsorption isotherm is a theoretical adsorption isotherm in the ideal case. The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution (Muhammad et al., 1998). The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as (Casey, 1997):

$$Q_e = X_m K C_e / (1 + K C_e) \quad - (2.2)$$

Where:

Q_e = adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent);

C_e = concentration of adsorbate in solution (mg/L);

X_m = maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent);

K = Langmuir constant related to energy of adsorption (L of adsorbent per mg of adsorbate).

The above equation can be rearranged to the following linear form:

$$C_e/Q_e = 1/X_m K + C_e/X_m \quad - (2.3)$$

The linear form can be used for linear regression of the experimental data by plotting C_e/Q_e against C_e . The Langmuir constants X_m and K can be evaluated from the slope and intercept of the linear equation.

2.10 Freundlich Adsorption Isotherm Model

The Freundlich isotherm, an earliest known relationship describing the adsorption equation, is for non-ideal system presented by Freundlich in 1906. The Freundlich isotherm is often expressed as (Casey, 1997):

$$Q_e = K_f C_e^{1/n} \quad - (2.4)$$

Where:

Q_e = adsorption density (mg of adsorbate per g of adsorbent);

C_e = concentration of adsorbate in solution (mg/L);

K_f and n = empirical constants dependent on several environmental factors and n is greater than 1.

The linear form of above equation is formed by taking the logarithmic of both sides as:

$$\ln Q_e = \ln K_f + 1/n \ln C_e \quad - (2.5)$$

The linear form can be used for linear regression of the experimental data by plotting $\ln C_e$ against $\ln Q_e$. The Freundlich constants can be determined from the slope and intercept of the linear equation (Muhammad et al., 1998).

2.11 Aqueous Heavy Metal Removal Observations and Mechanisms

Singh et. al. (2006) suggested that Pb uptake by the phosphatic material in their study followed the linear Langmuir model. The fit of the data to the Langmuir isotherm was observed to be generally good with some deviations at higher concentrations. They suggested that these deviations could indicate the possibility of other mechanisms in addition to precipitation and co-precipitation taking place simultaneously.

In an earlier study (Singh et al., 2001), Zn^{2+} sorption by phosphatic clay with different aqueous concentrations fitted well using the Langmuir model. The maximum sorption capacity was found to be 25.1 mg/g. In this sorption experiment,

the interaction of phosphatic clay with metal solution caused a decrease in solution pH as the amount of sorbed metal increased. Similar observation was found in a study on Zn^{2+} sorption by soils (Cameron et.al, 1997). The increase in Zn^{2+} sorption by the soils resulted in a decrease in soil solution pH. The decrease in pH could be partly due to the hydrolysis of Zn^{2+} to give $\text{Zn}(\text{OH})_2$ and H^+ and partly due to re-adjustment of charge on the soil colloid surfaces as ZnOH^+ ions are sorbed (Barrow, 1986).

The mechanisms or geochemical processes involve in Pb removal by soils or minerals are not clearly understood. Nriagu (1984) suggested a two-step reaction that involves the sorption of Pb on metal oxides, and a subsequent reaction with orthophosphate ions in solution to form lead phosphate as a solid. The most detailed studies involving calcium apatite are those of Suzuki et al. (1982), who proposed that Pb^{2+} in solution substitutes for Ca^{2+} in the apatite structure on a 1:1 basis. However, from the ionic radius point of view, the ionic radius of Pb^{2+} (0.126nm) is much larger than that of Ca^{2+} (0.108nm) (Faure, 1991) and that the crystal lattice parameters of the Pb apatite are significantly different from that of calcium apatite (Roberts et al., 1990). The substitution of Ca^{2+} in apatite structure by Pb^{2+} may not be that easy and on a 1:1 basis.

There are several possible reactions capable of removing Pb from solutions. Among others, surface adsorption, ionic exchange or substitution, and precipitation are the most possible mechanisms (Xu and Schwartz, 1994). In fact, Singh et al. (2006) deduced that Pb precipitation remained the dominant retention mechanism until the immediate supply of PO_4^{3-} was used up in the system.

Lead removal efficiency for phosphatic material was observed to be controlled mainly by the dissolution of its phosphatic clay associated fluoroapatite $[\text{Ca}_{10}(\text{PO}_4)_5\text{CaCO}_3(\text{F},\text{Cl},\text{OH})_2]$ followed by subsequent precipitation of geochemically stable pyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2]$, because these may possess high potential to interact with aqueous Pb during the sorption experiment (Singh et. al., 2006). The phenomenon was further confirmed by both X-ray

diffraction (XRD) and scanning electron microscopic (SEM) analysis of the phosphatic clay material after its interaction with aqueous Pb solutions at the highest concentration (approximately 200mg/L). SEM analysis revealed an amorphous to cluster of lead phosphate crystals.

The behavior of these can be summarized in terms of the following chemical reactions for the dissolution of hydroxyapatite (HAP) and the precipitation of hydroxypyromorphite (HPM) (Xu and Schwartz., 1994),

HAP dissolution:

HPM precipitation:

In general, the removal of aqueous lead by HAP is initially fast. In the study of Singh et al. (2006), 95.6ppm of Pb was almost completely removed from solution by hydroxyapatite after 2 min. They observed that the Pb sorption kinetics onto phosphatic clay was biphasic, i.e. initially fast reactions followed by slow and continuous Pb removal reactions. They deduced that the initial sharp decrease in solution pH might be combined hydroxylapatite dissolution/Pb-hydroxylapatite precipitation reaction rather than the dissolution or dissociation of CO_2 or release of protons via surface exchange between Pb^{2+} and H^+ . They also suggested that the slow reactions might include mechanisms like, surface precipitation or sorption to available sites, co-precipitation and diffusion to internal sites. Their studies concluded that it is likely that multiple slow reaction mechanisms were responsible for the slow-phase Pb sorption onto phosphatic clay, as the material contains a mixture of several minerals containing different types of sorption sites. It remained complicated to quantify the contribution of individual Pb removal mechanisms.

In their earlier study (Singh et. al., 2001), the observed loss of Pb from solution was coupled with a gain of Ca and formation of fluoropyromorphite, indicating two

potential mechanisms: apatite dissolution and precipitation of fluoropyromorphite or exchange of Pb with Ca within the apatite. They also suggested that if the correlation of Pb loss and Ca gained in the solution is nowhere near unity (1.0), then it would suggest other retention mechanisms in addition to cation exchange, such as surface complexation or others. Lead removal efficiency of phosphatic clay increased with (i) increasing pH, (ii) sorbent amount and (iii) decreasing ionic strength.

Metal sorption depends on pH because of resulting changes in metal species and surface charge of adsorbing media. Mineral surfaces become more negatively charged with increasing pH and surface groups that have lost protons may be able to sorb cations more readily (and anions less readily) from solutions.

Generally, studies related to the effects of ionic strength on Pb sorption are largely limited to pure mineral systems. In such systems, the decrease in Pb sorption with increasing ionic strength is attributed to competition between Pb and other cations for available sorption sites in the background electrolyte solution, thus reducing Pb uptake. This phenomenon is mainly due to (i) change in the activity of free Pb^{2+} and PbOH^+ due to ion pair formation and effect of ionic strength on pH, (ii) competition for the available sorption sites on clay surfaces, and (iii) changes in the electrostatic potential in plane of sorption.

2.12 Comparison of Lead, Cadmium and Zinc Interactions with Phosphatic Materials

Sandrine et al. (2007), Singh et. al. (2001) and Chen et al. (1997) studied the heavy metals (Pb, Cd and Zn) interactions with phosphatic clay. Their results showed that the amounts of metals sorbed onto phosphatic clay material decreased in the order of $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ in their batch equilibrium technique sorption experiments. They suggested that the sorption mechanisms for Pb, Cd and Zn might include co-precipitation. However, on the basis of available information, they were unable to confirm the formation of any new amorphous or crystalline phase formed after

sorption of Cd and Zn. Sorption isotherms for their studies were characterized by decreasing slopes as aqueous metal concentration increased beyond the threshold, indicating high affinity of the adsorbent for high concentrations of the adsorbate. They commented that simultaneous changes in solution pH and Ca concentration made it difficult to determine whether the increase in Ca concentration was the consequence of ion exchange with heavy metals, further phosphatic clay dissolution due to decrease in pH, or other mechanisms.

Results of desorption experiments conducted under a wide pH variation in extracting solution (pH range from 3 to 10), showed that a large proportion of metals sorbed stayed intact. Desorption rates were the exact opposite of sorbed rates i.e. $Zn^{2+} > Cd^{2+} > Pb^{2+}$. It seemed that the fluoropyromorphite formed during the Pb sorption process remained more stable than surface complexes of Zn and Cd. This suggested that the decrease in metal desorption with increase in sorbed amount may be accounted for by the increase proportion of less readily desorbed solid phases (like precipitates) formed during the sorption process.

LeGeroes and LeGeroes (1984) stated that cations with ionic radii smaller than Ca^{2+} (0.099 nm) have a lesser chance to be incorporated into an apatite structure compared with cations with larger ionic radii. Hence, precipitation of Zn^{2+} (0.069 nm) with Ca^{2+} would be less likely compared to the larger cations of Pb^{2+} (0.118 nm) and Cd^{2+} (0.097 nm).

2.13 Sequential Extraction

Although the sorption efficiency must be taken into account, the condition and future handling of the sludge after heavy metal sorption are also to be considered. Sequential extraction methods can be used to analyze the redistribution of metals after heavy metals sorption treatment. In general, it is noted that the non-residual fraction is more easily leached out than the residual fraction (Barona et al., 2000).

Selective sequential extraction (SSE), also known as sequential chemical extraction, was carried out on the samples to study the fractionation of the metal species. The modified 3-stages SSE scheme recommended by the Standards, Measurements and Testing programme of the European Union (SM&T – formerly Community Bureau of Reference or BCR) was adopted. A sample work flow is presented in Figure 2.1 for reference. This procedure was favored by many recent research works. (Helen et al, 2000, Maria et al, 2002, Valarie et al, 2006, Lim et al., 1997, Li et al., 2001, and Tokalioglu et al., 2003).

