

Mathematical model for reactive transport of heavy metals in soil column: Based on PHREEQC and HP1 simulators

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Abstract. Mining activities play a significant role in environmental pollution by producing large amounts of tailings which comprise heavy metals. The impressive increase in mining activities in recent decades, due to their high influence on the industry of developing countries, duplicates the need for a substantial effort to develop and apply efficient measures of pollution control, mitigation, and abatement. In this study, our objective was to investigate the effect of simulation of the leachate, pH and inflow intensity of transport of Pb^{2+} , Zn^{2+} , and Cd^{2+} through Lakan lead and zinc plant tailings, in Iran, and to evaluate the modeling efficiency by comparing the modeling results and the results obtained from previous column studies. We used the HP1 model and the PHREEQC database to simulate metals transport through a saturated soil column during a 15 day time period. The simulations assumed local equilibrium. As expected, a lower pH and inflow intensity increased metal transport. The retardation of heavy metals followed the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$ and the removal concentrations of Cd, Pb, and Zn at the inflow intensity critical scenario, and Cd and Pb at inflow acidity critical scenario exceeded the allowable EPA and Iranian's 1053 standard thresholds. However, although the simulation results generally agreed well with the results of the column study, improvements are expected by using multi-dimensional models and a kinetic modeling approach for the reactions involved. The results of such investigations will be highly useful for designing preventative strategies to control reactive transport of hazardous metals and minimize their environmental effects.

Keywords: lakan plant tailing; HP1; PHREEQC; heavy metals; Cd, Pb, and Zn; lakan lead and zinc plant

1. Introduction

Despite significant progress in science and technology, environmental problems are increasing at the national, regional, and international levels. Correlations between industrial activities and environmental contamination make it difficult to expect substantial industrial development without some impact on the environment. The production of inorganic wastes in mining operations has always been an important issue and a threat to the environment, especially the subsurface. The

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oxidation rates, even though capillary forces kept the local moisture content relatively high. Pot *et al.* (2005) used different physical and chemical equilibrium and non-equilibrium transport models to simulate the impact of various rainfall intensities on herbicide transport. Their study showed that physical/chemical, non-equilibrium conditions were dominant. Michel *et al.* (2007) used mathematical and empirical models to investigate nickel and cadmium transport in silty and sandy soils and concluded that a decrease in the pH increases the transport of heavy metals in acidic soils. Dolati Ardejani *et al.* (2008) investigated the pollutant problems associated with the waste produced by a coal washing plant using the Phoenix package to simulate pyrite oxidation and pollution generation from waste dump. Using HP1 model, Jacques *et al.* (2008) further presented that reducing the inflow intensity causes a decrease in the pH level, thereby promoting monovalent cations to adsorb on the cation exchange complex, and bivalent cations to adsorb into the soil solution. Simulating the effect of pH on Pb, Mn, Zn, and Ni transport using HYDRUS-1D, Chotpantarat *et al.* (2001) found that increasing the pH of the inflow solution increases the retardation of heavy metals. They also indicated that the use of a two-site model (TSM) for sorption produced a better match with measured heavy metal BTCs than linear or nonlinear Langmuir type equilibrium models. Grathwohl *et al.* (2013) introduced the featured catchments and describe a methodology of the Water and Earth System Science (WESS) by selecting samples. Maier *et al.* (2013) applied MIN3P to evaluate the water chemistry from the infiltration through soil into the unsaturated zone, transport through bedrocks and granular aquifers to a river to identify zones of steep concentration gradients and high dynamics under transient flow conditions. Their results indicated that subsurface water residence times range from approximately 2 to 2,000 years. Chen and Jiao (2014) applied the PHREEQC 2.0 to determine freshening time and hydrochemical of coastal groundwater in two brackish aquifers in Shenzhen, china. Their sensitivity analysis indicated that the freshening time was most sensitive to the pore water velocity in the aquifer, while the groundwater chemical composition was more sensitive to the values of cation exchange capacity of the aquifer. Nair *et al.* (2014) used two Surfaces complexation models, electrostatic (ES) and non-electrostatic (NES) models were employed to simulate the sorption behavior of U (VI) on quartz in the absence of Mg, Ca, and Sr and ES model in the presence of alkaline earth metals. The surface reaction constants (log K) for ES and NES models were fitted to experimental data by coupling PEST with PHREEQC. In U (VI)-Mg-quartz, U (VI)-Ca-quartz, and U (VI)-Sr-quartz systems, only the ES model describes the general trend of the experimental data. Beni *et al.* (2014) conducted experiments and modeling of the possible effects of iron oxide coatings on the reactive surface area of calcite in the column. The losses and gains of calcite in the column compartments provided the data basis for modeling the entire experiment with the reactive transport code TOUGHREACT using a kinetic rate law. The simulated calcite changing patterns in the most compartments are consistent with the experiments. Wuana *et al.* (2016) tested some toxic heavy metals from municipal waste dump soil by the castor plant under natural and single or mixed chelant-assisted scenarios in pot microcosms. They suggested that the mixed chelants could be considered as alternative treatments for enhanced phytoextraction and revegetation of degraded waste dump soils.

