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TECHNICAL COMMUNICATION

Effective Parameter Predictions in Metals Transport from the Zanjan Zinc Mine Tailings using PHREEQC

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Abstract The effects of grain size distribution, initial flow rate, and initial pH were simulated using PHREEQC to determine how these factors affect the transport of Cd, Ni, and Mn from the tailings of the Zanjan zinc (Iran) leaching plant. Not surprisingly, lower pH, higher flows, and smaller effective particle size increased metal transport. The simulation results generally agreed well with results from a previously conducted column study.

Keywords Geochemical modeling · Sensitivity analysis · Metal transport · PHREEQC · Mine tailing · Zanjan

Introduction

The Zanjan zinc leaching plant, located 12 km from Zanjan, Iran, processes ore from the affiliated Anguran mine into zinc sheet metal. The tailings or "cake" from this operation are enriched in nickel (Ni) and cadmium (Cd). The objective of this study was to determine how pH, flow rate, and grain size distribution affected Ni, Cd, and manganese (Mn) transport from these tailings, using the PHREEQC geochemical model.

Seuntjens et al. (2002) studied how physical and chemical properties affected field-scale Cd transport in a heterogeneous soil profile; using Monte Carlo simulations, they demonstrated that variations in field-scale Cd flux were dominated by variations in deposition rate and the parameters of the Freundlich sorption isotherm. Concas et al. (2005) concluded that a decrease in pH increased metal dissolution and transport from mine tailings. Tipping et al. (2006) used the CHUM-AM model to investigate the behavior of atmospherically-deposited metals in Cumbria, UK and concluded that the principal processes controlling cationic metals are competitive partitioning to soil organic matter, chemical interactions in solution, and chemical weathering.

Michel et al. (2007) applied mathematical and empirical models to investigate Ni and Cd transport in silty and sandy soils and concluded that a decrease in pH increases metals transport in acidic soils. Van der Grift and Griffoen (2007) investigated Cd and Zn leaching from polluted soil using unsaturated and saturated zone flow and reactive transport models and concluded that metal contamination depended on surface water load, geohydrologic and geologic structure, soil type, and dominant land use. Hanna et al. (2009) used PHREEQC to study zinc and lead transport in soils and concluded that the model can predict metal transport in acidic conditions, and that decreasing pH increases metal transport. Gordon et al. (2009) modeled Ni and Cd transport and found that decreasing pH increases Ni and Cd transport in silt and sandy soils. Horvath et al. (2009) showed that column leaching tests can be effectively used to investigate metal transport from mine tailings.

Materials and Methods

Simulation

PHREEQC.2 software (Parkhurst and Appelo 1999) was used to simulate different scenarios of discharge, grain size

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distributions, and pH for about 30 days. PHREEQC is a geochemical model that is used for water and soil environments. One dimensional transport with geochemical reactions can be simulated. The modeling efficiency (EF) was calculated for measured and modeled data using Eq. 1 (Loague and Green 1990):

$$EF = \frac{\sum_{i=1}^{n}(x_i - x_n) - \sum_{i=1}^{n}(y_i - x_i)}{\sum_{i=1}^{n}(x_i - x_n)} \tag{1}$$

where x, y, x^{-}, and N are measured value, modeled prediction, the arithmetic mean of measured values, and the number of measured and modeled values, respectively. When modeled predictions perfectly match the measured ones, EF is equal to 1. A negative value indicates that the modeled prediction describes the data less well than the mean of the observations.

Ni–Cd Cake Compounds

The deposited waste material has been studied using X-ray fluorescence (XRF) and by measurement of its physical properties (Hashem Zadeh 2003; Sedaghat 2007). Elemental analysis indicated that the material contains high concentrations of metals: 40.4 % zinc, 11.2 % Cd, 3.3 % Ni, 1.4 % copper, and 0.8 % lead. A 1 kg sample was sieved using 18, 35, 60, 80, 100, 120, 140, 170, 200, 230, and 270 mesh sieves. Sedaghat (2007) also conducted 30 day leaching tests on 1,441 g of the Ni–Cd cake in each of three 6 cm internal diameter columns; the height of tailings in each column was 40 cm (of the 50 cm column height). The effluent of each column was analyzed after 1, 3, 7, 13, 20, and 30 days. The results of that study were used in this study. Parameters such as rain events and acid leaching were simulated using PHREEQC. Equilibrium and exchange constants for chemical species of the tailings column were taken from the MINTEQ data base (Allison et al. 1990).