Figure 2.1 Modified BCR procedure workflow chart

Chapter 3

Materials & Methods

3.1 General Chemicals and Apparatus

All experiments were conducted in an air-conditioned laboratory condition. The temperature was approximately $25\pm 5^{\circ}\text{C}$ and humidity of approximately $70\pm 5\%$ throughout the day.

Labware used for each experiments were rinsed with tap water (and non-phosphate containing detergent if necessary), soaked in diluted HNO_3 overnight, and then rinsed with distilled water. Deionised water from Millipore DirectQ Water Purification Systems was used in rinsing and preparation of all solutions.

All chemicals used in the experiments were analytical reagent (A.R.) grade. The stock solutions of heavy metals were prepared using nitrates (i.e. $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$).

A reciprocal shaker was used (30 ± 2 rpm) where dynamic mixing was required in the experiments. Centrifugation was performed using a Kubota 8410 centrifuge at 3300 rpm for approximately 10min. The solid to liquid ratio for all sorption and desorption experiments were kept at 1:200 (e.g. 0.1g: 20ml).

All solutions/ supernatants were filtered through $0.45\mu\text{m}$ pore size membrane filters, preserved with concentrated HNO_3 acid, and kept in a fridge, prior to elemental analysis. Cations analysis was conducted using the Inductive Coupled Plasma (ICP) Emission Spectrometry (Model Optima 2000 DV – Perkin Elmer).

3.2 Preparation of Sludge

CaF₂ sludge was collected from a local flat panel display manufacturer, AFPD Pte Ltd. AFPD Pte Ltd produces a substantial amount of CaF₂ sludge through coagulation, and their daily sludge production rate was estimated at 10,000 kg of dewatered sludge per day.

Prior to the preparation of the sludge sample for tests, the sludge cakes was broken up into smaller pieces and dried in an oven set at 40±5°C for about 3 days (or until the moisture content of the soil reduced to less than 2%).

The dried sludge was lightly pounded manually using a stone mortar to loosen up the fine particles. The lightly pounded dried sludge was sieved through a 250µm sieve with the help of a mechanical shaker. The dried fines that passed through the 250µm sieve was collected and kept in air-tight plastic bags and containers for all testings. In this project, the maximum size of the sludge particles was limited to 250µm.

3.3 Sludge Characterization

Sludge characterization analysis was carried out on the sludge fines. Moisture content, pH, loss on ignition, XRD, particle size analysis, cation exchange capacity (CEC), surface charge density, BET surface area, and micropore volume analysis and chemical content analysis was carried out.

Table 3.1 summarizes the physical and chemical properties of the sludge fines used in this study:

Table 3.1 Properties of CaF₂ sludge

Sludge Property	Analysis	Remarks
Sludge Colour	Greyish White	
Moisture Content (Sludge Cake)	61.6%	BS 1337 (1990)
Specific Gravity	2.102	BS 1337 (1990)
Particle size distribution	Figure 3.1	(Malvern Microplus Mastersizer MAF5001)
pH at 22°C	7.22	US EPA Method 9045D (2002) (Mettler Toledo)
Elemental Concentration mg/Kg soil):		Atomic Emission Spectrometer (Perkin-Elmer USA ICP-AES 400)
Ca	336,052	&
P	94,257	Ion Chromatography (IC)
F	54,200	(Dionex ICS-1000 coupled with AS-15 resin column)
Al	3379	
Mg	908.0	
Si	2,112	
Na	5,326	
Fe	307.9	
K	141.0	
Ba	76.5	
Cr	5.65	
Cu	23.1	
Mn	47.6	
Ni	9.58	
Zn	71.0	
S	#N.D.	
Mo	N.D.	
As	N.D.	
Sr	N.D.	
Co	N.D.	
Ag	N.D.	
Pb	N.D.	
Cd	N.D.	
Loss on Ignition (%m/m):		Heiri et al. (1999)
Up to 550°C (Organic Content)	14.25%	
550°C to 950°C (Carbonate content)	3.48%	
CEC (cmol/kg)	36.226	US EPA Method 9081 (1986)
BET Surface Area (m ² /g)	31.63	(QuantaChrome Autosorb-1
BJH Micropore Volume (cm ³ /g)	1.905x10 ⁻²	Micropore : AS1C-LP)
SEM	Figure 3.4	JSM-6360 & JED-2300
Mineral Composition	Figure 3.2	X-Ray Diffractometer (XRD) (Bruker AXS D8 Advance)

#N.D. – Not Detected or below detection limit of equipment

3.3.1 Moisture Content

The moisture content of the sludge cake was determined by determining the amount of weight (water) loss of the fresh sludge cake sample, after being broken up and dried in the oven at around 100°C for a few hours, or until there was no further change in the weight of the sludge. (BS1377, Part 2, 1990)

The moisture content was calculated using the following equation:

$$\text{Moisture Content} = \frac{(M_{\text{wet}} - M_{\text{dry}})}{M_{\text{wet}}} \times 100 \% \quad - (3.1)$$

where

M_{wet} = mass of fresh sludge cake before drying in oven

M_{dry} = mass of sludge cake after drying in oven

The moisture content of the original sludge cake was 61.6%. Although steps had been taken to make sure that minimal moisture was loss between the time the sludge cake was collected and the day of testing, the actual moisture content on site would still be expected to be slightly higher due to unavoidable moisture loss during the delivery transfer and escape of moisture from the sludge containment bags.

3.3.2 Particle Size Distribution

The particle size distribution analysis of the sludge fines (after crushing and sieving) and synthetic hydroxyapatite (HAP) was analyzed with the Malvern Microplus Mastersizer – Model MAFF5001.

The master sizer consists of an optical unit to collect the raw data and measure the particles sizes, and a linked computer unit to run the Malvern software for analysis. The mastersizer works on the basis of the Mie theory, which was developed to

analyse the way light is scattered by spherical particles and which also deals with the way light passes through or absorbed by the fine particles.

In order to carry out the experiment, the samples have to be mixed with the dispersant liquid in a sample unit housed in the optical unit. The mixture was then pumped into a measurement cell to allow the analyzing laser beam to be passed through. A sweep snap-shot of the particles scatter pattern is then be taken by a detector. This detector is made up of many individual sub-detectors, which are responsible for collection of scattered light over a particular angle range. Generally, over 2000 sweeps are made for each sweep (i.e. 2ms). To allow data adjustment for background contamination in the dispersant liquid, the window and the optics, calibration is usually required by effecting the background measurement of the dispersant liquid.

The combined particle size distribution curve of the CaF₂ sludge and the synthetic HAP samples are presented in Figure 3.1.

(B)

Figure 3.1 Particle size distribution of CaF₂ sludge fines (A) Volume (%) vs Particle size (μm) & (B) Cumulative Volume (%) vs Particle size (μm)

As compared to the synthetic HAP samples, the CaF₂ sludge samples consists of finer particles. A majority of the sludge fines falls below the size of 20 μm, which accounts for more than 60% of the total volume as compared to the HAP samples which has 60% of the particles falling below 60 μm. The HAP sample has 100% of the particles falling below 250 μm, which supported the choice of choosing the sieve size 250 μm for the CaF₂ sludge.

3.3.3 pH of sludge

Sludge pH was measured using a glass electrode pH meter (Model Mettler Toledo) in an aqueous slurry (US EPA Method 9045D, 2002). The slurry was prepared by mixing the fresh sludge sample with ultra pure water, such that the solution to solid ratio was 2:1. The slurry was mixed using a magnetic stirrer to ensure that the slurry was homogeneous throughout.

The pH has a great effect on the solute concentration and sorption/desorption of contaminants in the sludge. pH adjustment during remediation can greatly reduce the mobility of some species or conversely dissolve contaminants for extractions.

The pH of the sludge slurry was measured to be 7.22 at 22°C. The sludge is almost neutral in pH (slightly alkaline), which is a favorable characteristic, as a cost effective sorbent for the removal of aqueous heavy metals from contaminated water as well as for in situ stabilization of heavy metal contaminated soils and sediments.

Being slightly alkaline, it could imply that there is not a substantial amount of H^+ ions present attracted to the sludge particles' surfaces. It is therefore advantageous in the efficiency of heavy metals sorption.

3.3.4 Elemental Concentration

In this project, the Inductive Coupled Plasma (ICP) Emission Spectrometry (Model Optima 2000 DV – Perkin Elmer) was used to determine the concentration of various heavy metal elements. ICP was used to measure the concentration of heavy metals of the spiked solution used in the experiments, and in the solution after adsorption and extractions.

Prior to ICP analysis, a strong acid (such as HNO_3) was added to preserve the samples and if required, the samples for analysis were digested/fused using the Microwave Digestion (closed vessels) method.

Procedures adopted in this project for sludge digestion/ fusion using microwave digestion (closed vessels) method (Model Anton Paar Multiwave 3000 – Perkin Elmer Precisely) was as follows:

0.1g or 0.2g of sludge sample was placed into the specific vessel tubes. Aproximately 4-6ml of concentrated HNO_3 acid was added into the vessels to

oxidize the biological materials. The vessels were sealed using the safety disks and placed into the 'bomb jacket' with an airtight screw cap. The vessels were then arranged onto the circular rotor and placed in the microwave for heating. The average time taken for heating was about 35minutes.

After cooling, the fused sample solution was transferred into a volumetric flask and diluted to volume with RO/DI water. (If required, hydrofluoric acid may be added to decompose the silicates and other residue deposits in a second stage of digestion before dilution.)

The diluted solution was filtered through a 0.45 μm Whatman filter paper. The filtrate collected were kept in polyethylene (PE) bottles and preserved in the refrigerator for further ICP analysis.

