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KINETICS OF METAL LEACHING FROM HEAVY METAL CONTAMINATED SOILS

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INTRODUCTION

The evaluation of the rate and extent of heavy metal leaching from contaminated real waste site soils is an important aspect in the design of soil washing processes. Although the technology of soil washing is well established in Europe, until recently it had been demonstrated only on a pilot scale in the United States. In January 1992, the first full scale soil washing system in the United States started operation at the King of Prussia Technical Corporation Superfund site at Winslow Township, New Jersey (1). Of the 498 Records of Decision published through 1991, only 18 specified soil washing as the primary remediation technology. Currently, models that may yield design information are not available and the soil washing technology is at an empirical level of development. This goal of this project was to develop a deterministic model to describe the kinetics of metal leaching from contaminated soils. Specific objectives of the project were to: 1) experimentally measure leaching kinetics under acidic conditions from real waste site soils, 2) determine through numerical simulation the fate and interactions of the various contaminant phases during the washing process, and 3) identify the rate controlling steps and gain insight into design and operational aspects of the washing process. The focus of the study was on Pb contaminated soils.

METHODOLOGY

BET analyses were conducted on the soil samples by a contract lab to obtain soil surface area, pore volume and pore diameter data. Sieve analyses (ASTM Method D422-63) were performed to obtain particle size distribution data from which the geometric mean was calculated and used for model simulations. A standard acid digestion procedure (EPA Method 3050) was conducted on soil samples to determine total Pb content.

A sequential extraction method developed by the DuPont Corporate Remediation Group (2) was used to determine the distribution of Pb in various geochemical phases. This technique was developed specifically for Pb contaminated soils. Soil samples were air dried and only material passing through a #10 sieve (2 mm mesh size) was used for analysis by sequential extraction. Pb was partitioned into the following ten fractions: 1) water soluble; 2) exchangeable; 3) Ag-displaceable; 4) carbonates; 5) Mn oxides; 6) organic; 7) amorphous Fe-oxide; 8) crystalline Fe-oxide; 9) sulfides; 10) residual. For modeling purposes, it was assumed that fractions 1, 2 and 4 form the easily leachable phase, and fractions 3 and 5 through 8 constitute an adsorbed phase. Phases 9 and 10 form the residual phase and were assumed to be immobile, even under strongly acidic washing conditions.

Bench scale soil washing experiments were performed to obtain kinetic data during acid washing of soils in a batch reactor system under vigorous mixing. pH was carefully controlled throughout the

experiments by means of pH controllers and an acid delivery system to maintain the set point pH. Typically, experiments were run at a liquid to solid (L/S) ratio of 20 (1.6 L of solution with 80 g of soil) with HCl as the extractant, although experiments at different L/S ratios were carried out. The L/S ratio changed slightly during the course of the experiments due to sampling and evaporation losses. During each experiment, samples were collected periodically up to 5 hours; a final sample was collected after 24 hours of washing. Samples were collected using a plastic syringe which was fitted with a filter holder containing a 0.22 µm membrane filter. The filtered sample was analyzed for metal content by flame atomic absorption spectroscopy. It was assumed that the filtered metal concentration was equal to the total dissolved metal species in solution. During the experiments, the solution conductivity also was measured periodically and used to calculate the ionic strength of the bulk solution.

Quality Assurance/Quality Control (QA/QC) procedures were followed throughout the study. For analysis of Pb by flame atomic absorption spectroscopy, calibration standards were checked every ten samples, matrix interference spikes were tested every twenty samples, and duplicate analyses were performed every ten samples. QA/QC for soil washing kinetic experiments involved analyzing blank samples collected at the beginning of each experiment to test for Pb contamination of glassware, mixing impellers, or sampling syringes, performing duplicate samples for 10% of the samples taken within an experiment, and duplicating 10% of the soil washing experiments performed.