Results and Discussion

Grain Size Distribution

Pore volumes differ with grain size distributions, so various scenarios of grain size distribution were simulated in PHREEQC. The first grain size distribution studied was a mixed grain size distribution, since this type of distribution exists in nature. The +18 and −18 to +60 grain size distributions represent a significant percentage (15 and 39 %, respectively) of the Ni–Cd cake in the sieved analysis (Sedaghat 2007). To investigate the effects of grain size distribution on metal transport from the tailings, the pH of the initial leaching solution was considered constant and neutral. The initial solution flow rate was 1 mL/min. The cation species that participate in the exchange and equilibrium reactions were defined by the software. The previously determined porosity coefficient for the mixed grain size distribution was +0.5 (Sedaghat 2007). Porosity corresponding to two other grain size distributions were calculated using soil mechanics Eqs. 2, 3, 4, and 5 (Das 2008).

$$K = 1 - 1.5D_{10}^2 \tag{2}$$

where K and D_{10} is the permeability (cm/s) and effective size (mm), respectively.

$$K = 1.4e^2K_{0.85} \tag{3}$$

where K, e, and $K_{0.85}$ permeability (cm/s), void ratio (dimensionless), and the corresponding value of a void ratio of 0.85 were calculated from Eq. (4):

$$K_{0.85} = 2.4622\left[D_{10}^2\left(\frac{e^3}{1+e}\right)\right]^{0.7825} \tag{4}$$

The relation between porosity (n) and e are defined in Eq. (5):

$$n = \frac{e}{1+e} \tag{5}$$

According to Eq. (5), the porosity for +18 and −18 to +60 grain size was 0.55 and 0.52, respectively.

Figure 1 compares the Cd concentration in the leachate from various grain size distributions of tailings in the PHREEQC simulation and the existing experimental data. The Cd concentration decreased sharply until the 7th day and then decreased at a much slower rate. The maximum leaching concentration was in the mixed grain size distribution and the minimum was associated with the +18 fraction mesh. As indicated in Fig. 2, the Ni concentration in the leachate behaved very similarly.

The model and experimental data for the Mn leachate concentrations agree well for the −18 to +60 and the +18 grain size distribution, but for the mixed grain size distribution, the model only agrees well with the experimental data after the 7th day. In general, as the grain size distribution was increased, the Mn concentration in in the leachate decreased (Fig. 3).

Flow Rate

To investigate metals transport at various pH and flow rate conditions using PHREEQC, we used one grain size distribution (mixed), since that distribution was the most critical in metal transport and exists in nature (Sedaghat 2007). Three flow rates (low, moderate, and high intensities) were selected to simulate natural processes. A flow rate of 0.5 mL/min produces a laminar flow and was the lowest rate that could be reliably produced in our

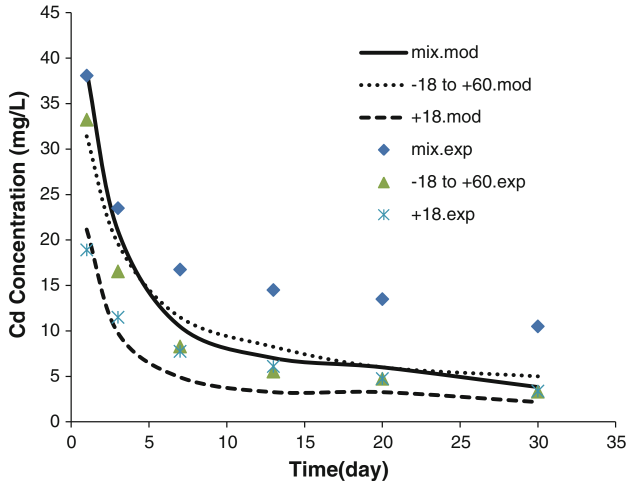

Fig. 1 Simulation and measured cadmium leaching concentrations with various grain size distributions. *Mod.* and *exp.* represents model and experiment respectively