We attempted to investigate the effect of aqueous pH conditions and inflow intensities on the sorption and transport of three heavy metal ions, Cd^{2+} , Pb^{2+} , and Zn^{2+} , using the HP1 numerical model, to evaluate the model's utility in simulating the transport of heavy metals and to investigate the sorption behavior of heavy metals in soil columns.

Table 2 Continued

Specific Volume	(ml)	110
Bulk density	(g./ml)	1.48
Specific density	(g./ml)	2.02
Solid fraction	-	0.73
Porosity	-	0.27

2.3 Transport model

We applied HP1 version 2.2 developed by Jacques and Šimůnek (2010) in our study. The HP1 reactive transport simulator, obtained by weak coupling of HYDRUS-1D and PHREEQC-2, was developed and designed to address multicomponent geochemical transport processes in the vadose zone. The software integrates a broad range of physical and biogeochemical processes, as described in the original manuals of HYDRUS-1D (Šimůnek *et al.* 2008a), PHREEQC-2 (Parkhurst and Appelo 1999), and HP1 (Jacques and Šimůnek 2010). HYDRUS-1D was originally designed mostly for simulating water flow, solute transport, and heat transport in one-dimensional variably saturated media. The program can numerically solve the Richards equation for saturated-unsaturated water flow and the Fickian-based advection-dispersion equation for solute and heat transport. In this software, the solute transport module also considers equilibrium and non-equilibrium advection-dispersion in the liquid phase, and nonlinear equilibrium physical and chemical sorption. Both of the HYDRUS-1D and HP1 models account for soil heterogeneity at the macroscopic scale by using scaling factors (Vogel *et al.* 1988), and at the microscopic scale by using dual-porosity or mobile/immobile type flow models (Fala *et al.* 2003, Šimůnek *et al.* 2003). HP1 implements a weak coupling method in which the governing equations for water flow, heat transport, and solute transport are solved sequentially. The multicomponent reactive transport equations are solved using a non-iterative sequential approach, meaning that the physical part is solved first without any chemical interactions, while the chemical reactions that are uncoupled in space and coupled to the components are solved subsequently (Jacques *et al.* 2008). A flow chart of the operator-splitting approach used in HP1 was described in (Jacques *et al.* 2006). Although operator-splitting errors may occur with this approach, Jacques *et al.* 2006 and Jacques *et al.* 2008 indicated that very accurate results can be determined by carefully selecting the spatial and temporal discretization.

2.3.1 Soil hydraulic properties

Six analytical models are available in HP1 to describe the soil hydraulic properties, including the function of Brooks and Corey (1964), Van Genuchten (1980), and Vogel and Cislérova (1988). In our study, the van Genuchten-Mualem (1980) was used to describe the water retention and hydraulic conductivity ($K(h)$) functions

$$\theta(h) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \quad (1)$$

$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \quad (2)$$

$$R = \frac{1 + \rho_b K_d}{\theta} \quad (9)$$

Where K_d is the partitioning coefficient of the solute [L^3M^{-1}], and v is the average pore water velocity [LT^{-1}].

2.3.4 Numerical simulation

The water flow and solute transport equations were solved numerically using the HP1 code (Jacques *et al.* 2010). The upper and lower boundary conditions for water flow were assumed to be a constant pressure head, and for solute transport to be a concentration flux boundary condition (third type) and a zero concentration gradient (free drainage), respectively. In the HP1 model, the Galerkin finite element method with a space weighting scheme was selected, while the time derivatives of the solute transport solution were approximated using a Crank-Nicholson finite difference scheme. We conducted all simulations over a period of 15 days. The modeling procedure was divided into two separated parts (as the experimental scenarios). Part one was considered to cover the simulation of the flow rate effect (the inflow solution assumed to be neutral), in which the flow rates were 0.5, 1, and 2 cc/min (cc stands for cubic centimeters), while in part two, the effect of inflow acidity is modeled by considering two different (0.12, and 0.29 g/L) inflow concentrations (for a 1 cc/min in flow rate). The boundary condition was specified as the experiment of Khodadadi Darban *et al.* (2012) which we selected the boundary conditions of our model the same as the experiments. Inflow rate was constant and the simulation column was in saturated flow condition. The rate of flow in outflow was zero. Acid concentration and pH of inflow were constant at the top of the column.

Fig. 1 indicates time of information and number of iterations.

