CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Gold mining industries have expanded all over the world, producing substantial amounts of waste that have become problematic to the environment. Heavy metals are leached from waste tailings generated during ore processing and when the tailings are placed in containment ponds. In addition, acid mine drainage at these sites results in an increase in the mobility of heavy metals into surface water and groundwater systems (Fetter, 1993 and Concas et al., 2005). Heavy metals, leached from abandoned mining sites and from tailings, can contaminate the soils, surface water and groundwater in the vicinity of the mining area and nearby areas, creating a potentially serious hazard for the surrounding environment and human health (Fetter, 1993; Cidu, et al., 2001; Yong, 2001; Sheoran and Sheoran, 2006; Trois et al., 2007). Construction defects, poor installation, and long-term aging of containment pond liners are typical reasons for metal leaching from containment ponds. The concentrations of these heavy metals vary from 100-10,000 ppm in mining wastes (Yong and Diperno, 1991) and concentrations in the leachate can vary from 0.1 μg L^{-1} to 55,000 mg L^{-1} (Moncur et al., 2005, Tarras-Wahlberg and Nguyen, 2006).

2.2 Examples of Contaminated Mining Sites

Salomons (1995) studied the environmental impact of metals released from gold mining activities in Brazil where mercury was used to concentrate the gold. The mining activities have resulted in high concentrations of mercury in sediments and fish with long-term consequences. Mercury concentrations in the sediments of lakes about 50 km. from the mining site ranged from 62 to 80 μg kg^{-1}, decreasing with depth to concentrations between 12 and 30 μg kg^{-1} which were similar to background concentrations reported for the area. The mercury concentrations in the lakes provided an indication of the wide dispersion of mercury through surface water and

the atmosphere. The highest Hg concentrations in fish were 2.7 $\mu g \ g^{-1}$ in carnivorous fish in the Madeira river and ranging from 0.01 to 2.19 $\mu g \ g^{-1}$ in eight fish species in the Itacaiunas-Paraobebas river system.

Babut et al. (2003) investigated the environmental impacts of small-scale gold mining in Dumasi, Ghana by collecting samples from river water, sediments, soils, vegetables and fish and evaluating the nature and extent of the mercury pollution in a selected river system and surrounding sites. Hg concentrations in groundwater ranged between 0.12 and 0.27 $\mu g \ L^{-1}$ while concentrations in river water samples were more variable ranging between 0.18 and 0.76 $\mu g \ L^{-1}$. In river sediments, mercury concentrations ranged from 0.64 to 8.5 $\mu g \ g^{-1}$, while mercury in sumps sediment ranged from 1.3 to 93.1 $\mu g \ g^{-1}$. The mercury concentrations in 15 types of fish collected in the vicinity of the main gold processing area ranged between 0.55 and 1.59 $\mu g \ g^{-1}$. The findings showed that mercury concentrations in the sediments and fish collected in Dumasi were rather high and widespread.

At an abandoned mine in southern Tuscany, Italy, soils at the site were contaminated with As (1,500-2,700 $mg \ kg^{-1}$), Hg (80-120 $mg \ kg^{-1}$) and Pb (200-240 $mg \ kg^{-1}$) (Macro et al., 2002). In addition, they found that the tailing waste has resulted in high metals contamination in waters downstream of the mine with Pb concentrations ranging from 0.001 to 0.904 $mg \ L^{-1}$, Hg concentrations ranging from 0.01 to 0.139 $mg \ L^{-1}$, and As concentrations ranging from 0.694 to 35.59 $mg \ L^{-1}$.

For a copper/lead mine in New Zealand, Pang (1995) found that a groundwater plume of metals (Cu, Pb, Zn, Cd, Fe, Mn) has moved about 1 km down gradient of the tailings pond. The results showed that heavy metals transport in the contaminant plume were estimated to be about 1.1 to 345 times slower than the groundwater flow and was in segregated zones with the following metals treavelling the fastest to the slowest: Fe << Zn < Cu < Mn < Pb << Cd.

Cidu et al. (2001) evaluated the increase in salinity in shallow groundwater of a Monteponi mine in Italy when deep aquifer water was mixed with the shallow aquifer of the mine. An increase in Cl⁻ from 0.13 to 12.9 $g \ L^{-1}$, resulted in the dissolution of Hg with concentration of Hg rising to 60 $\mu g \ L^{-1}$. The mine flooding also caused an increase in concentrations of other dissolved metals and mobilization

of metals in mine waste left in the surrounding areas.

Moncur et al. (2005) found that the discharge of a small mine drainage impoundment water into a small lake in Canadian Shield area, Manitoba has changed the composition of the lake water with the highest accumulation of dissolved metals and SO_4^{2-} in the lower portion of the water column of the lake, at concentrations up to 8,500 mg L^{-1} Fe, 20,000 mg L^{-1} SO_4^{2-}, 30 mg L^{-1} Zn, 100 mg L^{-1} Al, and increased concentrations of Cu, Cd, Pb and Ni as compared with background water.

At a contaminated mine site in North Wales, UK, Gao and Bradshaw (1995) found an improvement in the water quality of a nearby stream, Nant Gwydry, where stabilization work has been performed 14 years ago to minimize mine pollution. However, the Nant Gwydry was still a polluted stream and this stream contributed approximately 1 tonne of Zn, 0.2 tonne of Pb and 0.05 tonne of Cd per year to a larger downstream river, the river Conwy.