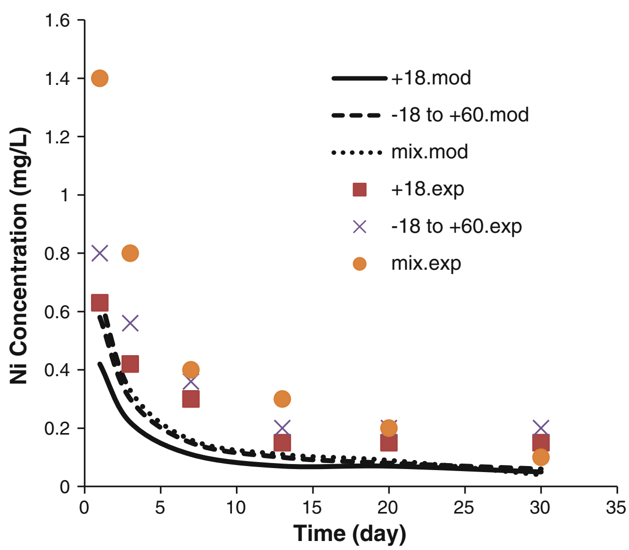

Fig. 2 Simulation and measured nickel leaching concentrations with various grain size distributions. *Mod.* and *exp.* represents model and experiment, respectively

laboratory, while 2 mL/min was set as the highest condition since flooding occurred in the column at higher flow rates (Sedaghat 2007). The maximum daily rainfall in Zanjan is 55 mm/day (Islamic Republic of Iran Meteorological Organization 1983). The number of time steps was defined for each flow rate in PHREEQC. The leachate concentrations of Cd, Ni, and Mn for each flow rate are presented in Figs. 4, 5, and 6. For all three metals, leachate concentrations from the tailings column decreased with increasing initial flow rates and the amounts declined with time during the 30 day period. Leachate concentrations plunged dramatically until the 7th day and then decreased

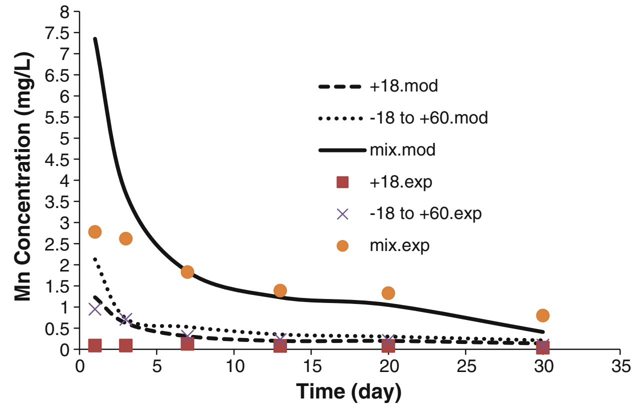

Fig. 3 Simulation and measured manganese leaching concentrations with various grain size distributions

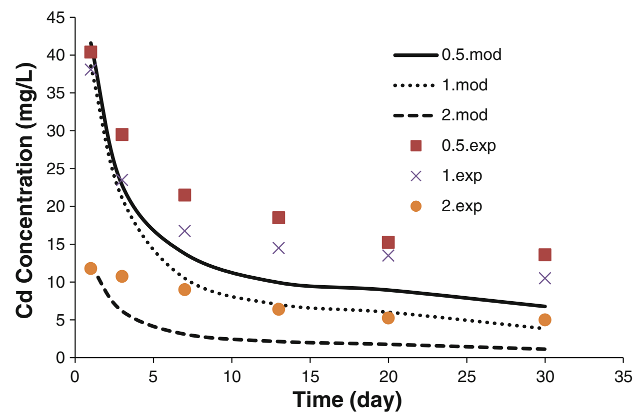

Fig. 4 Modeled and measured leaching concentrations of cadmium at various flow rates

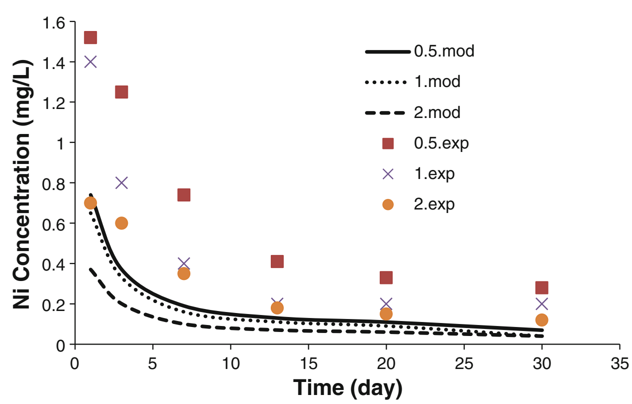

Fig. 5 Modeled and measured leaching concentrations of nickel at various flow rates

steadily. The model results are compared to the results of the column leaching tests (Sedaghat 2007). The simulation efficiencies for the various grain size distributions and flow rate scenarios are presented in Tables 1 and 2.

