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COMPETITIVE SORPTION OF MULTIPLE COMPONENT HEAVY METALS FROM GOLD MINING LEACHATE ONTO LATERITE SOIL

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ABSTRACT: It is important to understand the mechanisms of releasing of metal elements from mining industries in order to predict or estimate migration of these contaminants in the environment and initiate necessary policy for pollution control and prevention in groundwater aquifer systems. In this study, we focus particularly on assessing the competitive sorption characteristics of Pb, Zn, Ni, and Mn in batch equilibrium experiments using single and multiple metal solutions in natural laterite soil from the Northern Thailand. A series of batch tests was conducted to evaluate the effects of pH on sorption/desorption characteristics of metals and to estimate the sorption/desorption isotherms. Soil chemical processes were characterized using Linear, Langmuir, and Freundlich equations, and the results indicated that sorption isotherms were very well described by the Langmuir model. Pb had the greatest sorption capacity as estimated by the maximum sorption parameter (Q_{max}) of the Langmuir equation. Sorption characteristics were discovered to be dynamic processes, depending on interaction among multiple component heavy metals, soil properties, and concentrations of metals in the solution. Additionally, the impacts of variable water saturation on heavy metal migration were also explored by employing parameters obtained from previous experiments as input parameters in HYDRUS-2D model to simulate the migration of heavy metals through variable saturated porous media. The computer simulations revealed that the migration of the mixed contaminated plume was governed mainly by the mechanisms in unsaturated zone, rather than the hydraulic head gradient in the saturated zone. In addition, decreasing water contents resulted in higher retention time, promoted the late arrival of water fronts, and therefore could extend the contaminants' lifetime in the system. Drier soil retarded transport of metals particularly in shallow unsaturated zone, leading to the possible pathway for the contaminants may get back in the hydrologic cycle via plant root uptake.

Keywords: Groundwater, heavy metals, competitive sorption, water saturation, HYDRUS-2D, dynamic interaction, laterite

INTRODUCTION

The presence of heavy metals in surface water and groundwater has been a major concern to communities and municipalities. Concerns over contamination of groundwater and surface water by mining, have generated program to remediate contaminated soils. Metals can cause significant damage to the environment and human health as a result of their mobilities and solubilities. The ubiquitous nature of heavy metals, their toxicity even in trace quantities, their tendency to bioaccumulate in the food chain, and the stricter environmental regulations related to heavy metal discharges make it necessary to develop schemes for the removal of heavy metals from both wastewaters and landfill leachates. The selection of most appropriate soil and sediment remediation method depends on the site characteristics, concentration, type of pollutants to be removed, fate and transport of metals, and the end use of the contaminant medium.

Metals typically become groundwater problems under the following situations: (1) activities associated with plating industry (Ma et al. 1994), where a wide variety of metals are present at high concentrations in soluble forms; (2) sites with releases of radionuclides, due to unique health risks and the use of chelating and complexing agents, can have significant impact at very low concentrations; and (3) metals and high levels of inorganic Total Dissolved Solids (*TDS*) are associated with leaks from sanitary, solid and hazardous waste landfill, and mining. One of the most potentially toxic heavy metals is lead, as classified as soluble and strongly hydrating cations (McBride 1994). Lead is particularly toxic to higher animals, producing kidney and blood diseases among other health disorders. 'Sorption' is used to describe the removal of metals in solution by soil

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solid phase, including any retention mechanism that controls availability and mobility (Chen et al. 1997).

Many studies have been conducted on sorption of metals onto the crystal structure and chemistry of synthetic and mineral apatites (Chen et al. 1997; Wright 1990; McConnell 1973) as well as many toxic heavy metals were investigated (Minamisawa et al. 2004, Um and Papelis 2004; Schneider and Rubio 1999; Ma et al. 1994). Additionally, many studies have been devoted to study the sorption of metals onto hydroxides, especially iron hydroxides (Hayes and Leckie 1986; Dzombak and Morel 1990), aluminium hydroxides (Benyahna and Garnier 1999; Bowers 1983), silicon hydroxides (Meng and Letterman 1993), and kaolinite (Dalang et al. 1984). Soil pH, other factors such as the presence of competing ligands, the ionic strength of the soil solution and the simultaneous presence of competing metals are known to significantly affect sorption and leaching potential through soil profile (Kookama and Naidu 1998). However, research related to studying dynamic interactions as well as predicting fate and transport of multiple toxic heavy metals under variable water saturation conditions in subsurface environment, especially when competitive sorption/ desorption can occur is still very rare.

In this study, the influence of variable water saturation on dynamic interactions of multi-species metals from mine leachate was investigated at Akara gold mine, located 280 km north of Bangkok. During the years of mining, waste rocks were extracted and used in the construction of the Tailings storage facility (*TSF*) in three mine waste emplacements. During ore processing, 750,000 dry tons per year of tailings were generated and deposited at the *TSF*. These mine tailing was left in the form of particulate suspension (i.e., fine grained sediment-water slurry) after the valuable metals had been extracted. The shallow municipal wells are mainly located within the nearby villages, where most local people rely on groundwater. After preliminary investigation, these shallow wells probably intersect the shallow, unconfined, alluvial, clayey sand aquifers at depth between 1.5-7 m beneath land surface, and groundwater table is approximately 6 m below the surface. Surface soil was preliminarily examined, and found that soil pH was ranged from around 3 to 7, and the soil was classified as acidic to neutral. The metals level was considered to be relatively low for a mineralized area comparing to other mining sites around Thailand and all over the world. The preliminary results led to the semi-conclusion of acidic mine leachate condition.