MODEL DEVELOPMENT

Leaching of contaminant metal was assumed to take place from porous, homogeneous spherical soil particles of uniform radius, which were immersed in an extractant solution (Figure 1). As noted above, it was assumed for modeling purposes that metals in contaminated soils exist in three phases only: metal precipitates (primarily carbonates and other easily leachable forms, e.g., water soluble + ion exchangeable + carbonate fractions), adsorbed metal (e.g., metal adsorbed to soil surfaces + organic coatings + Fe/Mn oxides) and an immobile residual phase. Complexing anions (e.g. Cl^-) and H^+ ions in the extractant diffuse into the pores of a particle as a result of both pore and film diffusion. H^+ reacts with precipitated (M(s), e.g., $PbCO_3(s)$) and adsorbed ($\equiv$M, e.g., $\equiv Pb^+$) contaminant metal, and the resulting metal ions (M, e.g. Pb^{+2}) are released into the pore solution. Metal ions may also undergo complexation reactions due to the presence of complexing anion(s). Concentration gradients within the particles result in the diffusion of free and complexed metal ions out of the pores and into the bulk solution. Similar reactions occur at the particle surface, with only film diffusion controlling the movement of species in and out of the bulk solution. Because the leaching process is assumed to take place in a well mixed system, diffusion within the bulk solution is ignored.

Sorption is assumed to be a reversible process and is treated as a pseudo-first-order reversible reaction with respect to the metal phase,

$$[\equiv M] + [H^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M] + [\equiv H] \tag{1}$$

where, ratio $k_1/k_{-1} = K_{ads}$, the equilibrium constant for adsorbed metal.

For soil washing using acidic solutions, dissolution of metal carbonates is assumed to follow an irreversible reaction:

$$M(s) + H^{+} \xrightarrow{k_2} M + products \qquad (2)$$

While the model accounts for metal complexation, adsorption of metal complexes to the soil surface is ignored. The formation of metal complexes with Cl^-, for example, during soil washing with HCl is assumed to be rapid and is described by the equilibrium reaction,

$$M + Cl^{-} \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} MCl \qquad (3)$$

where $k_3/k_{-3} = K_{Cl}$, the equilibrium constant for the reaction.

Double layer effects are ignored because at higher ionic strength (> than about 0.1 M) the coulombic contribution to adsorption is constant in the acidic pH range (3).

The activity of adsorbed metal is assumed to be unity. Activity coefficients are calculated based on the Bronsted-Guggenheim equation and may vary with leaching time as ionic strength typically increases as ions are leached from the soil. Also, within the soil particle a radial gradient in ionic strength is assumed to exist that is the same as the simulated Pb gradient.

The model was formulated by linking the pore diffusion equation of each ion (4) with its corresponding chemical reaction. The transfer of metal from the particle surface to the bulk solution across the liquid film is assumed to follow Fick's first law of diffusion.

The resulting system of partial differential equations was transformed to a set of ordinary differential equations (ODEs) in time by using a finite difference (central difference) approach for the spatial derivatives. The resulting set of ODEs with the appropriate initial and boundary conditions was solved using an ODE solver. Details of the modeling approach are described elsewhere (5,6).

Model parameter estimates were based on laboratory measurements (soil particle size characteristics, Pb content and distribution, ionic strength), calculation (diffusion coefficients, activity coefficients), and data fitting. Equilibrium data were used to fit the equilibrium constant K_{ads} (equation 1) and a total site density, S_T. Kinetic data then were used to determine the rate constants k_1 (equation 1) and k_2 (equation 2) and a particle tortuosity factor. Parameters were fit by minimizing the sum of squares between measured and fitted data.

RESULTS

Fitted and measured data under pseudo-equilibrium conditions (24 hrs leaching) for four soils are shown in Figure 2. The data for each soil were fitted using two parameters, the metal adsorption equilibrium constant, K_{ads} and the total site density, S_T ($S_T = [\equiv H] + [\equiv Pb]$). The parameters, K_{ads} and S_T, estimated by the equilibrium modeling approach are soil specific. The values of the site density, S_T, across different soils falls within the range of site densities reported in the literature. The equilibrium constants, K_{ads}, across the soils are similar (Table 1). Differences across soils may be attributed to differences in surface characteristics, soil heterogeneity and site density. Considering the complexity of real waste site soils, the fit of the data is good, possibly because at low pH and the contaminant levels for these soils, the system is dominated by H^+ and Pb^{2+}.