Table 3.2 shows the background concentration of the various elements in the sludge. The relatively high concentration of Ca and P reflect the presence of apatites as its major constituents. The concentration of F will be assessed to confirm the presence of fluoroapatites.

The concentrations of the other heavy metals were insignificant, indicating that the sludge is relatively unhazardous. The sludge has very high concentration of Si, Na and Al, which is typical in most industrial wastewater sludge due to the high sand content.

Table 3.2 Elemental Concentration (Sludge)

Elements	Std. Dev. (mg/kg sludge)	Relative Std. Dev. (%)	Mean (mg/kg sludge)
Ca	16349	4.86	336,051.8
P	4925	5.23	94,256.7
F	2063	3.81	54,200.0
Al	0.127	0.47	3,379.0
Mg	0.017	0.24	908.0
Si	212.5	10.06	2,112.3
Na	383.3	7.20	5,326.2
Fe	0.012	0.47	307.9
K	0.003	0.24	141.0
Ba	0.0005	0.08	76.5
Cr	0.001	1.93	5.6
Cu	0.001	0.46	23.1
Mn	0.001	0.32	47.6
Ni	0.001	0.98	9.6
Zn	0.001	0.17	71.0
S	-	-	#<<
As	-	-	#<<
Mo	-	-	#<<
Sr	-	-	#<<
Co	-	-	#<<
Ag	-	-	#<<
Pb	-	-	#<<
Cd	-	-	#<<

#<<. – Not Detected(N.D.) or below detection limit of equipment

3.5.5 Loss on Ignition (LOI)

An ignition test can be used to approximate the organic content of the sludge samples. The loss on ignition reported includes organic matter and some soluble carbonate salts. The sequential loss on ignition test procedure adopted is adapted from a method reviewed by Heiri et al. (2001).

In this study, the sludge was dried at 100°C in an oven, combusted at approximately 550°C, and then ignited at approximately 950°C. Both loss on ignition at 550°C and

950°C were reported in this study. In first reaction, organic matter is oxidized at approximately 550°C to carbon dioxide and ash. In second reaction, carbon dioxide is evolved from carbonate at approximately 950°C, leaving oxide. The weight loss during the reactions is measured by measuring the samples before and after heat ignition.

The LOI is calculated using the following equations:

$$\text{LOI}_{550} = \frac{W_{100} - W_{550}}{W_{100}} \times 100\% \quad - (3.2)$$

$$\text{LOI}_{950} = \frac{W_{550} - W_{950}}{W_{100}} \times 100\% \quad - (3.3)$$

Where:

LOI_{550} is the LOI at 550°C,

LOI_{950} is the LOI at 950°C,

W_{100} is the dry weight of the sludge samples before organic combustion,

W_{550} is the dry weight of the sample after organic combustion at 550°C

W_{950} is the dry weight of the sample after ignition to 950°C

Loss on ignition for the sludge was 14.25% at 550°C (organic content) and 3.48% at 950°C (carbonate content).

Taking a weight of 44g/mol for carbon dioxide and 60g/mol for carbonate (CO_3^{2-}), the weight loss by LOI at 950°C should give the weight of the carbonate in the original sample theoretically.

3.3.6 Cation Exchange Capacity

CEC is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the sludge. The method used in this study was modified based on the procedure put forward in the Agronomy by American Society of Agronomy (Soil Science of America, 1982), suggested by Rhoades (1977).

In this study, the method adopted include the process of (i) saturation of cation exchange sites with 1M NaOAc and pH stabilization (pH 2~8) with HNO_3 or

NaOH, (ii) saturation of cation exchange sites with 1M NaCl 3 times (30min of agitation each for initial 2 times and then overnight for pH stabilization for the last time) and (iii) extraction with 0.5 M $\text{Mg}(\text{NO}_3)_2$ 3 times (overnight). Individual steps were conducted with the sludge:solution ratio of 1:2 in duplicates. The total Na^+ displaced into the solution was measured using the ICP-OES.

CEC is a measurement of the capability of the sludge to adsorb (and release) cations. It is an important parameter at sites contaminated by heavy metals, because heavy metals will often replace exchangeable ions such as sodium, potassium, calcium, and magnesium that exist naturally in the sludge.

Figure 3.2 indicates that the CEC of CaF_2 sludge is relatively constant (approximately 36.6 cmol/g sludge) in the pH range between 3.0 and 7.0. There is a slight dip in CEC when pH is <3.0 and a slight increase in CEC when pH is >7.0. The slight dip in CEC when pH is <3.0 could be attributed to the positive zeta potential detected (see Figure 3.7). A positively-charged surface offers less attraction to positive cations which results in reduced cation exchange interactions .

Figure 3.2 CEC of CaF_2 Sludge

3.3.7 Brunauer Emmett and Teller (BET) Surface Area and Micropore Volume

Quantachrome Autosorb Automated Gas Sorption System (Autosorb for Windows Version 1.20) was used in this research study to analyse the BET surface area and micropore volume (BJH Method Cumulative Desorption Pore Volume) of the sludge samples. The analysis includes the internal surfaces present in microcracks or pores open at only one end, thus giving surfaces areas and volumes that are typically two to three times higher than most common air permeability methods.

The BET surface area of the sludge fines was $31.63 \text{ m}^2/\text{g}$ sludge and the BJH micropore volume was $1.905 \times 10^{-2} \text{ cm}^3/\text{g}$ sludge. For comparison, synthetic hydroxyapatite powder was also analyzed. The BET surface area of HAP was $24.34 \text{ m}^2/\text{g}$ sludge and the BJH micropore volume was $1.633 \times 10^{-2} \text{ cm}^3/\text{g}$ sludge. At a higher surface area and micropore volume, the CaF_2 sludge fines should possess better adsorption efficiency than the synthetic HAP.

3.3.8 X-Ray Diffraction Analysis

The mineral phases of the samples were identified through x-ray diffractometer (XRD) measurements (Model: Bruker AXS D8 Advance), 34 kV, 20 mA. Powder XRD is one of the primary techniques used to examine the physio-chemical make-up of unknown solids.

The powdered sludge sample is placed in a holder and is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded by a detector.

Once the diffraction patterns are obtained, both manual matching of the peak positions (the reflection angles) and a computer-aided search for the compounds are performed.

The analysis conducted on the raw sludge samples is presented in an intensity -2θ format in Fig 3.3.

Figure 3.3 XRD analysis on CaF₂ sludge

The XRD analysis shows that the sludge contained primarily of hydroxyapatites (hydroxylapatites) and fluoroapatites. All these mineral compounds are very effective in heavy metals adsorption.

3.3.9 Scanning Electron Microscopy

Particle morphology of the sludge was assessed by scanning electron microscopy (SEM, JSM-6360) and elemental spectra were obtained using energy-dispersive X-ray spectroscopy (also known as energy dispersion spectroscopy (EDS), JED-2300) during SEM observations.

SEM/EDS elemental mapping observations as shown in Figure 3.4 (A) and (B) further reinforced the existence of apatites (even spread of Ca, P and F shown in Figure 3.4(B)) in the sludge.

Figure 3.4(A) Elemental spectrum of sludge obtained by energy-dispersive X-ray analysis

Figure 3.4(B) Back scattered SEM micrograph of sludge and SEM element dot map of F, P and Ca in sludge.

3.3.9 Zeta Potential

Almost all particulate or macroscopic materials in contact with a liquid acquire an electronic charge on their surfaces. Zeta potential is the electrical potential that exists at the shear plane of a particle, which is some small distance from the surface as illustrated in Figure 3.5.

Figure 3.5 Illustrations of Zeta Potential on a colloidal particle

The determination of the sludge particle zeta potential was conducted using a BrookHaven Zeta Potential analyzer. The particles were suspended (approximately 1g/L) in 1mM KCl electrolyte solution, with a pH range of 2 to 11. For each data 10 runs at 20 cycles per runs were conducted.

Figure 3.6 shows the zeta potential of CaF_2 sludge at various pH values. The zero point charge (ZPC) was at about pH 2.5. At pH above the ZPC, the zeta potential

would be negative. Negative zeta potential elements provide an important advantage for the application in removing heavy metals. Being negatively charged on the surface, the sludge particles can additionally attract and possibly precipitate positively charged cationic heavy metals.

Figure 3.6 Zeta Potential (mV) vs pH of CaF₂ sludge

3.4 Sorption Experiments

The respective contaminant stock solutions, containing Cd(NO₃)₂, Pb(NO₃)₂ and Zn(NO₃)₂, were prepared with RO/DI water according to the desired heavy metal loadings for the adsorption experiments. The solutions were then stored into 1-Litre PE bottles. From each batch of stock solutions prepared, about 20ml was kept for ICP analysis for heavy metals concentration. All pH adjustments were performed by addition of either HNO₃ or NaOH solution.

For adsorption experiments on the effect of background electrolyte, various quantities of KNO_3 powder were added to the stock solution to achieve the desired concentration (ranging from 0.005M to 0.1M).

All metal sorption studies were conducted using batch experiments. For typical sorption experiments, 0.1g of CaF_2 sludge fine powder ($<250\mu\text{m}$) was added into 50ml polycarbonate centrifuge tubes, each containing 20ml of contaminant solution to achieve a solid to solution ratio of 1:200(g/ml). To ensure uniform contact and mixing of the sludge powder and the solution, the capped tubes were placed in a reciprocating shaker at 30 ± 2 rpm for the desired duration. The time for typical sorption tests was 24 hr, and up to 72 ± 1 hr for kinetic studies. After the test, the pH of the suspension was monitored. A centrifuge machine (Kubota 8410) was utilized to separate the sludge from the solution at approximately 3300 rpm for about 10min. The supernatant were filtered through $0.45\mu\text{m}$ pore size filter and preserved in HDPE bottles. The filtrate were acidified with HNO_3 and stored in the chiller prior to ICP analysis.

The amount of adsorbed metals was taken as the difference between the amounts added initially in the contaminant stock solution, and that remaining after reacting for the desired duration. All measurements were conducted in duplicates or triplicates.