The primary objectives of this study are: (1) to explore the effects of the simultaneous presence of multiple component heavy metals on dynamic sorption behavior to laterite soil; and (2) to investigate the effect of environmental conditions such as soil moisture contents on migration of multiple species heavy metals from mining leachate. For this purpose, the study was divided into four parts. First, a series of leaching test was conducted to examine the amount and types of heavy metals as a potential threat from mine tailing soil. Second, a series of batch experiments was undertaken to generate equilibrium isotherms using single and multiple metal solutions. Third, the effect of heavy metal concentration on the competitive sorption behavior was examined. Finally, the transport and migration of the multiple species heavy metals under various soil moisture contents was investigated using a 2D numerical model (HYDRUS-2D) (Simůnek et al. 1999). Results were characterized and compared for different metal solutions using the Langmuir equation.

MATERIALS AND METHODS

Soils

The laterite soil samples were collected at 13 different locations distributed all over the area and ranged from the soil surface down to approximately 2 m deep. Each sample was air-dried and sieved through sieve number 200 prior to heavy metals analysis. The samples were collected and transported back to the laboratory and kept at 4°C prior to use. Table 1 presents the main soil characteristics of the porous media from laterite layer.

General Soil Analyses

Soil pH was measured in deionized water in triplicate. To analyze for total heavy metal contents in the Tailing, EPA method 3051 was employed in which the aqueous phase contaminant concentrations was analyzed via

Table 1 Soil characteristics of the laterite layer

pH-H_2O	5.4
Organic matter (%)	0.13
Clay fraction (%)	50.2
Sand fraction (%)	30.8
Silt fraction (%)	19.0
Natural water content	0.46
Specific gravity	2.73
CEC ($cmol_c$/kg)	8.2
Bulk density (g/cm^3)	1.10

ICP- OES (Inductively coupled plasma optical emission spectroscopy) on a Perkin Elmer OPTIMA 4300DV, and expressed as total dissolved metals in mass concentrations or in molar concentrations.

Sorption Experiments

Because Pb, Zn, Ni, and Mn were discovered at relatively high concentrations in the tailing found at the site and they were known to be toxic to human and environment, they were selected as representative metals in this study. The isotherm experiments of these metals from their single and multiple component solutions on laterite were undertaken using a batch equilibrium technique in triplicate with a constant solid to liquid ratio of 1:50 as recommended by USEPA (USEPA 1987). The experiments were individually performed by adding 0-100 ppm of Pb, Zn, Ni, and Mn (single or multiple-component solutions) 50 ml to 1-g of laterite sample in 60-mL polypropylene centrifuge tubes. To test for the impact of heavy metal concentration on competitive sorption among several metals, the systems with only one dominating metal were set up and the experimental matrix is presented in Table 2.

The samples were shaken on a platform shaker for 120 hours or less (until local equilibrium had been reached). Changes in sorbed metal concentration in the system were measured periodically. The suspensions were centrifuged at 6640×g for 20 minutes and the supernatants were removed by filtration through Whatman No. 42 filter paper. The solutions were analyzed for heavy metal by ICP-OES.

Langmuir Isotherm

The corresponding isotherms for each experiment were investigated by fitting the experimental observations to the Langmuir isotherm given by (Sparks 1995):

$$Q = \frac{Q_{\max}\ aC_e}{1 + aC_e} \tag{1}$$

where Q is the amount of heavy metal sorbed by the solid (mg/g$_{\text{sand}}$), C_e the equilibrium concentration in solution (mg/L), Q_{max} is the maximum sorption capacity (mg/g$_{\text{sand}}$) and a the bonding energy coefficient (mg/L). The optimal parameter values for Langmuir equation were determined by non-linear regression analysis, on the assumption of a constant relative error as the residuals revealed no systematic deviation. The goodness-of-fit for the isotherms was estimated by the coefficient of determination (R^2).

Table 2 Competitive sorption experiment with one dominating metal

System	Run	Metal Concentrations (ppm)			
		Pb	Zn	Ni	Mn
Pb Dominated	1	5	1.7	1.7	1.7
	2	10	3.3	3.3	3.3
	3	15	5	5	5
Zn Dominated	1	1.7	5	1.7	1.7
	2	3.3	10	3.3	3.3
	3	5	15	5	5
Ni Dominated	1	1.7	1.7	5	1.7
	2	3.3	3.3	10	3.3
	3	5	5	15	5
Mn Dominated	1	1.7	1.7	1.7	5
	2	3.3	3.3	3.3	10
	3	5	5	5	15

RESULTS

The results of overall regional groundwater analysis in Akara mine area revealed that several metal elements in the area exceeded Thai water standard as shown in Table 3.

Batch desorption experiments of several heavy metal species from tailing were conducted to estimate the amount of heavy metals that could be released from sorbed phase into aqueous phase and potentially contaminated groundwater resources as well as surface water in the nearby area. Additionally, the effects of solution pH on the release of heavy metals from tailing as a threat to the environment were also determined. The results are illustrated in Fig. 1 below.