2.3 Sorption of Heavy Metals onto Soils

Sorption is a dominant process that controls the mobility of contaminants in the subsurface (Chang et al., 2001; Liu et al., 2006). It is therefore, important to understand the sorption/desorption of heavy metals onto the soils. The amount of metal adsorbed has been shown to correlate with the soil properties such as pH, redox potential, zero point charge of soil, clay, soil organic matter (Lee et al., 1998; Adhikari and Singh, 2003), cation exchange capacity (CEC) (Adhikari and Singh, 2003), Fe and Mn oxides, and calcium carbonate content (McLean et al., 1992). Among these factors, soil pH has the greatest effect of any single factor on the solubility or retention of heavy metals in the soil. It has been shown that metals are sorbed more strongly at high soil pH resulting in lower solubility of metal ions in the groundwater and surface water (Elzahabi and Yong, 2001; Appel and Ma, 2002; Bin-Shafique et al., 2002; Adhikari and Singh, 2003).

2.3.1 Sorption isotherms

Linear sorption isotherm

Sorption is typically described using an isotherm where the mass of sorbate sorbed per mass of sorbent is plotted against the aqueous concentration of sorbate in equilibrium with the sorbed contaminant. By using a linear isotherm, the slope of the plot is given by the distribution coefficient, K_d (L mg^{-1}), as given in equation 1:

$$K_d = \frac{c^*}{c}$$

(1)

where

K_d = Linear distribution coefficient (L mg^{-1})

C_{eq} = Sorbate concentration in solution (mg L^{-1})

$C*$ = Amount of sorbate retained by soil (mg g^{-1})

Langmuir sorption isotherm

Non-linear isotherms are used when the ratios of the mass of sorbate sorbed per mass of sorbent and the aqueous equilibrium concentration are not a constant over the range of equilibrium concentrations. Sorption of inorganic contaminants on mineral surfaces is frequently nonlinear. The Langmuir isotherm was developed to describe the non-linearity of the relationship. The isotherm is based on the concept that a surface possesses a finite number of sorption sites and the surface can be saturated with the sorbate above a certain aqueous concentration (Fetter, 1993). The Langmuir isotherm is given as:

$$C^* = \frac{Q_{max} bC}{1 + bC}$$

(2)

where

Q_{max} = Adsorption constant related to the binding strength of the sorbate on the matrix surface (L mg^{-1})

b = Maximum amount of sorbate adsorbed by sorbent (mg g^{-1})

Freundlich sorption isotherm

Another isotherm describing non-linear sorption behavior is the Freundlich isotherm. The Freundlich sorption isotherm is an empirical relationship which is

widely applied to the sorption of various metals and organic compounds by soils.

$$C^* = K_f C^n \qquad (3)$$

where

K_f = Distribution coefficient (L mg^{-1})

n = Dimensionless constant

2.3.2 Factors affecting metal sorption

Adsorption of metals depends on the properties of the solid (i.e., the particle size, nature of inorganic oxide coating, organic carbon content, and zero point charge of the solid) as well as the properties of the liquid, including pH and the total dissolved metal concentrations (i.e., the sum of the free metal pool, inorganic ions as well as the concentrations of the complexing ligands) (Bin-Shafique et al., 2002).

2.3.2.1 Properties of soils

Composition of soil

The soil type and composition play a significant role in heavy metal sorption. In general, coarse-grained soils (e.g., gravel, sand and silt) exhibit a lower tendency for heavy metal adsorption than fine grained soils (e.g., clay). Fine-grained soil fractions such as clay minerals, iron and manganese oxyhydroxides, have large surface areas per unit mass and exhibit enhanced sorption properties (Shrama and Reddy, 2004). Clays are known to sorb heavy metals by specific sorption and cation exchange (Adhikari and Singh, 2003). Soil organic matter has a large number and variety of functional groups and high CEC values, resulting in enhanced heavy metal retention mostly by surface complexation, ion exchange, and surface precipitation (Kalbitz and Wennrich, 1998).

Point of zero charge

The adsorption of metals on a solid surface or mineral components of the solid surface is influenced by the surface charge of the solid surface (McLean and Bledsoe, 1992; Bin-Shafique et al., 2002; Shrama and Reddy, 2004). The point of zero charge (pzc) is the pH at which the net surface charge of the solid is zero. The pzc of some

of minerals and the effect of pH on the surface charge of the solid are shown in Figure 2.1 (Stumm and Morgan, 1995). The pH where there is no net zero surface change is represented by pH_{pzc}. For example, the pzc for kaolinite is 4. Increasing the pH above the pH_{pzc} would results in more negative charge, which in turn would increasing the sorption of metal cations on the sorbent.
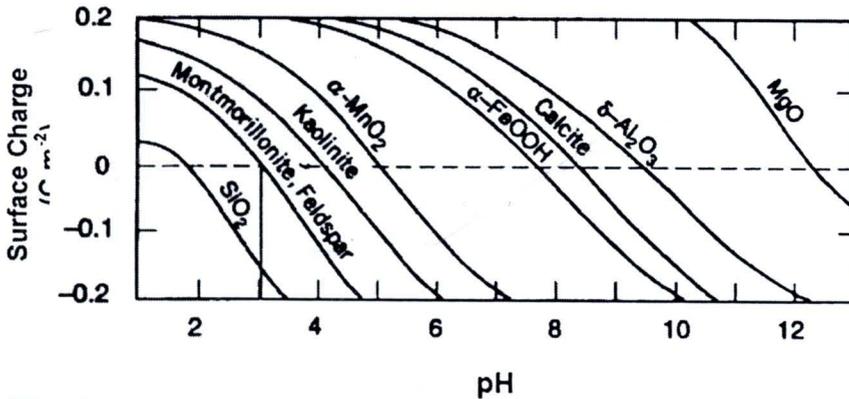