The residues in the centrifuge tubes were rinsed with approximately 20ml of DI water to remove excess supernatant. The suspension was centrifuged and the supernatant was drained out as much as possible. This procedure was also adopted prior to SSE studies to ensure that the heavy metals in the supernatant (in excess) were removed completely. The residues were dried in oven at $40\pm 5^\circ\text{C}$ and kept for XRD analysis.

3.5 Selective Sequential Extraction (SSE) Experiments

SSE, or known as sequential chemical extraction, was done on the sludge samples after treatment with the spiked solutions.

The modified 3-stage SSE scheme recommended by the Standards, Measurements and Testing programme of the European Union (SM&T – formerly Community Bureau of Reference or BCR) was adopted for the samples.

Table 3.3 BCR Selective Sequential Extraction (SSE) Scheme (modified).

Fraction	Extractant	Conditions	Presumed Extracted Phase
#1. Exchangeable, Water and Acid Soluble	0.11 M CH ₃ COOH (L/S = 40)	16 h Room temp	Metals bound to soil carbonates
#2. Reducible	1.0 M NH ₂ OH.HCl pH adjustment with HNO ₃ (L/S = 40)	16 h pH 2 Room temperature	Metals bound to oxides
#3. Organic/ Oxidizable	(i) 30% w/v H ₂ O ₂ (L/S = 5) (ii) 30% w/v H ₂ O ₂ (L/S = 5) (iii) 1.0 M NH ₄ OAc pH adjustment with HNO ₃ (L/S = 50) (Total = 40 mL)	(i) 85C, 1 h + 1 h evaporation (ii) 85C, 1 h + evaporation to near dryness (iii) room temp, 16 h pH 2	Metals bound to organic matter and sulfides
#4. Residual	HNO ₃	Microwave assisted digestion	Remaining portions not extracted by the above extractants

The SSE scheme adopted in this study would fractionate the heavy metals immobilized by the sludge into four fractions: (i) exchangeable, water and acid soluble (e.g. carbonates/ specifically sorbed fractions), (ii) reducible (oxide-bound), (iii) oxidisable (e.g. organic substances and sulphides), and (iv) residual. The SSE procedure is summarized in Table 3.3.

Chapter 4

Results and Discussion

4.1 Background

The effects of initial heavy metal concentration, pH variation on the sorption tests, ionic strength, time variation (kinetic studies) were evaluated using batch experiments. The results are presented in this chapter.

Typical experimental results have been presented by plots of the extracted metal concentrations from the aqueous solution. Extraction efficiencies were calculated by taking the ratio of the extracted metal concentration in solution to the total initial stock solution's concentration

4.2 Sorption Isotherms

The amount of heavy metals removed per unit mass of CaF_2 sludge (mg/g) was plotted as a function of equilibrium heavy metals concentration(ppm) for 24hrs heavy metals sorption experiments with 0.05M KNO_3 and without KNO_3 electrolyte solution.

Equations 2.2 to 2.3 were applied to plot the Langmuir adsorption isotherm. The linear form was used for linear regression of the experimental data by plotting C_e/Q_e against C_e , in which Langmuir constants X_m and K can be evaluated from the slope and intercept, respectively of the linear equation.

Equations 2.4 to 2.5 were applied to plot the Freundlich isotherm. By plotting $\ln C_e$ against $\ln Q_e$, the linear form is used for linear regression of the experimental data. The slope and intercept of the linear equation would then be obtained from the graph to obtain the Freundlich constants, k_f and n .

4.2.1 Lead Sorption Isotherms

As shown in Figure 4.1, the sorption isotherms are characterized by decreasing slopes as equilibrium Pb concentration increases, until a threshold is reached. This indicates high affinity of the sorbent at low concentrations of the sorbate. Similar observations were also observed with phosphatic clay (Singh et al., 1997 and 2006). However the present study showed more promising results of lead adsorption using CaF_2 sludge.

The presence of background ionic concentration of 0.05M KNO_3 does not seem to have any significant effect on the sorption capacity for Pb concentration below 1000ppm. For initial Pb concentration below 1000ppm, the sorption isotherms indicate that Pb sorption capacities of CaF_2 sludge with and without KNO_3 electrolyte solution are almost the same. However, for subsequent Pb concentration above 1000ppm, Pb sorption capacity of CaF_2 sludge without KNO_3 electrolyte solution is much bigger than the one with 0.05M KNO_3 electrolyte solution, almost twice as much sorption capacity for the highest Pb concentration. The maximum sorption was limited to 250 mg/g with the background ionic interference.

The decrease in Pb sorption with increasing background ionic strength could be attributed to competition between Pb and other cations in the background electrolyte solution for available sorption sites, thus reducing Pb uptake. With the addition of KNO_3 ionic strength, we can clearly observe the decrease in Pb sorption solution from Figure 4.1.

Figure 4.1 Sorption isotherms for Pb onto CaF₂ sludge

The equilibrium sorption data (Tables 4.1 and 4.2 show the adsorption test results for Pb without KNO₃ and with 0.05M KNO₃, respectively) were fitted to the linear form of the Langmuir equation and Freundlich equation, and are plotted in Figures 4.2 and 4.3.

Table 4.1 Batch adsorption test results for Pb without KNO₃

Intended Ce (ppm)	Ce (ppm)	24hr Ce (pp m)	Qe [1] (mg/g of CaF ₂ sludge)	Ce/Qe	lnCe	lnQe
30	30.58	0.207	6.07	5.03	3.42	1.80
150	154.3	0.415	30.78	5.01	5.04	3.43
600	595.7	0.563	119.03	5.00	6.39	4.78
1800	1850	10.64	367.87	5.03	7.52	5.91
3500	3644	1301	468.60	7.78	8.20	6.15

Table 4.2 Batch adsorption test results for Pb with 0.05M KNO₃

Intended Ce (ppm)	Ce (ppm)	24 hr Ce (ppm)	Qe [1] (mg/g of CaF2 sludge)	Ce/Qe	lnCe	lnQe
30	23.36	0.044	4.66	5.01	3.15	1.54
125	118	0.069	23.59	5.00	4.77	3.16
160	162.8	0.128	32.53	5.00	5.09	3.48
450	453.5	0.313	90.64	5.00	6.12	4.51
1500	1423	212.5	242.1	5.88	7.26	5.49
3500	3758	2540	243.6	15.43	8.23	5.50

(A) Langmuir isotherm for Pb 1-day adsorption

(B) Freundlich isotherm for Pb 1-day adsorption

Figure 4.2 (A) Langmuir isotherm for Pb adsorption and (B) Freundlich isotherm for Pb adsorption; 30~3500ppm Pb solution without KNO₃

Figure 4.3 (A) Langmuir isotherm for Pb adsorption; (B) Freundlich isotherm for Pb adsorption; 30~3500ppm Pb solution with 0.05M KNO_3

Table 4.3 summaries the comparison of the correlation coefficient (R^2) for data fitted using the Langmuir isotherm model and Freundlich isotherm model. The fit of data is observed to be closer to the Freundlich isotherm model (R^2 closer to unity)

than that using the Langmuir isotherm. This suggests that Pb sorption process by CaF₂ sludge is non-ideal linear adsorption.

Singh et al. (2006) suggested that the deviations from the Langmuir equation could also indicate the possibility of other mechanisms in addition to precipitation and co-precipitation. The presence of other minerals other than apatites may increase the sorption capacity for Pb.

Table 4.3 Linear equations for Langmuir and Freundlich isotherms for Pb soption

Langmuir isotherm			Freundlich isotherm	
	linear equation	correlation coefficient R ²	linear equation	correlation coefficient R ²
Without KNO ₃	Y = 0.0008x +4.4783	0.7936	y = 0.9387x -1.3264	0.9926
With 0.05M KNO ₃	Y = 0.0028x +4.1365	0.9219	y = 0.8201x - 0.7866	0.9594

Note: for Langmuir data x=Ce and y=Ce/Qe; for Freundlich data x=ln(Ce) and y=ln(Qe)

The Langmuir constant X_m (maximum adsorption capacity) and the Freundlich constant K_f were obtained from the linear Equations 2.2-2.5. The values are summarized in Table 4.4. Relative large X_m (up to 1250 mg/g without background ionic electrolyte) implies that the adsorption capacity of aqueous Pb by CaF₂ sludge in study is relatively good. The Freundlich constant, n, were larger than unity, further implying good adsorption of Pb onto the CaF₂ sludge.

Table 4.4 Comparison of the isotherm constants for Pb sorption

KNO ₃	Langmuir Constant X _m (mg/g)	Langmuir Constant k	Freundlich Constant K _f	Freundlich Constant n
Without	1250.000	5598	0.265	1.065
With 0.05M	357.143	1477	0.455	1.219

The CaF₂ sludge, contains not only pure apatites, such as hydroxyapatite and fluorapatite, but also some other unknown compounds as well. This made

deciphering the mechanisms of Pb sorption more complex. There are several possible reactions capable of removing Pb from the solutions. Among others, surface adsorption, ionic exchange or substitution and precipitation are most possible mechanisms (Xu, 1994).

4.2.2 Zinc Sorption Isotherms

The amount of Zinc removed per unit mass of CaF_2 sludge (mg/g) plotted as a function of equilibrium Zinc concentration (ppm) for 24hrs zinc sorption experiments with 0.05M KNO_3 and without KNO_3 electrolyte solution are shown in Figure 4.4.

Figure 4.4 Sorption isotherms for Zn onto CaF_2 sludge

Similar to the lead sorption isotherms, the sorption pattern is also characterized by decreasing slopes as equilibrium Zn concentration increases, until a threshold is reached. This indicates high affinity of the sorbent at low concentrations of the sorbate.

The trend seems to indicate approximately more than ten to twenty folds lower in adsorption capacity of Zn as compared to Pb. Here the threshold of the Zn seems to be below 25mg/g of sludge, which was much lower than the 450 mg/g of Pb sorption attained. Background ionic strength (0.05M KNO₃) does not seem to have any significant effect on the sorption capacity for Zn concentration below approximately 200ppm. With the background ionic interference, the sorption capacity seems to have been reduced by almost a third.