It is obvious from Fig. 1 that the desorption characteristics of Mn is pH dependent. Solution pH greatly affected metal desorption mechanisms from mine tailing as less Mn was discovered in the aqueous phase with increasing pH. Additionally, the aqueous metal concentrations (i.e, y-axis) in Fig. 1 reached plateau level after 48, 24, and less than 24 hours for pH 4, 7, and 10, respectively, indicating that the system reached local equilibrium conditions faster with increasing pH.

Sorption characteristics of single and multiple component heavy metals are shown in Fig. 2 below.

The total amount of metal retained by the solid phase was calculated from Eq. 2:

$$Q = \frac{(C_o - C_t)V}{W} \tag{2}$$

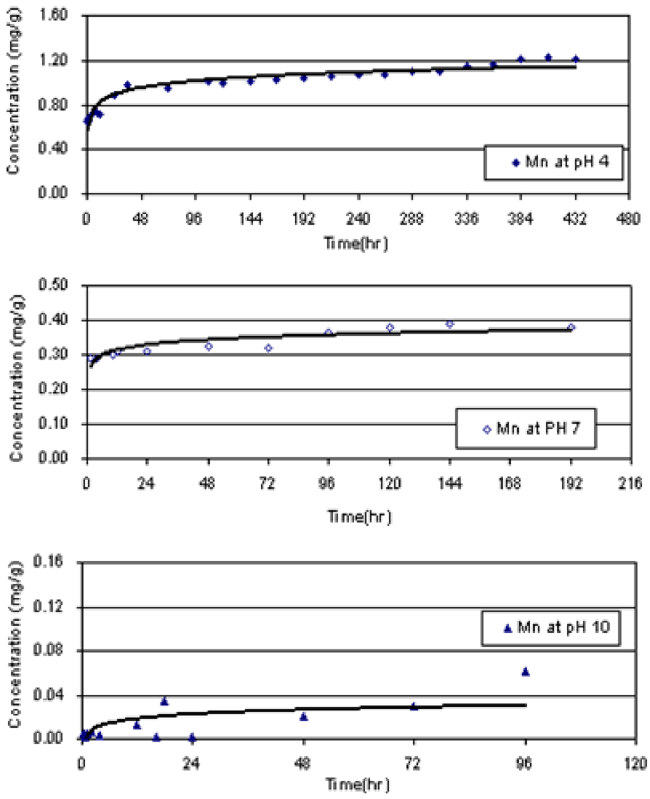

Fig. 1 Effects of pH on desorption and time to reach equilibrium of manganese (Mn)

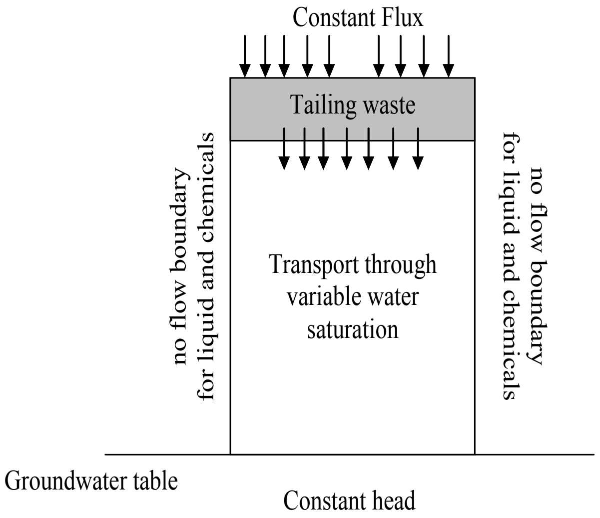

Fig. 3 Conceptual model and domain for numerical simulation of transport of heavy metals in unsaturated zone