Figure 2.1 Point of zero charge and the effect of pH on the surface charge of some common minerals (from Stumm and Morgan, 1995)

2.3.2.2 Properties of aqueous solutions

Effect of pH

Aqueous soil pH plays a major role in the sorption of heavy metals (Appel and Ma, 2002; Celardin et al., 2004) as it directly controls the solubilities of metals. Solubility of the metal hydroxides is a function of pH (Figure 2.2). The solubility of metal hydroxides decreases linearly with increasing pH (Stumm and Morgan, 1995). Many adsorption sites, for example, Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals, are pH dependent. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also, as the pH becomes more acidic, metal cations compete for available permanent charged sites with Al^{3+} and H^+ (McLean and Bledsoe, 1992).

Effect of ionic strength

Ionic strength can affect metal adsorption because of competition between the metals of interest and other species for the same adsorption sites. (Kookana, and Naidu, 1998; Miretzky et al., 2006). A concentrated electrolyte can swamp the

surface of the sorbent, limiting metal access to the sorption sites (Reed and Nonavinakere, 1992)
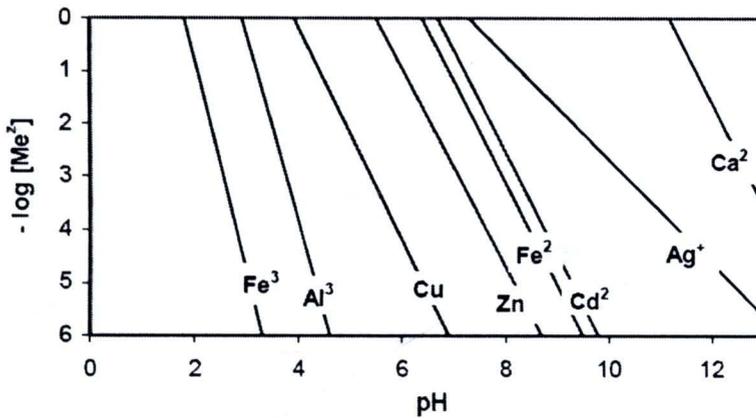

Figure 2.2 Solubilities of metal oxides and hydroxides (from Stumm and Morgan, 1995)

Effect of competing cations

The presence of other cations can significantly affect the sorption and mobility of the metal of interest in a system since cations compete with each other for sorption sites. Cavallaro and McBride (1978) found that sorption of Cu and Cd reduced in presence of 0.01 M CaCl$_2$ as compared to a system with no CaCl$_2$. The lower sorption of Cu and Cd was due to competition with Ca for available sorption sites.

Effect of complex formation

Metals cations form complexes with inorganic and organic ligands. The resulting association usually has a lower positive charge than the free metal ion, and may be uncharged or carry a net negative charge. In addition, ligands may change the solubility of metals, allowing a higher total metal to be in solution as compare to a system with no ligand. In general, the decrease in positive charge on the complexed metal reduces sorption to a negatively charged surface. The presence of ligands may increase metal migration depending on the result of the complex formation (McLean and Bledssoe, 1992; Gomes et al., 2001).

At low concentrations, metals are adsorbed by the specific adsorption sites. With increasing concentration of metals, the specific adsorption sites are saturated and the nonspecific sites are filled. Metals associated with these nonspecific sites exchange with other metal cations and are more potentially mobile (McLean and Bledssoe, 1992). Di Torro et al. (1986) found that the partition coefficient tends to decrease with increasing concentration. As a result, the fraction of the total concentration that sorbed on the sorbent often decreased when the total concentration increased, resulting in higher metal concentration in the aqueous phase.

2.3.3 Sorption of single heavy metals onto soils

Hooda and Alloway (1998) compared Cd and Pb sorption capacities of some selected English and Indian soils using batch equilibrium tests. The experiments were conducted using duplicate 1-g soil in 100 mL capacity polyethylene bottles and 25 mL of 0.002 M $Ca(ClO_4)_2$ containing different metals concentrations (0-10 mg Cd L^{-1} and 0-100 mg Pb L^{-1}). For both Cd and Pb, the English soil had the highest log K_f (3.939 and 5.738 L kg^{-1} for Cd and Pb, respectively) while the Indian desert soil had the lowest log K_f (1.880 and 3.055 L kg^{-1} for Cd and Pb, respectively). For both soils, the log K_f for Pb sorption (3.055-5.738 L kg^{-1}) were greater than the log K_f for Cd sorption (1.880-3.939 L kg^{-1}). Soil-metal sorption was found to be positively correlated with soil pH, organic matter, clay content, $CaCO_3$ content and CEC, but was negatively correlated with the sand content. Application of sewage sludge to the soils, especially English soil, increased Cd and Pb sorption.

The sorption characteristics of Pb onto fifteen Taiwan soils at different aqueous pH were investigated by Lee et al. (1998). The results showed that Pb sorption was highly pH dependent with an increase in partition coefficients for increasing pH values. The Langmuir isotherm described the sorption characteristics of Pb. The Tacha silty loam had the greater maximum adsorption capacity (43.9 and 143.2 mg g^{-1} at pH 4.5 and 6, respectively), and the Lichochen sand had the smallest maximum adsorption capacity (1.1 and 2.7 mg g^{-1} at pH 4.5 and 6, respectively). When correlated with soil properties, the organic matter played the most important

role in affecting lead sorption.