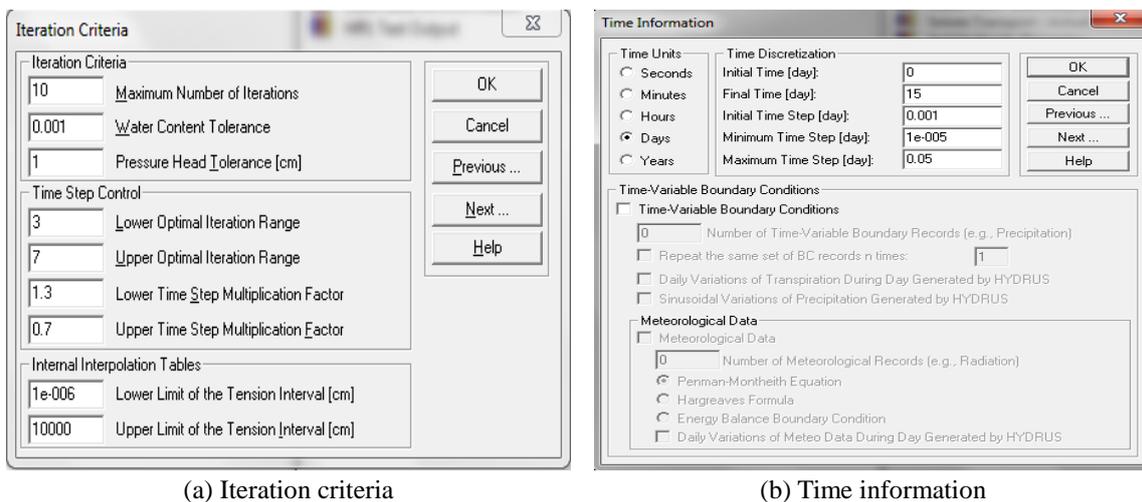


Fig. 1 Detail of simulation procedure

Simulating the transport using HP1 model, the Van Genuchten-Mualem (1980) was used to describe the water retention and conductivity functions. The upper and lower boundary conditions

Where x_i , y_i , x_n and n are measured values, model predictions, arithmetic means of the measured values, and the number of measured and modeled values, respectively. When model predictions perfectly match the measured data, EF is equal to 1. A negative value indicates that the predictions describe the data less than the mean of the observations.

3. Results and discussions

3.1 Inflow intensity

The first investigated parameter in our study was the inflow intensity (the inflow solution assumed to be neutral). Fig. 4 presents the effects of flow rate on the removal of Cd, Zn, and Pb. To simulate which happens in nature, we selected three flow rates 0.5 cc/min, as the slow flow rate, 1 cc/min, as the medium flow rate, and 2 cc/min as faster flow rate, which was similar to the experiments were carried out by Marzban (2008) and Khodadadi Darban *et al.* (2012). We achieved maximum removal of Cd, Zn, and Pb after three days at a flow rate of 0.5 cc/min (Fig. 4).

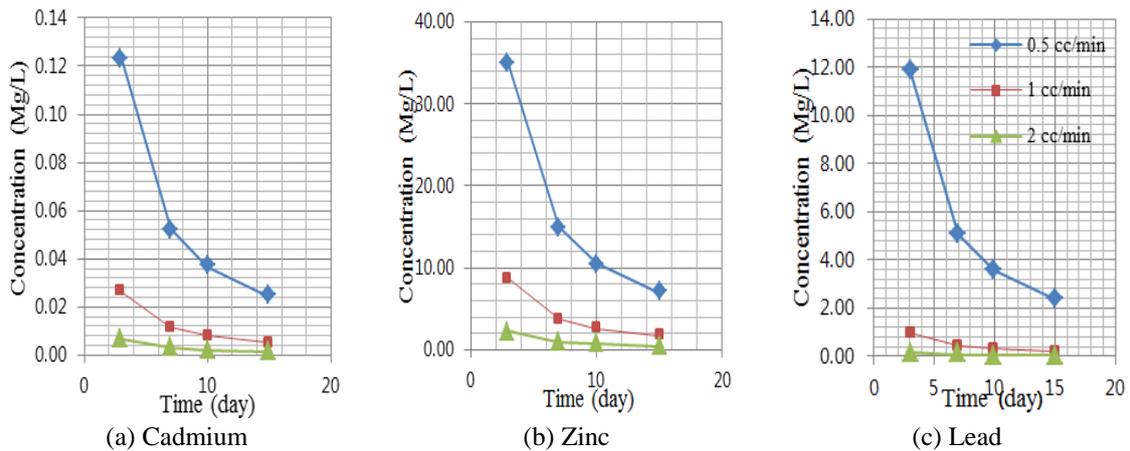


Fig. 4 the effluent concentration of Cd, Zn, and Pb from simulation columns for different flow intensities in different days