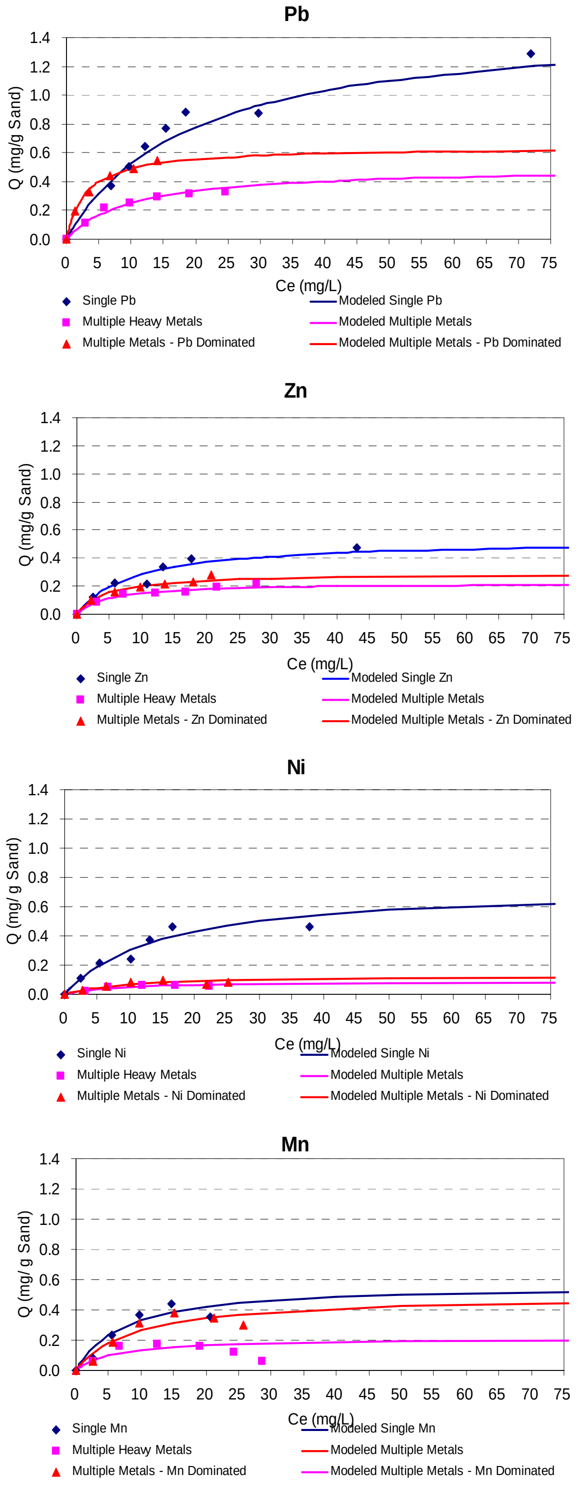

Fig. 2 Pb, Zn, Ni, and Mn sorption isotherms from both single (◆), multiple (■), and multiple with one dominating metal (▲). Solid lines are the best fits to the Langmuir model

Table 3 Chemical analysis of tailing soil samples

Parameter	Concentration (mg/g)	Minimum - Maximum Concentration (mg/g)
Aluminum	10.82	7.28-13.67
Arsenic	ND	ND
Barium	0.15	0.04-0.29
Bismuth	ND	ND
Boron	0.147	0.04-0.29
Cadmium	ND	ND
Calcium	41.80	24.21-51.76
Chromium	ND	ND
Cobalt	ND	ND
Copper	0.07	0.02-0.09
Iron	19.71	11.41-22.90
Lead	0.04	0-0.13
Magnesium	4.87	3.86-5.36
Manganese	2.49	1.67-2.84
Mercury	0.001	0-0.005
Nickel	0.07	0.05-0.11
Potassium	2.53	2.37-2.79
Silver	ND	ND
Sodium	0.41	0.33-0.45
Strontium	0.04	0.02-0.05
Zinc	0.17	0.05-0.28

where Q is the amount of metal sorbed per unit mass pf soil (mg/g sand), C_o and C_t are the metal concentrations in the initial solution and after the reaction time t, respectively (mg/L), V is the volume of the solution added (mL), and W is the air dried mass of laterite soil (g).

All heavy metals tested, both single and multiple initial metal solutions, were adequately described by the Langmuir equation with relatively high R^2 as tabulated in Table 4 for case 1 (single metal), case 2 (multiple metals), and case 3 (multiple metals with one dominating metal), respectively.

Pb adsorbed more onto laterite compared to other three metals tested as indicated by the higher Q_{max} values regardless of single or multiple component heavy metal solutions. Moreover, the higher binding affinity coefficient a of Pb was also the greatest among all the metals tested, indicating that Pb appeared to be related to sorption at high energy surfaces with lower dissociation constants. The experimental data also confirmed the role of metal coexistence on Pb, Zn, Ni, and Mn sorption, by reducing the sorption capacity of each metal. However, the lower Q_{max} and a values may reflect both the competitive sorption among the metals and also the saturation of the sorption sites in the system due to the coexistence of other metals. Therefore, the sorption behavior of case 1 (single metal) and case 3 (multiple metals with one dominating metal) may be compared.

The results from Table 4 indicated that the coexistence of multiple heavy metals in the solution reduced the sorption capacity and the binding affinity for Pb, Zn, and Ni. The sorption behavior of Mn was affected to a different extent as the maximum sorption coefficient Q_{max} decreased whereas the metal binding affinity a increased.

Adsorption isotherm parameters obtained from batch experiments were employed as initial input adsorption isotherm parameters (i.e., $K_d = Q_{max}*b$ [$M^{-1}L^3$] and $\nu = b$ [$M^{-1}L^3$]) for heavy metal transport modeling under variable water saturation conditions. Since HYDRUS-2D model cannot account for pH variation, the simulations were undertaken under constant pH conditions. The conceptual model was constructed with boundary conditions shown in Fig. 3 and mainly composed of several scenarios generated by computer simulations for estimating metal concentration from mine leachate that could potentially contaminate groundwater aquifer underneath the *TSF*. For this, we focused on estimating the maximum concentration level (according to Thai drinking water standard shown in Table 5) and time for heavy metals to reach groundwater table under various degree of saturation. Once heavy metals desorbed from tailing soil, they moved through pores as rainwater infiltrated through soil. Metals contained in tailing could dissolve in the percolating

Table 4 Parameters of Langmuir isotherm at a reaction time of 120 hours

Parameter	Conditions	Pb	Zn	Ni	Mn
C_0 (mg/L)	Case 1	0-100	0-100	0-100	0-100
	Case 2	0-25	0-25	0-25	0-25
	Case 3	0-25	0-25	0-25	0-25
C_e (mg/L)	Case 1	6.86-71.97	2.44-92.34	2.52-88.49	2.63-60.78
	Case 2	2.90-19.05	3.07-21.58	3.18-22.30	2.68-24.33
	Case 3	1.30-14.00	2.21-20.68	2.77-21.89	2.66-21.23
Q_{max} (mg/g)	Case 1	1.52	0.53	0.75	0.57
	Case 2	0.50	0.22	0.09	0.21
	Case 3	0.64	0.29	0.13	0.50
a	Case 1	19.15	8.34	15.03	7.28
	Case 2	9.78	4.98	8.57	5.88
	Case 3	2.99	4.46	9.64	8.65
R^2	Case 1	0.86	0.94	0.96	0.94
	Case 2	0.97	0.97	0.92	0.99
	Case 3	0.99	0.98	0.94	0.95