Muhammad et al. (1998) found that adsorption of Cu, Cr, Pb, Cd onto sand using batch experiments at pH 7.2 to 7.5 was described by Langmuir and Freundlich isotherms. The Langmuir maximum capacities (Q_{max}) were 719, 556, 833, and 139 mg g^{-1} for Cu, Cr, Pb, and Cd, respectively. While the Freundlich constant (K_f) for Cu, Cr, Pb, and Cd were 1.52, 0.36, 0.27, and 0.34 L g^{-1}, respectively. The adsorption capacity for metals onto sand for this study were found to be in the order of Pb > Cu > Cr > Cd.

Alumaa et al. (2002) studied the sorption of Cu, Pb, Cd and Cr for 10 different Estonain soils at low concentrations of 1.0 µg L^{-1} to 30 mg L^{-1}. The soil use was 2 grams in 10 mL of solution (ratio1:5). The linear distribution coefficient (K_d) varied from 57 to 63,000 L kg^{-1}. Sorption affinity arranged according to their K_d were in the order: Pb > Cr > Cu > Cd. Correlation of the K_d's with the soil properties showed that sorption of heavy metals was dependent on the soil organic matter and clay content and the concentration of Fe and Mn oxides. However, the work of Appel and Ma (2002) for the sorption of Cd and Pb onto three tropical soils (Mollisol, Oxisol, and Ultisol) from Puerto Rico showed that metal sorption was more dependent on the metal types than the soil composition. The experiments were conducted at constant ionic strength (0.01 M), varying concentrations (0-1.2 mM), pH values (2-7) and at a soil: solution ration of 1:100. In addition, they found that soil mineralogy was more important for Cd and Pb sorption than the quantity of organic matter and the external surface area in these soils.

Adhikari and Singh (2003) conducted sorption equilibrium experiments of Pb and Cd onto five agroecological zones (i.e., Vertic Ustochrept, Tyric Eutrochrept, Typic Ustipsamment, Typic Haplustalf, and Typic Ustorthent) of India. The experiments were employed at two different temperatures 25 ± 2 and 45 ± 2 °C to determine various thermodynamic parameters ($K°$, $\Delta G°$, $\Delta H°$, $\Delta S°$). They found that heavy metals sorption was described by Freundlich and the modified two surface Langmuir isotherms. The Langmuir sorption capacities (Q_{max}) were in the range from 62.5 to 132.5 mg kg^{-1} soil for Pb and 55.9 to 90.9 mg kg^{-1} soil for Cd. Sorption capacities of Cd and Pb were found to correlate with the soil pH, CEC, and organic matter. The Freundlich K_f constants ranged from 1.99 to 4.16 L mg^{-1} for Pb and from

0.90 to 2.81 L mg^{-1} for Cd. The sorption capacity of Pb was found to be 4-6 times higher than that of Cd. Thermodynamic parameters showed that sorption of Pb and Cd were spontaneous while Cd sorption was exothermic whereas Pb sorption was endothermic for all soils.

Oren et al. (2005) investigated the sorption of Zn onto two natural zeolites found in the regions of Gordes and Bigadic in Western Turkey. They found that an increase in external surface area of the zeolites has little effect on the sorption capacity. The sorption of Zn on both zeolites was found to be dependent on the pH. Sorption of Zn onto both materials was found to increase for increasing initial metal concentration. A plateau in sorption capacity was found for both zeolites which indicated unavailability of zeolite surfaces at certain concentrations. When the soil:solution ratio increased from 1:1 to 10:1 g L^{-1} zinc sorption decrease about 68 and 49 % for Gordes and Bigadic zeolite, respectively.

2.3.4 Sorption of binary or multiple heavy metals onto soils

The adsorption of Cd, Cu, Pb and Zn onto kaolinite in single and multi-metal systems as a function of pH in 0.01 M NaNO$_3$ solution was studied by Srivastava et al. (2005). Results showed the value of pH$_{50}$, pH at which 50% sorption occurs, followed the order of Cu < Zn < Pb < Cd in single-element system, but sorption order of Pb < Cu < Zn < Cd in the multi-element system.

Serrano et al. (2005) investigated the competitive sorption of Pb and Cd in batch equilibrium and kinetic sorption experiments using four soils from central Spain. Results of the study showed that the sorption isotherms can be described by Langmuir isotherm and the sorption kinetics can be described by an empirical power function. Sorption capacity of Pb and Cd were found to be reduced by the presence of both metals. The sorption capacity (Q_{max}) of Pb (2.33-12.9 mmol kg^{-1}) was higher than that of Cd (1.27-7.67 mmol kg^{-1}). The overall sorption processes of Pb and Cd in the smectitic soil (with the highest sorption capacity of the four soils) were slower than for the other three soils with a clay mineralogy dominated by kaolinite and illite. These results showed that sorption of Pb and Cd were dependent on clay mineralogy.

Arias et al. (2006) used batch experiments to study the competitive and noncompetitive adsorption of Cu and Zn onto acid soils at pH 5 with 0.01 M $NaNO_3$ as the background solution. Freundlich isotherm fitted the sorption data better than the Langmuir isotherm, possibly due to the heterogeneity of the sorbent surfaces. The K_f value ranged from 1.3 to 8.7 for Cu and from 0.1 to 1.4 for Zn. For both metals, K_f for soils developed over granite (2.3 for Cu and 0.1 for Zn) were smaller than for soils developed over amphibolites (5.1 for Cu and 0.6 for Zn), which have higher iron oxide contents. The value of n for Zn (average 0.6) was greater than for copper (average 0.3). Results of their studies showed that noncompetitive adsorption of Cu exhibited greater sorption than that of Zn, especially in the soils with the highest organic matter contents. Total metal adsorption from solutions containing both Cu and Zn at a 1:1 mole ratio was intermediate between the adsorption capacity of Zn and Cu of the same total aqueous concentration, indicating that these metals competed with each other.