The Zn sorption data had also been analyzed using the Langmuir model and Freundlich model (Cassey, 1997) to evaluate which one of the two models is more applicable for Zn sorption by CaF₂ sludge. The sorption test results for Zn without KNO₃ and with 0.05M KNO₃ (Table 4.5 and 4.6 respectively) were tabulated and were fitted to the linear form of the Langmuir equation and Freundlich equation. The equilibrium sorption datas were then plotted in Figure 4.5 and 4.6.

Table 4.5 Batch adsorption test results for Zn without KNO₃

Intended Ce (ppm)	Ce (ppm)	24hr Ce (pp m)	Qe [1] (mg/g of CaF ₂ sludge)	Ce/Qe	lnCe	lnQe
50	56.52	3.878	10.53	5.37	4.03	2.35
100	112.2	28.13	16.82	6.67	4.72	2.82
500	555.1	431.7	24.67	22.50	6.32	3.21
1000	1040	924.7	23.09	45.05	6.95	3.14
2000	2046	1925	24.17	84.62	7.62	3.19
3000	3067	2942	24.86	123.36	8.03	3.21

Table 4.6 Batch adsorption test results for Zn with 0.05M KNO₃

Intended Ce (ppm)	Ce (ppm)	24 hr Ce (ppm)	Qe [1] (mg/g of CaF ₂ sludge)	Ce/Qe	lnCe	lnQe
50	53.67	21.98	6.34	8.47	3.98	1.85
100	95.60	46.58	9.80	9.75	4.56	2.28
500	465.9	395.2	14.15	32.94	6.14	2.65
1000	807.7	730.4	15.47	52.21	6.69	2.74
2000	1991	1911	16.05	124.06	7.60	2.78
3000	3142	3059	16.46	190.83	8.05	2.80

Figure 4.5 (A) Langmuir isotherm for Zn adsorption and (B) Freundlich isotherm for Zn adsorption; 30~3500ppm Zn solution without KNO_3

Figure 4.6 (A) Langmuir isotherm for Zn adsorption; (B) Freundlich isotherm for Zn adsorption; 30~3500ppm Zn solution with 0.05M KNO_3

Table 4.7 summaries the comparison of the correlation coefficient (R^2) for data fitted using the Langmuir isotherm model and Freundlich isotherm model. It was observed that the fit of data is closer to the Langmuir isotherm model (R^2 closer to unity) than that using the Freundlich isotherm. This suggests that Zn sorption process by CaF_2 sludge followed an almost ideal Langmuir sorption model.

Table 4.7 Linear equations for Langmuir and Freundlich isotherms for Zn soption

Langmuir isotherm			Freundlich isotherm	
	linear equation	correlation coefficient R ²	linear equation	correlation coefficient R ²
Without KNO ₃	y = 0.0397x + 2.4624	0.9993	y = 0.1916x + 1.7835	0.797
With 0.05M KNO ₃	y = 0.0594x + 4.8392	0.9999	y = 0.2162 + 1.1815	0.8603

Note: for Langmuir data $x=Ce$ and $y=Ce/Qe$; for Freundlich data $x=\ln(Ce)$ and $y=\ln(Qe)$

The Langmuir constant X_m (maximum adsorption capacity) and the Freundlich constant K_f were obtained from the linear Equations 2.2-2.5. The values are summarized in Table 4.8. X_m value of approximately 25 mg/g of sludge was attainable, which implies that the adsorption capacity of aqueous Zn by CaF₂ sludge in study not as good as Pb which we had achieved (1250 mg Pb/g sludge without background ionic interference). In fact, it was even lower than Pb sorption with the presence of background ionic interference (357 mg Pb/g sludge). The Freundlich constant, n, were larger than unity, further implying good adsorption of Zn onto the CaF₂ sludge in study.

Table 4.8 Comparison of the isotherm constants for Zn sorption

KNO ₃	Langmuir Constant X _m (mg/g)	Langmuir Constant k	Freundlich Constant K _f	Freundlich Constant n
Without	25.189	62.03	5.951	5.219
With 0.05M	16.84	81.47	3.259	4.625

If the main sorption mechanism is mainly surface sorption as suggested by the almost linear Langmuir pattern, the retained Zn in the sludge might not be as stable as Pb.

During the sorption experiments, the interaction between the aqueous Zn²⁺ solution and CaF₂ sludge resulted in the reduction of Zn²⁺ concentration in the solution. It

was observed that the pH values of the equilibrium solution decrease slightly (by approximately 0.1~0.2) while the amount of zinc metals sorbed increases with increasing initial Zn^{2+} concentration. The observation that Zn^{2+} sorption was accompanied by a decrease in pH also agrees with the results of studies by Barrow (1986), in that the decrease in pH was partly due to hydrolysis of Zn^{2+} to give ZnOH^+ and H^+ and partly due to re-adjustment of charge on the colloid surfaces (such as ZnOH^+ ions) were sorbed.

Simultaneous changes in solution pH and Ca^{2+} concentration make it difficult to determine whether the increase in Ca^{2+} concentration was the consequence of ion exchange with Zn^{2+} , further dissolution of CaF_2 sludge due to a decrease in pH, or other mechanisms. According to LeGeroes and LeGeroes (1984), cations with ionic radii smaller than Ca^{2+} (0.099 nm) have less of a chance to be incorporated into an apatite structure compared with cations with larger ionic radii. Therefore, the sorption of Zn^{2+} (0.069 nm) is unlikely to be caused by the incorporation of Zn^{2+} into the apatite. Instead, based on zeta potential measurements, CaF_2 sludge has a negative charge when the solution pH is greater than 2.5 (Figure 3.6). Therefore, sorption could be caused mainly by the attraction of cationic heavy metal, Zn^{2+} to the CaF_2 sludge.

4.2.3 Cadmium Sorption Isotherms

As shown in Figure 4.7, trends similar to the Pb and Zn sorption isotherms was observed. For Cd concentration below approximately 3750ppm, the sorption pattern is also characterized by decreasing slopes as equilibrium Zn concentration increases, until a threshold is reached. This indicates higher affinity of the sorbent at low concentrations of the sorbate. However, the slope started to increase after 4000ppm, which is peculiar to the trend as observed for Pb and Zn. This upward slope trend might be due to over precipitation of the Cd nitrate in the solution which contribute to the overall removal of Cd in the solution. Hence, the sludge might have had reached its threshold capacity at approximately 50 mg/g and the remainder were actually attributed by self precipitation after 3750ppm.

The trend seems to indicate approximately more than 10 folds lower in adsorption capacity of Cd as compared to Pb, but almost doubled of Zn. Background ionic strength (0.05M KNO₃) does not seem to have any significant effect on the sorption capacity for Cd concentration below approximately 300ppm. With the background ionic interference, the sorption capacity seems to have been reduced slightly only by less than 10%.

Figure 4.7 Sorption isotherms for Cd onto CaF₂ sludge

The Cd sorption data have also been analyzed using the Langmuir model and Freundlich model (Cassey, 1997) to evaluate which one of the two models is more applicable for Cd sorption by CaF₂ sludge.

The equilibrium sorption data of Cd without KNO_3 and with 0.05M KNO_3 (Tables 4.9 and 4.10 respectively) were fitted to the linear form of the Langmuir equation and Freundlich equation, and are plotted in Figures 4.8 and 4.9.

Table 4.9 Batch adsorption test results for Cd without KNO_3

Intended Ce (ppm)	Ce (ppm)	24hr Ce (pp m)	Qe [1] (mg/g of CaF_2 sludge)	Ce/Qe	lnCe	lnQe
50	72.92	3.747	13.84	5.27	4.29	2.63
100	126.9	19.07	21.57	5.88	4.84	3.07
500	648.0	439.2	41.76	15.52	6.47	3.73
1500	1444	1188.9	51.03	28.30	7.28	3.93
2500	2751	2495	51.23	53.70	7.92	3.94
3500	3583	3324	51.73	69.25	8.18	3.95
5000	4952	4560	78.43	63.13	8.51	4.36

Table 4.10 Batch Adsorption Test Results for Cd with 0.05M KNO_3

Intended Ce (ppm)	Ce (ppm)	24 hr Ce (ppm)	Qe [1] (mg/g of CaF_2 sludge)	Ce/Qe	lnCe	lnQe
50	82.46	7.636	14.96	5.51	4.41	2.71
100	147.35	30.39	23.39	6.30	4.99	3.15
500	653.6	476.7	35.39	18.47	6.48	3.57
1500	1467	1242	44.94	32.64	7.29	3.81
2500	2657	2427	46.06	57.69	7.88	3.83
3500	3944	3692	50.46	78.18	8.28	3.92
5000	4952	4584	73.65	67.24	8.51	4.30

Figure 4.8 (A) Langmuir isotherm for Cd adsorption and (B) Freundlich isotherm for Cd adsorption; 50~5000ppm Cd solution without KNO_3

Figure 4.9 (A) Langmuir isotherm for Cd adsorption; (B) Freundlich isotherm for Pb adsorption; 50~5000ppm Cd solution with 0.05M KNO_3

Table 4.11 summaries the comparison of the correlation coefficient (R^2) for data fitted using the Langmuir isotherm model and Freundlich isotherm model. It was observed that the fit of data is closer to the Freundlich isotherm model (R^2 closer to unity) than that using the Langmuir isotherm. This suggests that Cd (like Pb) sorption process by CaF_2 sludge did not follow an ideal adsorption Langmuir isotherm model.

As discussed previously, Singh, et al. (2006) suggested that the deviations from the Langmuir equation could also indicate the possibility of other mechanisms in addition to precipitation and co-precipitation. The presence of other minerals other than apatites may increase the sorption capacity for Pb, which could be likely similar for Cd too.