Table 5 Some important input parameters for HYDRUS 2D simulations

Dispersivity, cm	60
Residual Water Content	0.092
Saturated Water Content	0.456
Initial volumetric water content	0.114, 0.228, 0.342, 0.456
Bulk Density, g/cm^3	1.10
Saturated Hydraulic Conductivity, m/s	1.47 x 10^{-6}
Effective diffusion coefficient, (m^2/s)	3.31 x 10^{-10} for Pb 2.46 x 10^{-10} for Zn
Mechanical dispersion, (m^2/s)	2. x 10^{-9}
Darcy velocity, m/s	1.97 x 10^{-9} (0.062 m/yr)
Initial Metal Concentration, mg/L	20 for Pb 35 for Zn
Maximum Concentration Level (i.e., Thai Drinking Water Standard), mg/L	0.01 for Pb 5 for Zn

water, move vertically, and eventually reached the water table. Metal contaminant fluxes were assumed to be steady state and estimated based on 2 year data of pumping rate of seepage wells under the *TSF*. The final estimated Darcy flux in the year 2004 to 2005 was 0.011 mm/day with the maximum value of 0.17 mm/day. Some important input parameters for HYDRUS-2D simulations are presented in Table 5.

The modeled water retention curve generated in HYDRUS-2D is also displayed in Fig. 4. The diffusion coefficient in this particular case is not constant and depends greatly on the degree of saturation. Therefore, we defined the effective diffusion coefficient (D_e) (Lide 2002) for heavy metals as a product of diffusion coefficient (D^*) and tortuosity factor (τ [-]) as shown in Eq. 3:

$$D_e = n(\tau D) = nD^* \tag{3}$$

where n is the porosity of the medium, D is termed the molecular diffusion coefficient of a chemical in a fluid environment (L^2T^1) is, and D^* is the bulk diffusion coefficient (L^2T^1).

The Tortuosity τ can be estimated from an empirical equation developed by Millington and Quirk (1961):

$$\tau = {(n_W)^{7/3}}\big/{n^2} = {(S_W n)^{7/3}}\big/{n^2} \tag{4}$$

In this study, the governing flow equation under variable water saturation in laterite soil was estimated by using the Richard's equation:

$$\frac{\partial\theta(h)}{\partial t} = \frac{\partial}{\partial z}\left(K(h)\frac{\partial h}{\partial z} + K(h)\right) \tag{5}$$

where t is time [T], z is a vertical coordinate [L] positive upward, θ is volumetric water content [L^{3}L^{-3}], and h represents the soil water matric pressure head [L], respectively.

The unsaturated soil hydraulic properties in this paper are assumed to be described by (van Genuchen 1980):

$$S_e(h) = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1 + |\alpha h|^n)^m} \tag{6}$$

$$K(\theta) = K_S S_e^{0.5}[1 - (1 - S_e^{1/m})^m]^2 \tag{7}$$

where S_e is effective water content [-], K_S is the saturated hydraulic conductivity [LT^{-1}], θ_r and θ_s represent residual and saturated volumetric water contents [L^{3}L^{-3}], respectively, and α [L^{-1}], n [-] and m $\left(= 1 - \frac{1}{n}\right)$ [-] are empirical coefficients.

The transport of heavy metals in variably-saturated laterite soil is estimated by using the convection-dispersion equation which can be expressed by:

$$\frac{\partial(\rho s)}{\partial t} + \frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D\frac{\partial c}{\partial z} - qc\right) \tag{8}$$

where s is the solute concentration associated with the solid phase of the soil [MM^{-1}], c is the solute concentration of the liquid phase [ML^{-3}], ρ is the bulk density [ML^{-3}], D is the solute dispersion coefficient [L^{2}T^{-1}], and q is the volumetric fluid flux density [L^2 T^{-1}].

The computer simulation using HYDRUS-2D revealed the results of variation in water saturation to the migration of multiple component metals in saturated zone as shown in Fig. 5. The figure is plotting moisture content in soil (y-axis) versus time to reach the required metal concentrations (x-axis) at different depth from

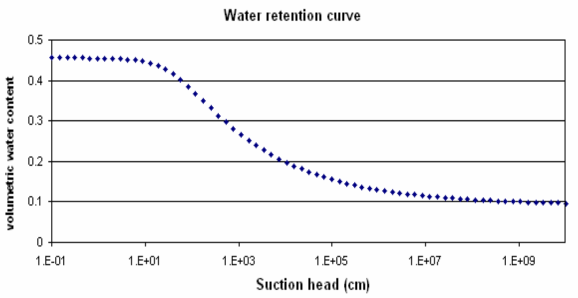

Fig. 4 Modeled water retention curve

ground surface. Since water table in Akara mine area was approximately 6 m below ground surface, the simulation was done at different depth from ground surface with 1 m increment (i.e., from 1 m to 5 m). The results indicated transport and migration of multiple component metals depended on soil water content. Take Zn at pH 4 at 1 m deep as an example, with increasing soil water content by 25% (from ~0.3 to > 0.4), it took two orders of magnitude shorter for Zn to pass through the soil matrix to reach a certain concentration at a certain depth in the environment.