Model calibration results to kinetic data for two of the waste site soils studied are shown in Figure 3.

For each of the soils, one set of model parameters describes the range of pH conditions shown. From Table 2 it is observed that the kinetic parameters, k_1 and k_2, for the four soils are in relatively close agreement. The slight variation between the values of the kinetic coefficient from one soil to another may be due to inherent differences in these soils or the manner in which lead geochemical phases were combined for modeling purposes. The dissolution coefficient, k_2, for the soils studied are close to those reported by Tuin and Tels (7). However, lack of available literature values hinder additional comparisons. From the calibration results it is also observed that the soil particles have a tortuosity greater than unity (Table 2), which is consistent with values reported in the literature. The similarity in model parameter estimates across different soils may be due to the similarity in Pb distribution across different soils. Although the parameters estimates are soil specific, they apply to leaching data at pH 1 to 3 and a range of ionic strength from 0.01 to 0.6M.

A sensitivity analysis was undertaken to gain insight to the relative importance of parameters affecting metal leaching. The analysis showed that model simulations were most sensitive to metal geochemical phase distribution (i.e., precipitated vs adsorbed) and metal location (i.e., surface vs pores). These results, in addition to sensitivity to pH (see Figure 3) indicate the importance of chemical factors in influencing leaching from real waste site soils.

While preliminary modeling efforts were successful in simulating metal leaching under acidic conditions, the effects of a strong ligand (i.e., EDTA) were not modeled successfully.

CONCLUSIONS

A numerical model, developed to simulate the removal of lead from soils, was applied to experimental data from four waste site soils based on parameters which were estimated through a combination of independent experiments, literature correlations and mathematical optimization. The lead contaminant pool was divided into easily leachable, adsorbed and residual phases based on sequential extraction data. The parameters obtained from the model calibration are consistent to those observed in the literature for adsorption of Pb to mineral surfaces. The similarity in the parameters estimated by the model may be due to similar geochemical phase distribution of lead across the soils. The results obtained show that the model is capable of matching experimental data over a range of solution pH (pH 1 to 3) and ionic strength (0.01 to 0.6M).

Although the model matched the experiment leaching data well, improvement in its performance can be further achieved by better characterization of metal geochemical phases distribution. Quantifying the radial distribution of metal across the particle would also improve the model performance. The effect of strong ligands on metal leaching was not adequately described and needs to be incorporated in the model.

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TABLE 1. EQUILIBRIUM MODEL CALIBRATION RESULTS

Parameters	Soil 1	Soil 2	Soil 3	Soil 4
S_T (sites/nm^2)	1.95	1.95	7.65	0.53
K_{ads}	3.38×10^{-3}	1.42×10^{-3}	1.30×10^{-3}	2.08×10^{-4}
r^2	0.99	0.99	0.99	0.99
Std. Error (mg Pb/L)	11	1.5	8.3	1.0

TABLE 2. KINETIC MODEL CALIBRATION RESULTS

Parameters	Soil 1	Soil 2	Soil 3	Soil 4
k_1 (L/mol-min)	0.644	0.019	0.39	0.134
k_1 (L/mol-min)	10.4	11.6	9.03	9.97
Toruosity	13.6	21.8	1.5	1.74
r^2	0.99	0.95	0.96	0.97
Std. Error (mg Pb/L)	2.28	4.45	3.97	0.57