Table 4.11 Linear equations for Langmuir and Freundlich isotherms for Cd sorption

Langmuir isotherm			Freundlich isotherm	
linear equation		correlation coefficient R^2	linear equation	correlation coefficient R^2
Without KNO_3	$y = 0.0139x + 7.5266$	0.9096	$y = 0.3478x + 1.2985$	0.9336
With 0.05M KNO_3	$y = 0.0148x + 8.6063$	0.91	$y = 0.319x + 1.4305$	0.9399

Note: for Langmuir data $x = \text{Ce}$ and $y = \text{Ce}/Q_e$; for Freundlich data $x = \ln(\text{Ce})$ and $y = \ln(Q_e)$

The Langmuir constant X_m (maximum adsorption capacity) and the Freundlich constant K_f were obtained from the linear Equations 2.2-2.5 (chapter 2). The values are summarized in Table 4.12. X_m value of approximately 72 mg/g without background ionic electrolyte and approximately 67.6 mg/g with 0.05M KNO_3 background ionic electrolyte. Both these values were below the maximum capacity as observed in Figure 4.7. This further reinforce that the difference in the threshold capacity might be due to excess precipitation at higher concentration ($> 3750\text{ppm}$). The Freundlich constant, n , were larger than unity, further implying good adsorption of Cd onto the CaF_2 sludge in study.

Table 4.12 Comparison of the isotherm constants for Cd sorption

KNO ₃	Langmuir Constant	Langmuir	Freundlich	Freundlich
	X _m (mg/g)	Constant k	Constant K _f	Constant n
Without	71.942	541.5	3.664	2.875
With 0.05M	67.57	581.5	4.181	3.135

Similarly to the behavior of Pb sorption, deciphering the mechanisms of Cd sorption was more complex. In addition to the precipitation mechanisms, there exist the possibility of other sorption mechanisms capable of removing Cd from the solutions, such as surface adsorption, ionic exchange or substitution and co-precipitation.

4.3 Heavy Metals Removal Kinetics

Heavy metals removal kinetics experiment was conducted with heavy metals stock solution of approximate desired concentrations. No background electrolyte was added into the solution. The test was conducted up to approximately 72±1hrs (ie 4320±60min). The amount of heavy metals removed (ppm), amount of Ca detected in the solution and the pH of the suspension was plotted as a function of time (min).

4.3.1 Lead Removal Kinetics

Lead removal kinetics experiment was conducted with Pb solution of approximately 4860ppm. The concentration of Pb and Ca detected in the solution and the pH of the suspension was plotted as a function of time (min) as shown in Figure 4.10.

Figure 4.10 Changes in chemistry during kinetic experiment with 4860ppm of Pb

The results show a biphasic characteristic. The two stage time dependent Pb removal was very similar to the results observed for phosphatic clay material and other pure apatite minerals (Singh, et al., 2006). The reaction was very fast initially and then followed by slow reaction. Within the first 4 hrs, approximately 30% of the aqueous Pb was removed (Table 4.13).

Fast reactions were most likely due to initial precipitation of Pb and P as a pyromorphite during aqueous Pb interaction with the sludge. In addition, surface sites were more readily available initially for chemical reactions. (Eqn 2.6 and Eqn 2.7). The initial sharp increase of suspension pH may be due to a combination of HAP dissolution and HPM precipitation. The increase in solution pH (Table 4.13 and Figure 4.10) after 5min reflected that H^+ concentration in solution decreased, indicating the HAP dissolution reaction (Eqn 2.6) is more dominant than HPM precipitation (Eqn 2.7). The addition of Pb^{2+} into the solution will consumed the $H_2PO_4^-$ that formed HPM, thus accelerated the dissolution rate of HAP, and more Ca^{2+} ions were released into solution. Therefore a rise in Ca^{2+} ions in the solution was detected.

The second stage showed a slower reaction behavior. These results suggest, that the dissolution of HAP was slower than that the precipitation of lead phosphate and hence the dissolution step controls the overall Pb removal reaction rate. HPM precipitation slowed down with time goes on. With more and more phosphate released from HAP dissolution been used by Pb forming precipitation, the whole reaction became more inhibited by HAP dissolution. Thus HPM precipitation slowed down while dissolution of HAP released more phosphate. Then H^+ producing rate decreased, the H^+ concentration in solution will also decrease. With a decreasing concentration of H^+ in the solution, pH will also gradually increase. The gradual increase of suspension pH indicated slow HAP dissolution, therefore decreasing the rate of Pb^{+} uptake, which inhibited the possibility of pH drop. This also caused a depletion of protons which caused the pH to rise in the solution. Since diffusion to internal site may be required to reach available sorption sites in the second stage, it may be also the cause of slow reaction rate in the later stage.

Table 4.13 Pb sorption, 5000ppm, without KNO_3

Initial Pb concentration,				
Time, min	ppm	After sorption, ppm	Pb removal rate %	pH
0	4861	4861	0.00	4.7
5		3976	18.21	5.1
15		3938	19.01	5.2
60		3805	21.73	5.2
240		3432	29.40	5.3
1440		2235	54.03	5.3
4320		767.3	84.22	5.4
		Time, min	Ca desorption, mg/g	
		0	0.00	
		5	21.09	
		15	25.35	
		60	31.24	
		240	43.25	
		1440	82.21	
		4320	134.85	

The mechanism of aqueous Pb removal by CaF_2 sludge was further verified by X-ray diffraction analysis (Figure 4.11). The shift of the peaks of X-ray diffraction confirmed the formation of HPM and lead phosphates after interaction with Pb solution ($\sim 4860\text{ppm}$).

Figure 4.11 XRD patterns of CaF_2 sludge without and after interaction with 4860ppm Pb solution for 24hrs. Mineral abbreviations: AP, apatites; HP, hydroxyl-pyromorphite; LPF, lead phosphate fluoride.

This is consistent with the deduction that the mechanisms of aqueous Pb removal by CaF_2 sludge are the combination of HAP dissolution and HPM precipitation to form pyromorphite.

4.3.2 Zinc Removal Kinetics

Zinc removal kinetics experiment was conducted with Zn solution of approximately 367ppm. The amount of Zn (ppm), amount of Ca detected in the solution and the pH of the suspension was plotted as a function of time(min) as shown in Figure 4.12.

Figure 4.12 Changes in chemistry during kinetic experiment with 367ppm of Zn

The results show a biphasic characteristic like Pb sorption. The reaction was very fast initially and then followed by slow reaction. Within the first 4 hrs, approximately 25% of the aqueous Zn was removed. By 1440min (24hrs), reaction has almost reached a plateau at approximately 20mg/g of Zn sorbed per sludge.

Fast reactions are most likely due to initial precipitation of Zn and P as a metal phosphate during aqueous Zn interaction with the sludge, and surface sites on the sludge were more readily available initially by the Zn ions for chemical reactions. (Eqn 2.6 and Eqn 2.7). The initial sharp increase of suspension pH may be due to a combination of HAP dissolution and phosphates precipitation.

The decrease in the concentration of Zn^{2+} will lead to an increase concentration of Ca^{2+} in the solution. This behavior can be explained by the following two chemical reactions for the dissolution of hydroxyapatite (HAP) and the precipitation (Xu et al., 1994):

HAP dissolution:

Zn Phosphate (ZP) precipitation:

These reactions are written in terms of H_2PO_4^- with the pH encountered in this test (from pH 2 to 7), H_2PO_4^- is the dominant phosphate ion.

After 5 mins, there was an increase in solution pH (Table 4.14 and Figure 4.12). This indicates that H^+ concentration in solution has decreased, reflecting the possibility of HAP dissolution reaction being more dominant than ZP precipitation. With the addition of Zn^{2+} into the solution and formation of ZP after reaction with the H_2PO_4^- , the dissolution rate of HAP accelerated and more Ca^{2+} ions were released into solution in the first 360 mins.

The second stage showed a slower reaction behavior quite like the case for Pb as discussed before. After 1440mins, the removal rate of Zn^{2+} and release rate of Ca^{2+} become almost stagnant. The dissolution rate of mineral components into the solution might have greatly reduced. At this stage, the dissolution of HAP is slower than that the precipitation of Zinc phosphate, and as more phosphate released from HAP dissolution was being used by Zn to form precipitates, the whole reaction became more inhibited by reduced HAP dissolution. Then as H^+ producing rate decreased, the H^+ concentration in solution will also decrease, resulting in a gradual

increase in pH. A depletion of protons might also caused the pH to rise in the solution. Since diffusion to internal site may be required to reach available sorption sites in the second stage, it may be also the cause of slow reaction rate in the later stage, like for the case of the Pb sorption.

Table 4.14 Zn Sorption, 367ppm,without KNO₃

Initial Zn concentration,		Zn removal			
Time, min	ppm	After sorption, ppm	Zn sorption, mg/g	rate %	pH
0	366.6	366.6	0.00	0.00	4.7
5		327.1	7.91	10.78	5.0
15		326.1	8.11	11.06	5.6
30		320.2	9.28	12.65	5.7
60		309.7	11.39	15.53	5.3
120		307.9	11.74	16.01	5.6
360		288.6	15.61	21.29	5.9
1440		265.7	20.18	27.53	6.0
1590		268.7	19.58	26.71	6.3
1860		268.5	19.62	26.75	6.3
2880		255.7	22.18	30.24	6.2
3060		259.3	21.47	29.28	6.3
3300		262.5	20.83	28.41	6.2
4380		252.5	22.83	31.13	6.2

Time, min	Ca desorption, mg/g
0	0
5	10.21
15	9.40
30	10.19
60	10.48
120	11.79
360	16.99
1440	17.14
1590	17.54
1860	17.26
2880	17.76
3060	18.19
3300	18.75
4380	19.36

The mechanism of aqueous Zn removal by CaF_2 sludge was further verified by X-ray diffraction analysis (Figure 4.13). The changes of the peaks of X-ray diffraction confirmed the formation of HPM and lead phosphates after interaction with Zn solution (~367ppm).