The competitive sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in mine soils from two mines in the province of A Coruña, Galicia, Northwest Spain was investigated by Vega et al. (2006). The retention selectivity sequences showed the Pb was the preferred retained metal, followed by Cr, and the other metals in the sequence were Ni, Cd, and Zn. Heavy metals were found to be weakly sorbed by the soils as shown by the desorption of the metal.

According to literature review of batch sorption experiments of heavy metals onto soils, most recent studies have used batch experiments to investigate the effect of environmental conditions, such as the presence of simultaneous metals, pH conditions, ionic strength, and metal concentrations as well as the effects of sorbent properties, texture of soils, size of sorbent, and clay mineralogy on metal sorption behaviors.

2.4 Transport of Heavy Metals in Soils

It is essential to understand the processes that affect the transport (migration) and fate of the contaminants in the soils and groundwater (Sharma and Reddy, 2004). The three major processes affecting the fate and transport of contaminants in the subsurface are physical, chemical and biological processes.

2.4.1 Physical processes

The physical processes impacting the transport of contaminants or metals in the subsurface are advection, diffusion and dispersion.

Advection: Advection refers to the contaminant's movement by flowing water in response to the hydraulic gradient.

Diffusion: Diffusion refers to the movement of contaminants under a chemical concentration gradient. Diffusion can occur even when the fluid is not flowing or is flowing in a direction opposite to the contaminant's movement. In porous media, diffusion in pore water cannot proceed as fast as it can in bulk water because the ions must follow longer pathways as they travel around mineral grains. To account for this, the effective molecular is used incorporating the tortuosity effects in soil.

Dispersion: This process expresses the non-uniform velocity of the fluid Difference in fluid velocities which causes mixing of contaminants and fluid along the flow path. This mixing is also called mechanical dispersion. Mixing that occurs along the direction of the flow path is called longitudinal dispersion. Mixing of contaminants in a direction normal to the flow path is called transverse dispersion.

The two processes of mechanical dispersion and effective molecular diffusion are combined and represented by the hydrodynamic dispersion coefficient, D_j (cm^2 hr^{-1}) which can be described in the longitudinal and transverse direction as:

$$D_L = \alpha_L v + D_m$$
$$D_T = \alpha_T v + D_m \tag{4}$$

where

D_L = Longitudinal dispersion (cm^2 hr^{-1})

D_T = Transverse dispersion (cm^2 hr^{-1})

α_L = Longitudinal dynamic dispersivity (cm)

α_T = Transverse dynamic dispersivity (cm)

v = Average velocity of groundwater flow (cm hr^{-1})

D_m = Effective molecular diffusion coefficient for the solute of interest in soil water (cm^2 hr^{-1})

For the first term in Eq. (4), mechanical dispersion is assumed to be the

product of the average groundwater velocity, v (cm hr^{-1}), through the porous media and the dispersivity, α_j (cm). The second term represents the effective molecular diffusion coefficient (cm^2 hr^{-1}), incorporating the tortuosity effects in soil. Molecular diffusion in groundwater typically occurs slowly and can usually be neglected.

2.4.2 Chemical and biological processes

Processes responsible for the change in the contaminants' concentration are chemical reactions, biodegradation and radioactive contaminant decay. Chemical processes can include chemical sorption, hydrolysis, redox reaction, complexation, abiotic decay while biological process includes biodegradation, transformation and mineralization, which are not important for metals.

2.4.2.1 Chemical process

Chemical Sorption refers to contaminants attached to mineral grains and organic matter in the soil where the sorbate reacts with the sorbent. Desorption of the sorbent usually results in a different sorbate. Chemical sorption defines the contaminant distribution between the solution and solid phase.

Hydrolysis is a chemical transformation process where an hydroxyl group is added to the compound which is more likely to be important for organic compounds (unlikely for metals).

Redox is measured in terms of Eh. The redox reaction is characterized by the redox potential (Eh). The redox reactions involve transfer of electrons which may change the oxidation state of metals. In soils, redox reactions can be mediated by naturally occurring microorganisms.

Complexation is described as the process of an ion or molecule complexing with ligands, which can include both organic and inorganic species. Complexes may be charged or uncharged, and the solubility of the metal ion can be affected accordingly.

Abiotic decay is the degradation of contaminants in the environment by chemical reaction such as photolysis, hydrolysis which is unlikely for metal ions.

2.4.2.2 Biological processes

Biodegradation, an oxidation-reduction reaction is mediated by microorganisms, must be considered for organic contaminants but not for metals. This can occur in the following ways: aerobic biodegradation and anaerobic biodegradation. Aerobic biodegradation occurs under aerobic or oxic environmental conditions in which oxygen acts as the electron acceptor. Anaerobic biodegradation occurs under anaerobic or anoxic conditions in the absence of oxygen.