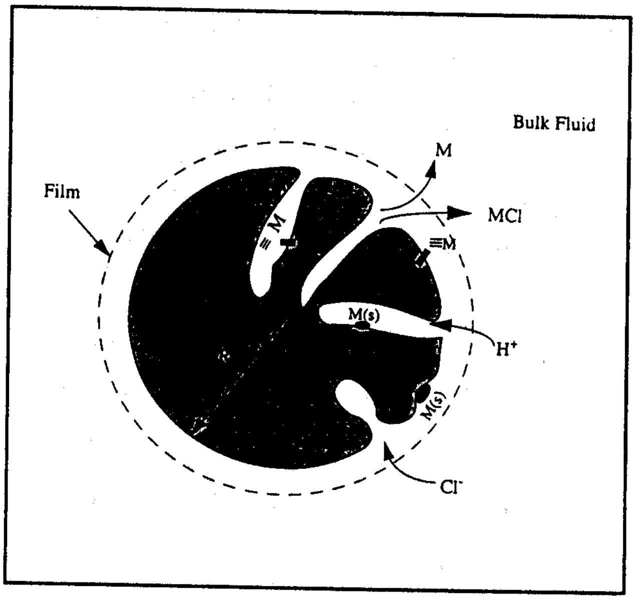

Figure 1. Conceptualization of metal leaching.

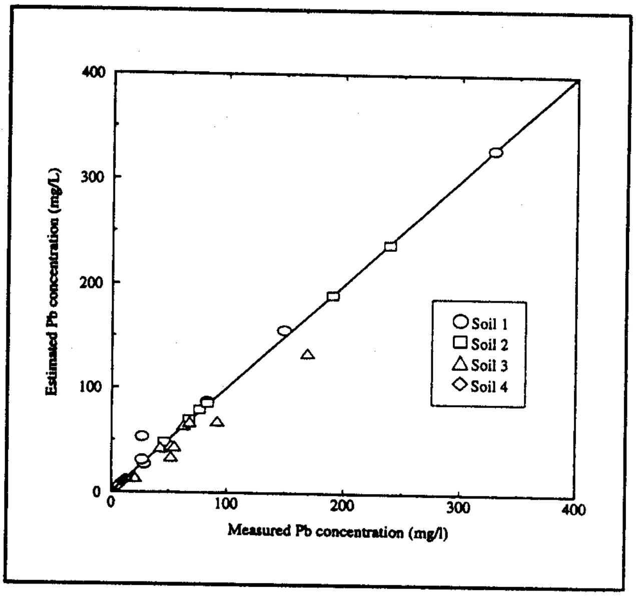

Figure 2. Equilibrium model calibration results.