When comparing between different metal species (i.e., Zn and Pb), the simulation results indicated that Pb traveled faster compared to Zn, leading to a much shorter time required to reach the maximum concentration level (i.e., Thai drinking water standard, 0.01 ppm for Pb and 0.5 ppm for Zn) at a specific depth in subsurface. However, Pb's front took a longer time to travel compared to Zn's at the same concentration level, supporting the previous batch observations that the sorption capacity of Pb was higher than Zn. Multiple metals fronts could travel faster compared to the single metal fronts of the same metal species as shown in the simulation results in Fig. 5. For example, Zn at 1 m deep under pH 4 conditions in the multiple heavy metal system took about twice less time to pass through the soil matrix to reach a certain concentration, compared to Zn in the single metal system. This finding indicated that metal sorption capacity the multiple metal system was reduced compared to its original stage in the single metal system.

Water fronts at each depth under various soil moisture contents were plotted in Fig. 6. The figure is plotting final water content (y-axis) as a function of time (x-axis) under various initial soil moisture contents. The results demonstrated that increasing initial soil moisture content led to an early arrival of water front at each depth. Furthermore, at the same initial soil water saturation, the time required to reach a certain final soil moisture content in the unsaturated zone depended mainly on the vertical location of the domain. Let's take the system with initial soil moisture content of 50% of its maximum value as an example here, the results in Fig. 6 demonstrated that it took 600 days and 400 days at 3 m and 2 m deep from ground surface, respectively, for the final soil water content to increase to 0.3. Moreover, the water front profile at 6 m deep did not really respond to the change in initial water content as can be noticed from flat water front profiles simulated by the model.

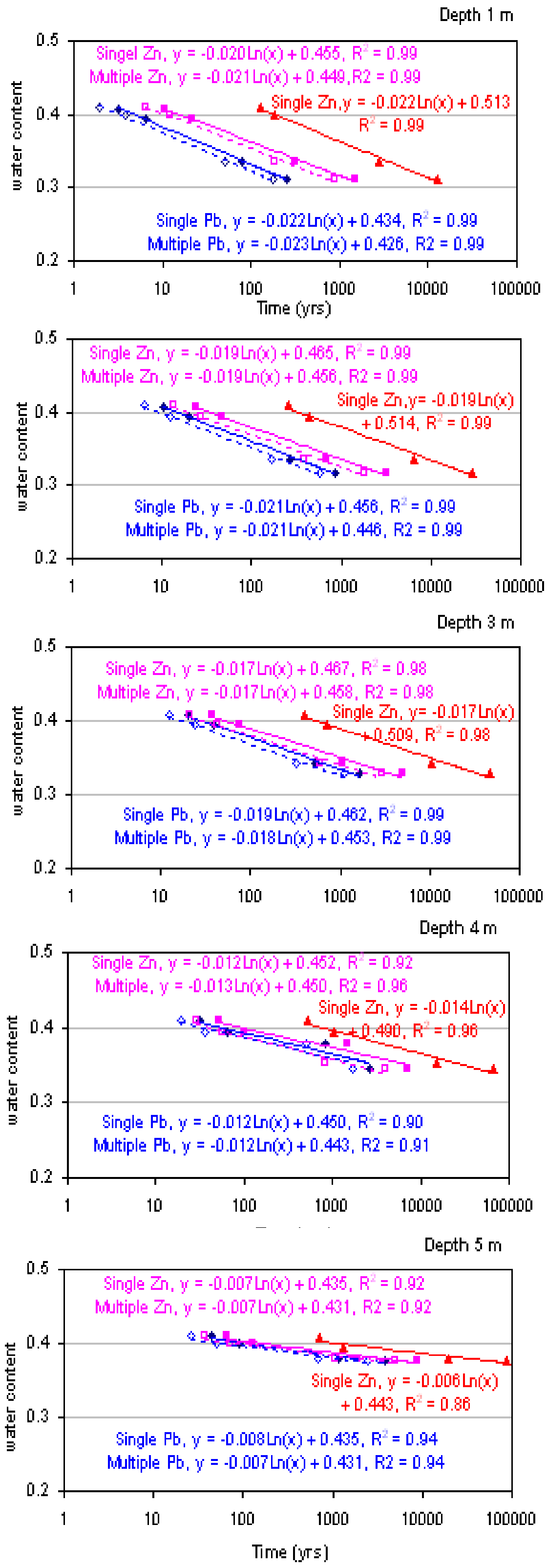

Fig. 5 Effects of variable soil moisture content on transport and migration of multiple component heavy metal in unsaturated zone.