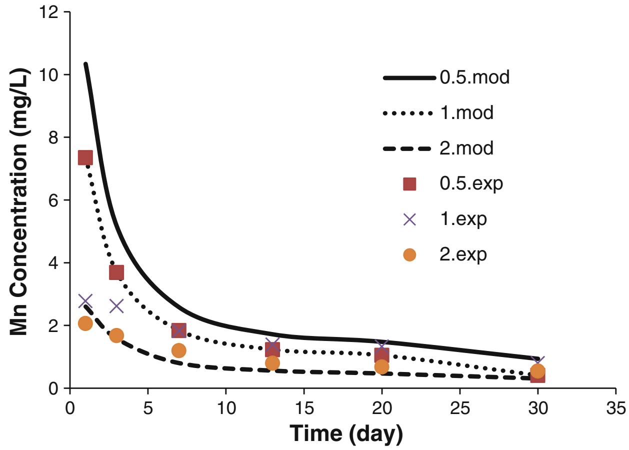

Fig. 6 Modeled and measured leaching concentrations of manganese at various flow rates

Table 1 Simulation efficiency with various grain size distributions

Grain size distribution	+18	−18 to +60	Mix
Cadmium	0.82	0.93	0.61
Nickel	0.36	0.45	0.3
Manganese	0.49	0.84	0.44

Table 2 Simulation efficiency at various flow rates

Flow rate	0.5	1	2
Cadmium	0.22	0.61	0.21
Nickel	0.62	0.3	0.2
Manganese	0.74	0.7	0.44

Initial pH

We used the same initial pH conditions (5, 6, and 7) in the model as were used in the leaching study, which were intended to simulate the effects of acidic rainfall. The cation species that would participate in the exchange and equilibrium reactions were defined by the software. The reactive transport parameters were determined using a 1 mL/min flow rate, which represents moderate rainfall intensity in Zanjan (Sedaghat 2007), and a mixed grain size distribution. The number of time steps and the pore water flow velocity were determined based on the observed tailings pore volume and flow rate. The leaching concentrations of Cd, Ni and Mn were predicted using PHREEQC for the three different pH conditions after 1, 3, 7, 13, 20, and 30 days.

The leachate concentrations plunged dramatically with time. Decreasing pH increased the solubility of all three metals, as illustrated in Figs. 7, 8, and 9. The simulation efficiencies for the pH scenarios are presented in Table 3.

Comparing Our Results with Other Research

Michel et al. (2007) investigated Ni and Cd removal in acidic sandy and silty soils using empirical and mathematical modeling. The simulation efficiency of their study was between 0.35 and 0.85 % in different scenarios. They did not compare results of modes with experiments and the effects of chemicals or other parameters were not considered.

Hanna et al. (2009) studied the effects of increasing pore water flow on zinc and lead transport in soil using PHREEQC and observed weak compatibility between predicted and measured results. They concluded that this was because the software failed to consider the strong metal-binding capacity of the soil.

In this study, there were a good agreement between model prediction and experimental data in most scenarios. However, the proportion of leaching volume to tailings

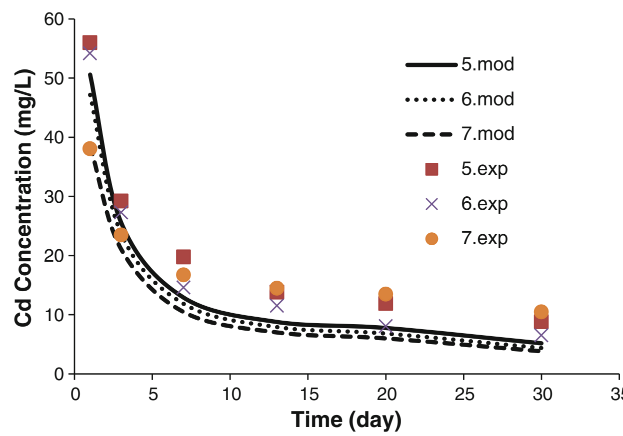

Fig. 7 Modeled and measured leaching concentrations of cadmium over the pH range of 5–7