Tranformation processes, such as biotransformation and radioactive decay, are very common and have major influence on the movement of contaminants in porous media. Exampls of solutes undergoing various transformation reactions and migration in soil include various nitrogen species such as ammonia and, organic phosphates. (Casey and Šimůnek, 2001)

2.4.3 Contaminant transport

Contaminant transport equation

The transport and reaction of the contaminant in a water saturated porous medium can be described using a one-dimensional advection-dispersion equation including sorption and decay as shown (Fetter, 1993):

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} - \frac{\rho}{\theta} \frac{\partial c^*}{\partial t} \pm \left[\frac{\partial c}{\partial t} \right]_{rxn} \qquad (5)$$

where

c = Concentration of solute in liquid phase (mg L^{-1})

t = Time (hr)

D_L = Longitudinal dispersion coefficient (cm^2 hr^{-1})

v_x = Average linear groundwater velocity (cm hr^{-1})

ρ = Bulk density of aquifer (g cm^{-3})

θ = Porosity of media

c^* = Amount of solute sorbed per unit weight of solid (mg g^{-1})

rxn = Subscript indicating a biological or chemical reaction of the solute (other than sorption) (mg L^{-1} hr)

The first term on the right hand side of the above equation represents the dispersion of the solute in groundwater, the second is the advection of the solute, the third term is the transfer of the solute from the liquid phase to the solid phase by sorption, while the last term indicates a change in the concentration of the solute with time due to biodegradation, chemical reactions or radioactive decay.

For a conservative chemical that undergoes no reaction or sorption onto soil, the equation in one dimension is written as follows:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} \qquad (6)$$

For a continuous injection of a conservative chemical in a one–dimensional flow field, the longitudinal dispersivity can be estimated from the chemical breakthrough curve (concentration with time) and the average flow velocity by using the eq. (6).

2.4.4 Nonequilibrium processes

Conceptual and mathematical models of sorption are often simplified by assuming the establishment of local equilibrium assumption (*LEA*). However, data that deviates from that predicted by *LEA* models have been reported, indicating nonequilibrium sorption in the system (Brusseau, 1992). It is a challenge to develop nonequilibrium models to investigate and understand the transport behaviors of contaminants in soil columns and in the field. As stated earlier, transport of contaminants in groundwater system could be affected by physical nonequilibrium processes (i.e., caused by aquifer heterogeneity, preferential flow) or/and chemical nonequilbrium processes (i.e. caused by hysteretic sorption). The nonequilibrium processes of solutes (only non-equilibrium sorption processes) for one-dimensional, steady water flow condition (Brusseau et al., 1989) are presented below.

General nonequilibrium formulation

The two-site or two-region nonequilibrium models (Nkedi-Kizza et al., 1984; Warrick, 2001) can be written as (dimensionless):

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} + \omega(C_2 - C_1) \qquad (7)$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \tag{8}$$

where β is a partitioning between the equilibrium and nonequilibrium phases, R is a retardation factor, C_1 and C_2 are dimensionless equilibrium and nonequilibrium concentrations, P is the Peclet number which is the ratio of advective flux versus dispersive flux, ω is a mass transfer coefficient, and the subscripts 1 and 2 refer to the equilibrium and nonequilibrium phases, respectively. T, X, P, and R are dimensionless terms defined as:

$$T = \frac{vt}{L}, \quad X = \frac{x}{L}, \quad P = \frac{vL}{D}, \quad R = 1 + \frac{\rho_b K_d}{\theta} \tag{9}$$

where

T = Relative pore volume (dimensionless)

x = Distance (L)

L = Colume length (L)

v = Average pore water velocity (L T^{-1})

D = Hydrodynamic dispersion coefficient (L^2 T^{-1})

For the physical nonequilibrium model, the remaining dimensionless parameters are:

$$\beta = \frac{\theta_m + f\rho_b K_d}{\theta + \rho_b K_d}, \quad \omega = \frac{\alpha L}{\theta v}, \quad C_1 = \frac{C}{C_0}, \quad C_2 = \frac{C_{im}}{C_0} \tag{10}$$

where f is the fraction of mobile water and α is is a first-order mass transfer coefficient (d^{-1})

Whereas for the chemical nonequilibrium model:

$$\beta = \frac{\theta_m + f\rho_b K_d}{\theta + \rho_b K_d}, \quad \omega = \frac{\alpha(1-\beta)RL}{v}, \quad C_1 = \frac{C}{C_0}, \quad C_2 = \frac{S_2}{(1-f)K_d C_0} \tag{11}$$

where f is the fraction of equilibrium sites and α is a first-order kinetic rate coefficient (d^{-1}). S_2 is solid phase concentration at site 2.

2.4.5 Transport of heavy metals in soil

In general, batch experiments are used to obtain equilibrium sorption isotherms so as to estimate the solid sorption capacity for any selected heavy metals present in the aqueous phase. Batch experiments assumed a completely mixed condition which maximizes contact between the metals and the sorbent. Batch experiments are useful as a first estimate in predicting the fate of the metals. Use of column experiments however may better approximate the field conditions, providing information that is not available from batch experiments (Miretzky et al., 2006). To evaluate the fate and transport of heavy metal in groundwater, the sorption parameters and the retardation factors are estimated from the breakthrough curves using the miscible displacement technique (Chang et al., 2001; Leitão, 2003). In most heavy metal pollution episodes, several metals are released simultaneously into the subsurface environment; therefore, it is important to understand the retention of these heavy metals in the presence of other metals. In the past, most studies have focused on the competitive sorption of heavy metals in soils under equilibrium conditions using batch sorption experiments. A few studies investigated the competitive transport of heavy metals in column experiments, for which reduction in retardation was possible due to competitive sorption (Tsang and Lo, 2006).