DISCUSSIONS

In Akara mining process, the oxidation stage produces acidic water which favors a release of heavy metals from the mineralized zone mainly including lead (Pb), copper (Cu), nickel (Ni), iron (Fe), manganese (Mn), and zinc (Zn). The mechanism for the release is believed to be due to the infiltration of surface water to the tailing pit creating oxidation environments which causes the release. Once the release occurs, water containing heavy metals can migrate further downward, and eventually contaminate the groundwater supply underneath. In this paper, an attempt to investigate the effects of soil moisture content on the transport and mobility of multiple component heavy metals in laterite soil and the dynamic competitive sorption behavior of the multiple component heavy metals in laterite soil are reported. The evaluation processes started with testing the leaching of heavy metal components from tailing soil collected from Akara mine area due to infiltrating water. Desorption studies in Fig. 1 are extremely important, particularly for already contaminated soil, to predict the fate and mobility of contaminants in such soil and to develop sound and cost-effective remediation strategies. The results demonstrated that decreasing in pH led to a significant release of heavy metals into the environment, suggesting that under acidic mine drainage conditions found at Akara mine area could promote more mobility of multi-component heavy metals. This observation may be explained by the competition between metal anions and proton (H^+) in the aqueous solution at low pH conditions, resulting in smaller fractions of heavy metals can sorb onto adsorbent surfaces. In addition, the presence of inorganic anions such as carbonate, phosphate, and sulfide in the soil water can influence the soil's ability to fix metals chemically (Diatta 2002). These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence. It was also observed that desorption was a more difficult process than adsorption and that not all of the adsorbate was desorbed (i.e., the reactions appear to be partially irreversible). Such apparent irreversibility may result in the adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide (Verburg and Baveye 1994). The time-dependent desorption behavior from laterite soil in this case could be ascribed to heavy metals being trapped in soil micropores, which resulted in a tortuous and slow release process (Sparks 1995). This interesting observation clearly stimulates the need of conducting further studies at macroscopic scale to determine the mechanisms for sorption-desorption phenomena as macroscopic measurements and models done in this work revealed some important information about sorption/desorption phenomena only but no mechanistic or molecular information could be explained.

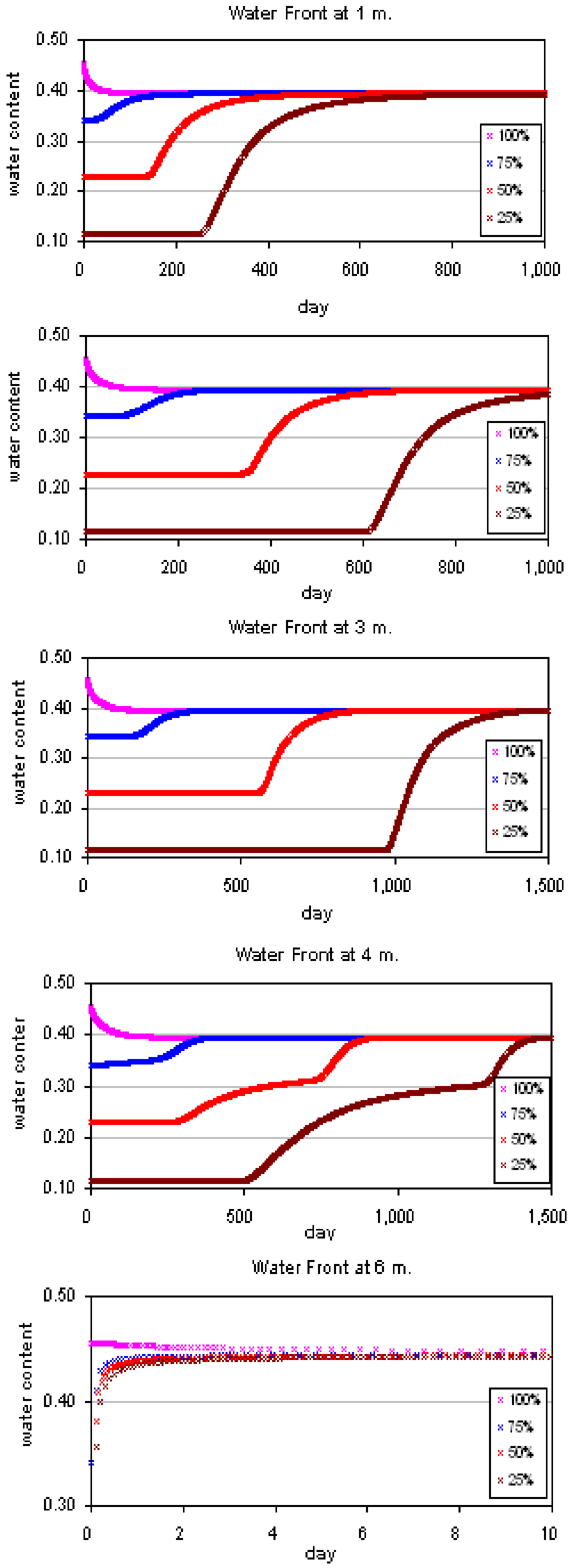

Fig. 6 Effects of variable soil moisture content on transport and migration of multiple component heavy metal in unsaturated zone

Next the adsorption parameters of multiple component heavy metals onto laterite soil were determined in single and multiple component heavy metals solutions. The sorption isotherm is extremely important in assessing the mobility of dissolved and sorbed chemicals, including heavy metals, in soil environments. Analysis of the adsorption data shown in Fig. 2 by employing a well-documented adsorption isotherm theory, demonstrated that sorption isotherms of Zn and Pb fit the Langmuir adsorption model as shown in Fig. 2. For this, the relatively high correlation coefficient R^2 values in most cases were observed from this study, indicating that transport and migration of heavy metals in unsaturated zone was governed mainly by their sorption capacity and/or other immobilizing mechanisms such as precipitation.