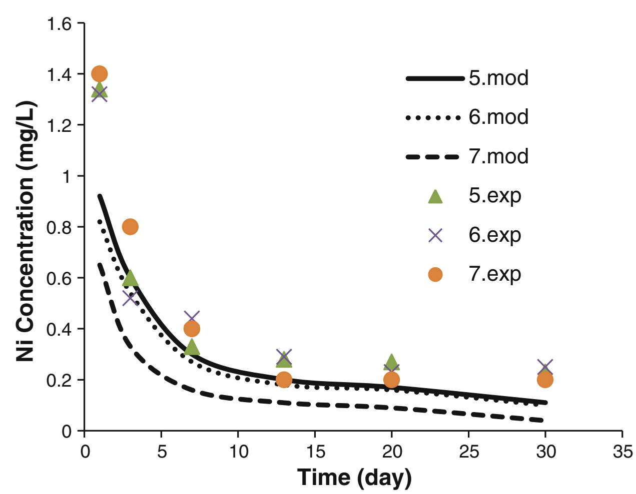

Fig. 8 Modeled and measured leaching concentrations of nickel over the pH range of 5–7

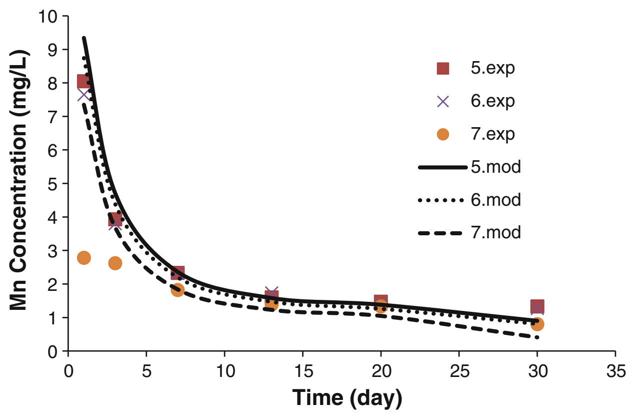

Fig. 9 Modeled and measured leaching concentrations of manganese over the pH range of 5–7

Table 3 Simulation efficiency at various pH values

pH	5	6	7
Cadmium	0.91	0.93	0.61
Nickel	0.76	0.64	0.3
Manganese	0.98	0.97	0.44

column pore volume was high in all of the scenarios; this may explain the observed differences between the results of the predicted model and the column test. Poor agreement in some scenarios could also be due to PHREEQC's use of a linear cation retardation factor. Retardation is an activity of a cation species in an exchange reaction, which is defined by Eq. 6 in PHREEQC:

$$R = \frac{1 + CEC}{C} \tag{6}$$

where R is retardation, CEC is the cation exchange capacity expressed in (Mol/kg water), and C is the species concentration (Mol/kg water). In some scenarios, e.g. lower pH, chemical reactions could compensate for the effects of linear retardation and improve the compatibility between modeled and measured data.

Conclusion

In general, metal transport predicted using PHREEQC for various scenarios of grain size distribution, rainfall, and acidity of simulated rainfall matched the results of the laboratory column studies fairly well and illustrate that geochemical modeling may be an alternative method to investigate metals transport from mine tailings in various environmental situations. In all cases, modeled effects of increased grain size, lower flow rates, and higher initial pH simulated the decreased concentration of metals leached from the Zanjan tailings. The maximum simulated concentrations of Cd, Ni, and Mn were associated with a mixed grain size distribution, and the minimum was for a +18 mesh grain size distribution. Generally, model predictions for the effects of pH and grain size distribution variations were more compatible than the effects of flow rate variations. Of the three metals considered, the modeled Ni concentrations were the least compatible in the different scenarios. Incompatibility in some scenarios may be due to an assumption by PHREEQC of linear cation retardation.

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