Kookana and Naidu (1998) conducted batch and column experiments (16 mm internal diameter and 100 mm length) to investigate the chemical interactions of Cd in two variable charged soils, an Oxisol and Alfisol, in the presence of Ca and Na salts with varying ionic strengths. For an increase in $NaNO_3$ concentration from 0.03 M to 0.15 M in the background solution, movement of Cd through the Oxisol soil column was four times faster in the 0.15 M solution. For both soils, the transport of Cd with the same ionic strength was faster in the presence of $Ca(NO_3)_2$ than in the presence of $NaNO_3$.

Plassard et al. (2000) studied the impact of initial concentration on the metal retention and distribution of three heavy metals (Cd, Pb, and Zn) in a carbonated soil using batch tests and unsaturated column tests. Metal uptake at high initial concentration was greater than at lower initial concentration, but was retained less strongly. The quantity of metal retained, and calculated from the effluent profiles

were 2.20 µmol g^{-1} for Cd, 2.35 µmol g^{-1} for Zn, and 2.46 µmol g^{-1} for Pb. The experimental results showed that the measured retentions of all three metals were lower for column tests than in batch tests which may be due to preferential flows in the column tests.

Chang et al. (2001) assessed the transport of Cu and Cd in a lateritic silty-clay soil column (10 cm length and 2.54 cm diameter), using a numerical model with a retardation factor estimated from linear and non-linear sorption isotherm. From the breakthrough curve of chloride (Cl$^-$) in each column, the longitudinal dispersivity was estimated to be about 6.14 and 8.15 cm for Cu and Cd, respectively. The linear isotherm distribution coefficients (K_d) were estimated from the breakthrough curve to be in the range of 5.33 to 9.63 L kg^{-1} for Cu and 2.71 to 5.04 L kg^{-1} for Cd. The Langmuir sorption capacities (Q_{max}) derived from batch tests of Cu (740.5-918.3 mg kg^{-1}) were higher than that of Cd (527.9-744.1 mg kg^{-1}). The values of log K_f ranged from 156.3 to 184.5 L kg^{-1} for Cu and from 30.5 to 53.9 L kg^{-1} for Cd while the values of Freundlich constant (n) ranged from 0.32 to 0.40 for Cu and 0.53 to 0.60 for Cd. They found that Langmuir sorption isotherm described well the equilibrium batch test data, but the breakthrough curves of these two metals can be explained using the Freundlich isotherm in the transport model.

The effects of contaminant aging on Cd transport in an undisturbed contaminated soil column could be explained using the Freundlich isotherms with the log K_f ranging from 1.5 to 26.1 L kg^{-1} and the Freundlich constant (n) ranging from 0.31 to 0.89 for Cd (Seuntjens et al., 2001). The Cd transport was described as an advection-dispersion process and the mobile-immobile transport model used to estimate the parameters showed that 16-22% of the water in the column was immobile.

Leitao (2003) conducted column experiments for Cu, Ni, and Zn to study metal competitive sorption in two soils, Sertã and Mortãgua soils. Cu was found to be completely sorbed through soil columns of both soils. Sorption capacity of Ni onto both soils was found to be lower than that of Cu and Zn, confirming the results of batch sorption experiments. The retardation factors for ternary (Cu-Zn-Ni) system were in the order of Cu (11.36 and 26.07 for Sertã and Mortãgua, respectively) > Zn (11.36 and 4.35 for Sertã and Mortãgua, respectively) > Ni (none). Ni and Zn in the

column were found to be almost equally distributed along the soil column length whereas Cu was found to be mainly sorbed in the upper part of the column.

Liu et al. (2006) studied the transport of 3 heavy metals (Cd, Zn, and Ni) in Taoyuan red soil with sand, silt, and clay content of 168, 400, and 432 g (kg soil)$^{-1}$. Dispersion coefficients using a one dimensional convective-dispersive model were 6.23×10^{-8} m^{2}s^{-1} for Cd, 3.62×10^{-8} m^2 s^{-1} for Ni, and 2.33×10^{-7} m^2 s^{-1} for Zn. They found that the retardation factors in decreasing order, were Cd (37.10) > Zn (27.52) > Ni (30.28), and the mobilities of metal in the soil, in increasing order, were Ni > Zn > Cd.

Miretzky et al. (2006) conducted soil column experiments to determine the effect of ionic strength, the electrolyte type, flow rate, bed height, and metal concentrations on the sorption/desorption of Zn in a sandy loam soil under saturation condition. The retardation factors were found to be 479, 520, and 523 at flow rates of 0.12, 0.09, and 0.07 mL min^{-1}, respectively indicating that retention of Zn slightly increased with decreasing flow rates, which may be due to non-equilibrium processes.

Antoniadis et al. (2007) conducted batch sorption and column experiments to measure the distribution coefficients (K_d) of Ni, Zn, Cu in clay by using a laboratory centrifuge. From both tests, the mobility of metals was in the order of: Ni > Zn > Cu. Sorption of metals was found to be less in the presence of other metals than in single metal system where the $K_{d, Ni}$ decreased by 3.3 times and $K_{d, Zn}$ decresed by 3.4 times, while Cu decreased by only 1.2 times in the presence of either Ni or Zn.

According to literature review of transport of heavy metals, studies using column experiments investigated the environmental factors, such as, ionic strength, flow rate, level of concentrations on only single metal transport in soils, but there are not many studies applying column experiments to investigate effects of pH conditions under acid mine drainage conditions, the presence of simultaneous metals in systems, effect of total metal concentrations, and metal types, on metal transport behaviors through mine soils.