Figure 4.13 XRD patterns of CaF_2 sludge without and after interaction with 367ppm Zn solution for 24hrs. Mineral abbreviations: AP, apatites; ZP, Zinc Phosphates.

This verified that the mechanisms of aqueous Zn removal by CaF_2 sludge are the combination of HAP dissolution and precipitation to form zinc phosphates.

4.3.3 Cadmium Removal Kinetics

Cadmium removal kinetics experiment was conducted with cadmium nitrate solution of approximately 750ppm. The amount of Cd removed (ppm), amount of

Ca detected in the solution and the pH of the suspension was plotted as a function of time (min) as shown in Figure 4.14.

Figure 4.14 Changes in chemistry during kinetic experiment with 750ppm of Cd

The Cd sorption rate shows a biphasic characteristic (two stage time dependent Cd removal) The initial reaction was extremely fast for the first 5 min, and then followed by a slow reaction. Within the first 5min, approximately 25% of the aqueous Cd was removed from the solution (Table 4.15).

The fast reactions could be due to initial ion exchange with the cations such as Ca and Na in the sludge. This is shown by the observation that there was a release of Ca in the solution in the same trend as Cd sorption (a steep release of Ca with the steep sorption of Cd from solution). Then subsequently the release of Ca slowed down, indicating that other mechanisms other than ion exchange could be contributing to the continued sorption of Cd in the solution, e.g. precipitation of Cd and P as cadmium phosphate during aqueous Cd interaction with the sludge.

No significant trend for pH was observed after the sorption reaction at various times. There is a slight increase of pH from 5.9 to 6.4 after the first 5 mins of

reaction, followed by very gradual increase in pH value as the reaction time increases.

The slight increase of suspension pH may be due to a combination of HAP dissolution and cadmium phosphate ($\text{Cd}_3(\text{PO}_4)_2$) precipitation. The increase in solution pH (Table 4.15 and figure 4.14) after 5min indicated that H^+ concentration in solution decreased, which further suggested that the HAP dissolution reaction (Eqn 2.6) would be more dominant than $\text{Cd}_3(\text{PO}_4)_2$ precipitation (Eqn 2.7). The addition of Cd^{2+} into the solution reacted with the H_2PO_4^- and formed $\text{Cd}_3(\text{PO}_4)_2$, thus accelerated the dissolution rate of HAP, and more Ca^{2+} ions were released into solution. Hence, a rise in Ca^{2+} ions in the solution was observed.

The second stage of Cd sorption showed a slower reaction rate. This suggests that the dissolution of HAP was slower than that the precipitation of cadmium phosphate and hence the dissolution step controlled the overall Cd removal reaction rate. As more phosphate was released from HAP dissolution, the reaction became more affected by $\text{Cd}_3(\text{PO}_4)_2$ dissolution. Then as H^+ producing rate decreased, the H^+ concentration in solution will also decrease. With a decreasing concentration of H^+ in the solution, pH will also gradually increase. The gradual increase of suspension pH after the first 5 mins indicated slow HAP dissolution, therefore decreasing the rate of Cd^{2+} uptake, which inhibited the possibility of pH drop. This also caused a depletion of protons which caused the pH to rise slightly in the solution. Since diffusion to internal site may be required to reach available sorption sites in the second stage, it may be also the cause of slow reaction rate in the later stage.

Table 4.15 Cd sorption, 750ppm, without KNO₃

Time, min	Initial Cd concentration,		Cd adsorption, mg/g	Cd removal	
	ppm	After Adsorption, ppm		rate %	pH
0	745.9	745.9	0.00	0.00	5.9
5		562.3	36.71	24.61	6.4
10		567.6	35.65	23.90	6.4
30		553.0	38.57	25.86	6.4
60		525.9	43.98	29.48	6.3
120		518.0	45.57	30.55	6.3
360		483.7	52.42	35.14	6.5
1440		392.3	70.71	47.40	6.5
1590		394.8	70.22	47.07	6.6
1860		383.4	72.50	48.60	6.7
2880		347.9	79.59	53.36	6.6
3060		352.1	78.74	52.79	6.8
3300		348.6	79.45	53.26	6.7
4380		327.6	83.64	56.07	6.7
		Time, min	Ca desorption, mg/g		
		0	0		
		5	16.36		
		15	17.86		
		30	17.73		
		60	18.62		
		120	19.85		
		360	21.37		
		1440	26.43		
		1590	27.35		
		1860	27.16		
		2880	28.63		
		3060	28.81		
		3300	28.74		
		4380	30.22		

The mechanism of aqueous Cd removal by CaF₂ sludge was unable to be further verified by X-ray diffraction analysis (Figure 4.15). The changes of the peaks of X-ray diffraction did not show any significant new peaks (with no significant morphological differences) after interaction with Cd solution (~750ppm). This could be due to that the cadmium-containing apatite that was formed which had similar XRD peak patterns with the calcium-apatites in the sludge, or that the new crystalline solid phases did not have a significant weight mass to be detectable by the XRD equipment.

Figure 4.15 XRD patterns of CaF_2 sludge without and after interaction with 745ppm Cd solution for 24hrs. Mineral abbreviations: AP, apatites.

4.4 Sorption of Heavy Metals as a Function pH

Sorption studies were conducted at various pH (2-8) to study the effect of pH on the sorption efficiency. The concentration of heavy metals chosen was in the region of approximately below 50% efficiency and was deemed to have little influence by the KNO_3 background electrolyte interference. The effectiveness of sorption (%) of various lead as a function of varying pH are plotted.

4.4.1 Sorption of Lead as a Function of pH

The effectiveness of sorption of various lead as a function of varying pH are shown in Figures 4.16. The concentration of lead used was approximately 3760ppm.

Figure 4.16 Pb Sorption Test at Various pH Values

Metal sorption depends on pH because of resulting changes in metal species and surface charge of adsorbing media. Mineral surfaces become more negatively charged with increasing pH and surface groups that have lost protons may be able to sorb cations more readily (and anions less readily) from solutions.

Generally, higher pH resulted in higher Pb adsorption by CaF₂ sludge. For instance, Pb adsorption was 223.62mg/g in pH 3 to 749.11mg/g in pH 8. This again verified two steps reaction model that had discussed before. More H⁺ released by HPM precipitation was neutralized at high pH, thus more and more precipitation would occur at high pH.

At high pH(>7), precipitation was already observed in the stock solution before adding to the sludge. This also contributed to the high Pb removal result for pH 8. The magnitude of the decrease of Pb concentration at high pH (7~8) is about

1900ppm. Almost 50% of aqueous Pb was removed by lead hydroxide formation in the solution). Comparing with Pb removal rate by CaF_2 sludge ranging from 93.40% to 99.66% for pH 7 to 8, it could be concluded that under high pH, CaF_2 sludge could contribute significantly to the overall Pb removal by the formation of lead hydroxides.

However, one exception was noted at pH 2, where the highest Pb removal (99.8%) occurred. When CaF_2 sludge was added to Pb solution of pH 2 a different precipitation took place almost instantaneously. At pH 2, the CaF_2 sludge was likely to be dissolved in the solution and hence released more dissolved phosphate and fluoride ions into the solution to form precipitates with the lead cations. This precipitates that formed were likely to be of pyromorphite-type minerals, which are highly insoluble under the extreme acidic conditions.

4.4.2 Sorption of Zinc as a Function of pH

The effectiveness of sorption of various zinc as a function of varying pH are shown in Figures 4.17. The concentration of lead used was approximately 367ppm.

Generally, higher pH resulted in higher Zn sorption by CaF_2 sludge. For instance, Zn adsorption ranged from 17.22mg/g at pH 2 to 72.82mg/g at pH 8. This again verified two steps reaction model we had discussed before. More H^+ released by HPM precipitation was neutralized at high pH, thus more precipitation would occur at high pH. Zinc phosphates is more insoluble under alkaline conditions

Figure 4.17 Zn Sorption Test at Various pH Values

According to Figure 4.17, there is a significant increase in the sorption of Zn^{2+} when the pH was increased from 2 to 3, followed by an almost constant removal rate from pH 3 to 6.5. Between pH 6.5 and 8, the removal rate increases significantly from 40.1% to 99.3%.

When compared with the CEC chart obtained (as discussed in chapter 3), the study shows that Zn^{2+} sorption is closely related to cation exchange capacity (CEC) of the CaF_2 sludge. Between pH 2 and 3, CEC increases therefore Zn^{2+} sorbed increases; from pH 3 to 6.5, the CEC is relatively constant hence the Zn^{2+} sorbed rate is constant. It can also be observed that the sorption capacity by the CaF_2 sludge has reached its threshold after pH 3 since it is almost constant. Precipitation was also observed during the adjustment of pH to 6.5, 7 and 8 before the sorption process. Therefore, continual increase in the removal of Zn^{2+} after pH 6.5 is most likely due to the formation of $\text{Zn}(\text{OH})_2$, which corresponds to a zinc hydroxides solubility chart presented by David et al. (1994). This contributed to the high Zn removal result for pH 8.

4.4.3 Sorption of Cadmium as a Function of pH

Sorption studies of Cd were conducted at the various pH (2-8). The effectiveness of sorption of various zinc as a function of varying pH are shown in Figures 4.18. The concentration of Cd used was approximately 350ppm.

Figure 4.18 Cd Sorption Test at Various pH Values

Generally, higher pH resulted in higher Cd sorption by CaF_2 sludge from pH 2 to pH 3. For instance, Cd sorption was 12.95mg/g at pH 2 to 32.29mg/g at pH 3. For pH values higher than 3, the sorption seemed to be rather constant at 50%.

Comparing with the CEC chart obtained (Figure 3.2), Cd^{2+} sorption was observed to be closely related to CEC of the CaF_2 sludge under the various pH. Between pH 2 to 3, CEC increases which corresponds to an increase in Cd^{2+} sorbed. Between pH 3 to 8, the CEC is relatively constant hence the Cd^{2+} sorbed rate is constant. It can also be

observed that the sorption capacity by the CaF_2 sludge has reached its threshold after pH 3 since it is almost constant.