Table 3 the effluent concentration of Cd, Zn, and Pb from simulation columns for different flow intensities on day 15

Element/inflow intensity (cc/min)	0.5	1	2
Cd (mg/l)	0.02	0.005	0.001
Zn (mg/l)	6.97	1.73	0.45
Pb (mg/l)	2.37	0.19	0.03

The total removal concentrations of these metals were 0.12, 34.85, and 11mg/l, respectively (Fig. 4). The higher leach ability in lower flow rates could be justified by having sufficient time for the reactions between the soil solid phase and the soil solution. The removal concentrations of

achieved after three days using the input solution with a pH of 5. The removal concentrations of these three metals were 0.4, 16.38, and 1.21 mg/L, respectively. Zn and Cd are considered mobile mainly in dissolved forms (Weber *et al.* 1991), whereas Pb considered as low or non-mobile in soils. The lower removal concentrations of Cd and Pb, compared to Zn in both inflow intensity and acidity scenarios, is likely due to precipitation of Cd and Pb species, especially at lower pH levels. The higher removal of metals with decreasing pH is reasonable because higher pH indicates lower quantities of H⁺ ions and an increase in the retardation factor of heavy metals as indicated by Chotpantararat *et al.* (2001), among many others. Table 5 presents the removal concentrations of the three metals after 15 days.

For the two difference pH, the simulation of the outflow concentrations after 15 days reached approximately zero. Table 6 describes the experimental and simulated concentrations of Cd, Zn, and Pb after 7 days. Table 7 indicates the simulation efficiencies for different pH levels. Comparing the simulated model with the experimental results, we achieved the highest efficiency for Cd removal concentrations, followed by Zn and Pb.

Table 5 the effluent concentration of Cd, Zn, and Pb from simulation columns for pH5 and pH6 on day 15

Element/pH	pH=5	pH=6
Cd (mg/l)	0.04	0.02
Zn (mg/l)	2.62	2.44
Pb (mg/l)	0.24	0.07

Table 6 the experimental and simulated removal concentrations of heavy metals

Element	pH=6 (Experiment) mg/l	pH=6 (Simulation) mg/l	pH=5 (Experiment) mg/l	pH=5 (Simulation) mg/l
Cd	0.041	0.054	0.053	0.08
Zn	4.47	5.24	5.46	5.32
Pb	0.039	0.15	0.078	0.052

Table 7 the Model efficiencies for the heavy metals removal concentrations at two pH values

Element/pH	pH=6	pH=5	Average
Cd	0.80	0.69	0.75
Zn	0.77	0.5	0.63
Pb	0.79	0.29	0.54

Permissible limits for concentrations of zinc, lead, and cadmium in groundwater, according to the U.S. Environmental Protection Agency US EPA (Weber *et al.* 1991) are 5, 0.005, and 0.01 ppm, respectively. The results in Table 4 (for inflow intensity scenarios) indicate that the concentrations of Cd, Zn, and Pb in solution exceeded the EPA limits. The results in Table 6 (for inflow acidity) indicate that the concentration of Cd and Pb exceeded the allowable limits. They also exceeded the Iranian standard for drinking water (Standard1053). Similar findings were reported by Khodadadi Darban *et al.* (2012). Heavy metal retardation followed the order Zn²⁺>Pb²⁺>Cd²⁺. The same results for similar conditions were reported by Wu *et al.* (1998), except

- The retardation of heavy metals followed the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$.
- Decreasing pH values and inflow intensities produced higher metal removal concentrations.
- The removal concentrations of Cd, Pb, and Zn at the inflow intensity critical scenario, and Cd and Pb at inflow acidity critical scenario exceeded the allowable EPA and Iranian's 1053 standard thresholds.
- Predicted early removal concentrations did not successfully match the observed data, likely due to the presence of sharp solute fronts, failure to establish local equilibrium, insufficient time for complete soil solid phase and soil solution reactions (the presence of macropores), or temporal variations in the physical properties. Some of the differences could be attributed also to the formation of complexes at the beginning of simulations.
- Differences between modeling and experimental results for some scenarios could also be attributed also to uncertainty in the values of some parameters, simplification of the transport process to one dimension, ignoring the effects of macropores and other transport mechanisms occurring in soils (such as bioturbation), or uncertainty in the dominant chemical processes and their parameters. In this study, lack of detailed data was the main barricade for improving the results.
- PHREEQC and HP1 models have approximately the same modeling efficiency for the Cd reactive transport simulations.

More research is needed to explore the various physical-chemical and biological processes that control the potential solubility of toxic metals from mine tailings. The use of two- and three-dimensional models, as well as kinetic modeling, is recommended to more accurately simulate reactive transport in actual field conditions.

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