2.4.6 Equilibrium/ nonequilibrium modeling

Using batch and column experiments to study the effect of pore water velocity (5-214 cm hr^{-1}) on sorption of Cd onto a homogeneous nonaggregated porous medium at pH 6, Bajracharya et al. (1996) found that the sorption of Cd was fairly constant (10-12 l kg^{-1}) with different flow rates, suggesting that nonequilibrium processes did not occur in the flow-through system. However, the column-determined sorption coefficients were found to be higher than the batch-determined sorption coefficients for similar solid-to-liquid ratio.

Darland (1997) performed saturated sand column experiments using an AsO$_4$ pulse at different pore water velocities of 0.2, 1.0, 10, and 90 cm hr^{-1} and found that local equilibrium assumption (*LEA*), based on either linear or nonlinear sorption, did not adequately explain AsO$_4$ transport for any pore water velocities. Apparent sorption rate coefficients for n^{th}-order kinetic model estimated from column tests were found to increase for increasing pore water velocities. However, the apparent equilibrium distribution coefficient K_f was found to decrease with increasing pore water velocities, indicating a decrease in the distribution coefficient of AsO$_4$ onto sand for increasing pore water velocities.

Physical nonequilibrium conditions were found by Seuntjens et al. (2001) in their column studies where indigenous Cd and freshly applied Cd were leached simultaneously from undisturbed samples of three Spodosol horizons. A mobile-immobile transport model estimated the mobile fraction to be about 80 % of the total water content. The model results indicated that mass transfer between sorption sites and the liquid was limited by diffusion rather than by kinetic sorption.

Pang et al. (2002) investigated the effects of pore-water velocity (3-60 m day^{-1}) on chemical nonequilibrium on Cd, Zn, and Pb transport in alluvial gravel columns. The symmetric breakthrough curves of tritium (^3H_2O) indicate that physical nonequilibrium did not occur in these column studies. The breakthrough curves of metals showed long tailings, indicating that occurrence of chemical nonequilibrium in the metal transport. The breakthrough curves were fitted using CXTFIT curve fitting program with a two-site model. The results showed that the partitioning coefficient

(β), forward rate (k_1), and backward rate (k_2) were positively correlated with pore-water velocity (PWV); whereas the retardation factor (R), mass transfer coefficient (ω), and ratio of k_1/k_2 were inversely correlated with pore water velocity. The retardation factors were found to be 26-289 for Cd, 24-255 for Zn, and 322-6377 for Pb.

Tsang and Lo (2006) conducted column, batch kinetics, and sequential extraction experiments to investigate the effect of binary competition on the transport of Cu and Cd in soils. Both single and binary metal transport behaviors of Cu and Cd in column tests were evaluated by equilibrium and nonequilibrium models. The experimental results showed that the specific sorption of Cd oxide and organic matter fractions were displaced by Cu. Cd transport were found to change from nonequilibrium in a single-metal system to equilibrium in a binary-metal system. From an engineering point of view, Cd may cause a larger extent of contamination than Cu under competitive condition due to reduction of sorption and equilibrium transport behavior.

Most studies have applied linear/nonlinear and equilibrium/nonequilibrium models to describe heavy metal transport in single metal systems. Some studies attemped to describe nonequilibrium processes of metal transport behaviors in various flow rates of single metal systems. However, there have been very few studies using linear/nonlinear and equilibrium/nonequilibrium models to assess heavy metal sorption and transport in mine soils with the presence of more than one metal at various concentrations and metal types in the system.

2.4.7 HYDRUS-1D Modeling

HYDRUS-1D is a Microsoft Windows-based modeling environment for the analysis of water flow and solute transport in various saturated porous media (Šimůnek et al., 2008). The program may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. The software package includes the one-dimensional finite element model, HYDRUS-1D, for simulating the movement of water, heat, and multiple solutes (nonlinear and nonequilibrium solute transport, volatile solutes) in a variety of saturated media. The

model includes a parameter optimization algorithm for the inverse estimation of a variety of soil hydraulic and/or solute transport parameters and may be supported by an interactive graphics-based interface for data-preprocessing, and graphic presentations of the results. The interaction between the solid and liquid phases can be described by linear/nonlinear and equilibrium/nonequilibrium sorption models. HYDRUS-1D does not have a multi-component modeling capacity; thus, each contaminant has to be modeled independently. HYDRUS-1D can be used to estimate sorption parameters from column studies under different environmental conditions using both linear/nonlinear and equilibrium/nonequilibrium sorption models. These parameters are estimated by minimizing the sum of the squared errors (SSE) between the experimental data and model-simulated data.

2.5 Summary

Most of the studies conducted investigate the sorption and transport of single heavy metal in aquifer materials. In recent years, many researchers conducted batch sorption experiments to investigate and elucidate the effects of environmental conditions, such as the simultaneous presence of metals, initial metal concentrations and pH conditions on metal sorption behaviors on soils. Although we know that more than one heavy metal is released simultaneously from several industries to the surrounding soil, surface water and groundwater, not many research have conducted column experiments, to describe the effects of simultaneous presence of metals in the system. Mine activities generated wastes that can potentially leaching several heavy metals to the environments, especially when acid mine drainage occurs. However, there are not many studies conducted to study heavy metal transports through mine soils and their surrounding soils. Specifically, the fate and transport of heavy metals at a particular site, the Akara Mine in Thailand, is unknown and the risks posed by these metals to residents near the mine need further investigation. There is a need to investigate and understand heavy metal transports from the mine tailings and in surrounding mine soils under different environmental conditions, such as, pH conditions of the mine environment, and the effect of simultaneous presence of heavy metals on the sorption and transport of the metals.