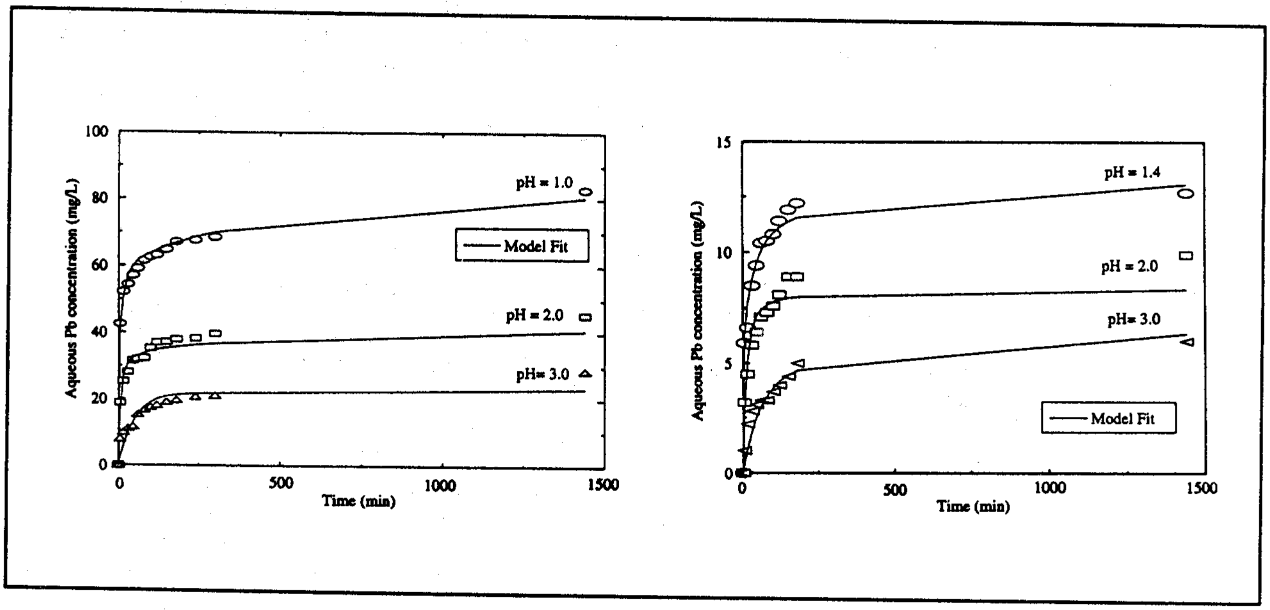

Figure 3. Kinetic modeling results for two waste site soils.

INTRINSIC BIOREMEDIATION OF CHLORINATED SOLVENTS AT THE ST. JOSEPH, MI AQUIFER - LAKE MICHIGAN INTERFACE

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1. INTRODUCTION

The anaerobic aquifer at the St. Joseph, MI National Priority List (NPL) site has been contaminated with trichloroethylene (TCE) of up to 160 mg/L, which in the last decade has been shown to have dechlorinated to cis- and trans-dichloroethylene (DCE), 1,1-dichloroethylene, vinyl chloride (VC), ethylene, and ethane. Previously, it was established that the occurrence of these products was due to intrinsic bioremediation, based on both laboratory investigations (1,2) and temporal monitoring of the groundwater , which showed significant levels of ethene and methane (3-5).

The flux of all alkyl halides into Lake Michigan is of major public concern due to the suspected carcinogenicity of VC. Moreover, as the plume moves towards and emanates into the aerobic surface water, the dominant redox conditions can be expected to change due to wave action and vertical seepage which promote the interchange of oxygen-rich lake water with the anaerobic groundwater. This phenomenon is likely to have an impact on the microbial community structure, and thus the biodegradative processes. The current presentation provides the results of field investigations at the interface with Lake Michigan, and presents some preliminary results on the fate of chlorinated solvents at a simulated interface between earobic and anaerobic conditions using using both experimental and modeling approaches.

2. METHODOLOGY

Off shore sampling was conducted using a truck-mounted Geoprobe chained on a 80' x 30' barge, which could be anchored using steel spuds (The Probing Times, 1994). The barge was put in place with the help of a tugboat, and an on-shore surveying team. Barge locations were based on a previously determined offshore survey plan, generated based on ground penetrating radar (GPR) and sonar measurements (B. Sauck, Eastern Michigan University). The four sampling points were approximately 100 m off shore at a depth of approx. 15', which corresponds to the expected hydraulic connection between the aquifer and Lake Michigan. A specially designed drill pipe was centered with a two-inch PVC sleeve, which was anchored with a steel plate in the lake sediment surface. A 0.5' vertically slotted screen well point was advanced to depths of up to 21 feet into sand and silt layers in 15-20' of water off shore, at depth intervals of 2-3'. Water samples were collected and analyzed for conductivity, pH, inorganic redox couples, methane, ethane, ethene, and chlorinated volatile hydrocarbons. Sediment samples were collected in the more reduced regions, were saturated with anaerobic groundwater, and shipped to the University of Michigan laboratories, where they were transferred to an anaerobic chamber.

On shore sampling was conducted using a Geoprobe with a 1' screen, which was driven into the beach sands using an 80lb electric hammer to depths of up to 32'. Groundwater samples were collected at 3' depth increments, and sediment samples were collected from the most reduced zones at 17-20'. The locations of the barge and the beachhead sampling points are shown on Figure 1, relative to the five previously developed transects on shore (modified from Wilson et al., 1994).