Langmuir parameters Q_{max} and a were well correlated for Pb regardless of whether the metal was applied in single or multiple solutions because Pb had the highest sorption capacity compared to Zn, Ni, and Mn based on the highest estimated maximum sorption parameter Q_{max} and binding affinity a. However, when Pb was applied in multiple metal solution with one dominating metal, Langmuir parameters Q_{max} and a were no longer well correlated.

The $\left(Q_{\max}/Q^{*}_{\max}\right)_i$ ratios were greater than unity (Q_{max} and $Q_{max}{}^{*}$ are the maximum sorption capacity in single and multiple heavy metal solution, respectively), suggesting that the simultaneous presence of multiple metals reduced sorption through competition for sorption sites (Serrano et al. 2005). The experimental observations revealed that $(Q_{\max}/Q^{*}_{\max})_{Ni} > (Q_{\max}/Q^{*}_{\max})_{Pb} > (Q_{\max}/Q^{*}_{\max})_{Mn} > (Q_{\max}/Q^{*}_{\max})_{Zn}$ suggesting that Ni sorption was more affected by the simultaneous presence of competing metals than other metals. This tendency of Pb to be effectively competed for sorption sites on solid surfaces has been described in the presence of other metals such as Cd (Fontes and Gomes 2003) and Cu (Christl and Kretzschmar 1999).

The bonding energy coefficient (a and a^* for single and multiple metal solutions, respectively) varied with metal solution and concentration, although Pb showed greater affinity than other metals regardless of the single or multiple metal solutions (Table 4). This finding is in agreement with Serrano et al. 2005. While binding strength, or affinity constant (a) estimates made from sorption isotherms should be considered qualitatively (Sparks 1995), lower a values appear to be related to sorption at low energy surfaces with high dissociation constants. The increasing isotherm a value for Mn in the presence of other competing metals may indicate that serious competition for sorption sites promotes the retention of Mn on more specific sorption positions. As a result, although maximum sorption coefficient Q_{max} decreased slightly, the metals were held more strongly. The reduction in both Q_{max} and a values may be explained by the high metal load, resulting in the saturation of sorption sites on solid surfaces.

Comparison of sorption isotherms of cases 1 (single metal) and 3 (multiple metals with one dominating metal) in Fig. 2 revealed the irregular sorption behavior of Pb as the steeper slope was observed for case 3 during the early stage, indicating that lead was initially more rapidly sorbed in the coexistence with other metals in the solution. Overall, this initial rapid reaction that Pb underwent in multiple metal solution is the characteristic of heavy metal sorption on pure components and soils and has been attributed to adsorption on high affinity surface sites (Glover et al. 2002) or on sites with higher bonding strength with the metal (McBride 1999). Consequently, the increment in the initial Pb sorption rate in multiple component metal solution could indicate that the competitive sorption forces Pb retention on more specific sorption sites for this metal.

The analysis of water fronts profile at each depth under various initial soil moisture content conditions (Fig. 5 and 6) revealed that the wetter the laterite soil in the environment the more heavy metal mobility we should expect. The simulation of water fronts at 6 m deep from ground surface did not illustrate the effects of initial soil water contents at all due to the presence of water table that is located in the vicinity at 6 m deep into the ground. The presence of groundwater table would saturate the system, and soil moisture contents would reach its saturated condition rather quickly no matter what the initial soil moisture contents were. More importantly, the results in Fig. 6 indicated that initial soil moisture content affected the water front profile more significantly at the shallow depths.

It is important to note that HYDRUS-2D numerical model was run for a relatively long time because metals naturally could travel quite slowly in subsurface environment as they tended to sorb more onto the soil matrix surfaces. The correlations shown in the figure suggested the effects of water content on time to reach the maximum concentration level for each metal. The steeper slopes of the plots between final water contents versus time to reach a certain metal concentration with increasing depth responded to the previous comment that initial soil moisture contents did greatly affect the mobility of multi-species heavy metals in the shallow unsaturated zone. This shallow depth zone is known for its biological and vegetation root uptake activities to take place, therefore may yield a potential for toxic heavy metals to be removed from the subsurface environment via biodegradation and biosorption (Minamisawa et al.

2004). On the other hand, the return of heavy metals to surface via vegetation root uptake may raise an alarm to public health concern regarding the accumulation of heavy metals in agricultural products. This study thus provides a basis for understanding the possible application of bioremediation and phytoremediation to remove multiple component heavy metals in subsurface environment, where there has been interest in the use of natural plants in treating heavy metal polluted effluents during the past two decades (Schneider and Rubio 1999).

CONCLUSIONS

This paper focused on investigating the effects of environmental conditions such as pH and soil moisture content on the transport and mobility of single and multiple component heavy metals in laterite soil and the dynamic competitive sorption behavior of the multiple component heavy metals through a series of equilibrium batch experiments and numerical simulations using HYDRUS 2D.

From all the findings here in this paper, it may be concluded that the sorption behavior of Pb, Mn, Zn, and Ni in laterite soil is significantly affected by the coexistence of other metals and the environmental factors including soil moisture contents. Thus, the competitive sorption as well as water saturation should be considered to correctly assess their potential bioavailability, toxicity, and leachability in unsaturated subsurface environment as these factors are imperative not only from the point of view of the residence time of the toxic heavy metals in the root zone (thereby their accumulation or plant uptake) but also for their potential to further contaminate groundwater underneath.

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