4.5 Selective Sequential Extraction (SSE) Experiment

SSE was carried out to investigate the proportion of exchangeable, acid soluble, reducible, organic/oxidizable and residual fractionation of sludge metals. A summary of the SSE procedure carried out in this study is given in Table 3.3.

The various fractionations of Pb, Zn and Cd in the sludge after sorption treatment at various pH was plotted and presented in Figure 4.19, in terms of percent fractionation.

(A)

(B)

(C)

Figure 4.19 Fractionation % for Sorption Test at Various pH Values of (A) Pb at ~3800ppm loading, (B) Zn at ~350ppm loading and (C) Cd at ~350ppm loading

From Figure 4.19(A), almost all (>99%) of the sorbed Pb resides in the very stable residual fraction across all pH conditions tested. This suggested that the hydroxylpyromorphite formed remained very stable even under acidic condition. Hence it further confirmed the effectiveness of the sludge in retaining Pb for remediation works.

Figure 4.19(B) shows that the exchangeable/acid soluble fraction (in %) seems to follow the same trend as the sorption efficiency as presented in Figure 4.6 before. Conversely, the residual fraction of the Zn sorbed follows a reverse trend in terms of percent fractionation in the sludge. The reducible (oxide-bound) and oxidizable (organic-bound) fraction remains rather consistent across all pH condition, fluctuating between 6% to 10% for the former and 22% to 28% for the latter (except at pH value 8, where a dip in oxidizable fraction was also observed).

Figure 4.19(C) shows that the sorbed Cd in residual fraction of the sludge can only be found in pH 3 to 8 (consistently between 21% to 25%). However, only negligible amount of sorbed cadmium at pH 2 are detected. This suggested that the residual fraction of the sorbed Cd in the sludge cannot stay insoluble under extreme acidic conditions, which explains the dip in sorption efficiency at pH 2 as presented in Figure 4.18 before.

To study further on the fractionation of sorbed Zn and Cd in the sludge, the following charts of fractionation in terms of mg of heavy metals/ g of sludge were plotted (Figure 4.20). Pb was not discussed as almost all of the sorbed Pb resides in the very stable residual fraction.

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(A)

(B)

Figure 4.20 Fractionation (mg/g) for Sorption Test at Various pH Values of (A) Zn at ~350ppm loading and (B) Cd at ~ 350ppm loading

Figure 4.20(A) shows that approximately 13 to 16 mg of Zn sorbed per g of sludge were in the reducible (oxide-bound), oxidizable and residual fractions across all pH conditions from pH 3 to pH 8. The only big fluctuation is the exchangeable fraction which started at approximately 1.8mg/g at pH 2, 8~12mg/g at pH 3 to 7, and then increased significantly to almost 50mg/g at pH 8. This trend correspond closely with the Zn sorption efficiency. This suggests that the main mechanism of Zn sorption is mainly due to formation of reducible, oxidizable and residual fraction. The solubility of the exchangeable/acid soluble fraction formation under various pH conditions is the determining factor on the efficiency of Zn sorption from the solution.

From Figure 4.20(B), it was observed that approximately 21.3 ± 0.7 mg of Cd sorbed per g of sludge are in the oxidizable and residual fractions across all pH conditions from pH 3 to pH 8. The reducible fraction was observe to be at around 10.6mg of Cd/g of sludge at pH 3 and increased slightly as the pH increased, achieving approximately 12.3mg/g at pH 8. Like Zn, this trend suggest that the main mechanism of Cd sorption is also mainly due to formation of reducible, oxidizable and residual fraction. The solubility of the exchangeable/acid soluble fraction formation under various pH conditions is also the determining factor on the efficiency of Cd sorption from the solution from pH 3-8. The only exception is at pH 2, only approximately half of the average (across pH 3-8) sorbed Cd was detected in the exchangeable/acid soluble, reducible and oxidizable fraction, and negligible amount was detected in the residual fraction. This suggest that the sludge is not as effective in Cd removal under extremely acidic condition, most probably due to the solubility of the residual fraction that would have had been formed under higher solution pH conditions.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

This project characterized the CaF_2 sludge and assessed its sorption capacity for Pb, Zn and Cd. The important parameters controlling aqueous metals removal, i.e., initial metal ion concentrations, ionic strength, solution pH, and heavy metals removal kinetics were evaluated using batch experiment.

The isotherms constants for the three heavy metals studied, without ionic strength and with 0.05M KNO_3 ionic strength were determined as summarized in Table 5.1 and 5.2. Generally, the presence of background ionic strength in the solution reduces the sorption efficiency of heavy metals, as metals competed with other ions for sorption sites on the sludge. However, the effect was negligible for lower concentrations of heavy metals (approximately <1000ppm for Pb, <200ppm for Zn and <300ppm for Cd). The L-shape of the sorption isotherms graphs indicate higher affinity of sorbent at low concentration of the sorbate.

The isotherms were compared and evaluated with both the Langmuir and Freundlich isotherm model. It was found that the Pb and Cd sorption followed the Freundlich isotherm model with correlation coefficient near unity. The deviation from the Langmuir linear isotherm indicates that there is a possibility of other sorption mechanisms in addition to monolayer surface precipitation and co-precipitation. Although Zn followed the Langmuir linear isotherm model, apparent sorption mechanisms remained complex as evidenced from the sorption and desorption behaviors.

Table 5.1 Comparison of the isotherm constants for heavy metals sorption without KNO_3

	Langmuir Constant X_m (mg/g)	Langmuir Constant k	Freundlich Constant K_f	Freundlich Constant n
Cd	71.94	541.5	3.664	2.875
Zn	25.19	62.03	5.951	5.219
Pb	1250	5598	0.265	1.065

Table 5.2 Comparison of the isotherm constants for heavy metal sorption with KNO_3

	Langmuir Constant X_m (mg/g)	Langmuir Constant k	Freundlich Constant K_f	Freundlich Constant n
Cd	67.57	581.5	4.181	3.135
Zn	16.84	81.47	3.259	4.625
Pb	357.1	1477	0.455	1.219

By comparing the isotherms constants of Pb, Zn and Cd sorption, we are able to conclude that the amount of metals able to be removed by the sludge decrease in the order of $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The conclusion that Zn^{2+} sorption mechanism was closer to the monolayer sorption model (Langmuir sorption model) could be the reason for the sludge to have the lowest sorption efficiency for Zn^{2+} .

To study the heavy metal sorption efficiency with respect to time, kinetics studies on the heavy metal sorption was carried out. The results show that the heavy metal sorption kinetics generally follow a biphasic characteristic. Major changes in the metal concentrations occurred in two distinct stages: a rapid decrease in heavy metal concentration in the solution followed by a slow heavy metal uptake by the sludge as a function of increasing reaction time. The initial fast reactions were most likely due to chemical reaction with readily accessible surface sites on the sludge by the metal ions. Since diffusion to internal site may be required to reach available sorption sites in the second stage, it may be also the cause of slow reaction rate in

the later stage. Among the studied metals, decreases in Pb initial concentration remained the highest followed by Cd and Zn.

Heavy metals removal by the sludge as a function of pH was studied for the pH range of 2-8. As expected, Pb and Zn concentration in the contaminant solution was greatly reduced at high pH (>7), partly due to formation of Pb and Zn precipitates (lower solubility under alkaline condition). However, it was interesting that an Pb removal for Pb was very high when the pH was extremely acidic (pH 2). A different kind of precipitated floc formed almost instantaneously when added to the sludge. This could be explained by the formation of highly insoluble pyromorphite-type minerals under extremely acidic conditions. Zn removal efficiency remained unchanged from pH 3-7 and dropped by approximately 15% under extremely acidic condition (pH <3). Cd removal efficiency remained unaffected by the pH, from pH value 3-7. Similar to Zn, Cd also observed a reduction of efficiency by approximately 20% (half of maximum) when under extremely acidic condition (pH <3).

From the XRD analysis, the formation of pyromorphite and zinc phosphates after reaction of the aqueous heavy metals with the sludge confirmed the precipitation is one of the dominant mechanisms for Pb and Zn removal from aqueous solution. However the sorption mechanism for Cd could not be confidently deciphered from the XRD peaks pattern obtained after reaction as no obvious evidence of new crystalline solid phase was observed.

Selective sequential extraction (SSE) tests show that more than 99% of Pb sorbed is in the very stable residual fraction, regardless of the pH condition. The SSE results also show that the main mechanism of Zn sorption is mainly due to formation of reducible, oxidizable and residual fraction. The solubility of the exchangeable/acid soluble fraction formation under various pH conditions is the determining factor on the efficiency of Zn sorption from the solution. Like Zn, the SSE charts suggest that the main mechanism of Cd sorption is also mainly due to formation of reducible, oxidizable and residual fraction. The solubility of the exchangeable/acid soluble

fraction formation under various pH conditions is also the determining factor on the efficiency of Cd sorption from the solution from pH 3-8. The only exception is at pH 2, only approximately half of the average (across pH 3-8) sorbed Cd was detected in the exchangeable/acid soluble, reducible and oxidizable fraction, and negligible amount was detected in the residual fraction. These results further confirmed the effectiveness of the CaF_2 sludge in retaining Pb for remediation works. Further treatment might be necessary to stabilize the non-residual fractions of Zn and Cd sorbed onto the sludge.

5.2 Recommendations for Future Works

This study has evaluated the Pb, Zn and Cd sorption capacity of CaF_2 sludge. The sorption characteristics of other heavy metals uptake can be studied. A study of the competitiveness of various heavy metals uptake is also possible.

Other important parameters controlling aqueous metals removal, such as organic and inorganic ligands interference, sludge to liquid ratio can also be evaluated using batch experiments.

The use of actual heavy metal laden industrial wastewaters or leachate from contaminated sites can be used to verify the results obtained in this study under controlled conditions.

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