Metal transport parameters in residual soil with different structures percolated by an acidic solution

Eduardo Pavan Korf, Gláucia C. dos Santos & Nilo Cesar Consoli
Federal University of Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil

Rafael Tímbola, Antonio Thomé, Pedro Domingos Marques Prietto
University of Passo Fundo, Passo Fundo, Rio Grande do Sul, Brazil

ABSTRACT

Acidic and inorganic materials in residual water represent a common effluent from industrial activities such as mining. These effluents impact the environment due its acidic properties and the presence of metals. Among the factors that influence the migration of these pollutants to subsurface the soil structure deserve further investigation. The objective of this study was determine and evaluate the transport parameters for Cd, Ni, Cr, Zn, Cu, Mn and Pb metals in an acid multispecies solution in a residual soil with an undisturbed and remoulded structure. Column tests were conducted to determine the R_d and k_d. Upon comparison between the structures, the results referring to k_d and R_d did not show a significant variation. A significant increase in the magnitude of values obtained from the undisturbed structure was observed, and only the values for the Cr metal did not increase.

RESUMEN

Materiales ácidos e inorgánicos en aguas residuales representan un efluente común de las actividades industriales como la minería. Estos efluentes impactan al medio ambiente debido a sus propiedades ácidas y la presencia de metales. Entre los factores que influyen en la migración de estes contaminantes bajo la superficie, la estructura del suelo merece mayor investigación. El objetivo de este estudio fue determinar los parámetros de transporte de Cd, Ni, Cr, Zn, Cu, Mn Pb en una solución ácida de múltiples especies en el suelo residual con una estructura original inalterada y outra modificada. Pruebas de columna fueron hechas para determinar R_d y k_d. Para las estructuras, los resultados de k_d y R_d no mostraron variación significativa. Un aumento significativo en la magnitud de los valores obtenidos para la estructura modificado fue observada, y sólo los valores para el metal Cr no aumentaron.

1 INTRODUCTION

Acidic and inorganic materials in residual water represent a common effluent from industrial activities such as mining (coal and mineral deposits), electroplating, casting and the handling of chemical substances in general. These effluents, if not well managed, may generate environmental pollution and have a negative impact on soil, superficial and underground water and ecosystems.

The mining activities are the industrial process that most contribute to generation of effluents. Mining generates serious environmental problems both in the metal extraction processes and coal extraction because it involves the transport of great volumes of solid material, which are waste generated as a result of low content of available ore. Usually, the waste are disposed without any concern about retaining the percolation of storm water and the consequent generation of leachate with acidic and inorganic characteristics, which is called acid mine drainage (AMD). AMD is generated by oxidation as well as by chemical and biological processes associated with sulfide ores (e.g. FeS2), and it has a high leach capacity of chemicals present in the tailings. These drainages are characterized by an extremely low pH, a high electric conductivity and high concentrations of Al, Fe, Mn, among other metals at low concentrations (Cd, Cr, Cu, Ni, Pb, Co, Hg), semimetals (As) and several inorganic constituents. These components promote an increase in acidity once they become part of the hydrolysis reactions. (Achterberg et al. 2003, Johnson and Hallberg 2005, Akcil e Koldas 2006, Nieto et al. 2007, Campaner and Luiz-Silva 2009, Equenuddin et al., 2010)

The metals when inserted in the environment may cause serious damage to toxicity in exposed organisms, because metals may be inserted in the food chain due to their high mobility. Krishna and Govil (2008) have claimed that contamination by metals may lead to both acute and chronic high toxicity, persist in an environment, high mobility and accumulate in organisms due to their liposolubility. Additionally, metal compounds, even in small amounts, may be toxic to plants and animals (Diels 2002, Lafuente et al. 2008).

Studies are needed to provide an understanding of the control mechanisms of AMD metallic compounds on the soil, so they help in the decision making process in relation to the pollutants management and control in contaminated subsurface areas, which are to geration environmental problems (Achterberg et al. 2003, Johnson and Hallberg 2005, Akcil e Koldas 2006, Kalin et al. 2006). Such studies should be conducted with the objective of monitoring the contamination plumes migration and carried out environmental models studies. Additional studies might also accelerate immobilization and decontamination projects or suspend such

procedures for verifying effectiveness of natural attenuation processes (for example see Sarmiento 2009).

The migration of pollutants to the subsurface is influenced by several factors that may determine the movement of metal through the soil. These factors are described by physical and biophysical-chemical processes, which are represented by the theoretical model shown in Eq. (1). The differential equation represents the transport rate of a pollutant ($\partial C/\partial t$) in a one-dimensional flow (x). The physical process, in general, involves diffusion and mechanical dispersion phenomena, and one may be predominant over the other. In Eq. (1), the summation of those two processes is called hydrodynamic dispersion (D_h). This phenomenon is characterized in the diffusive part by molecular diffusion coefficient (D^*), which is represented by the direct relationship between the coefficient diffusion in free solution (Do) and a physical-chemical factor called tortuosity (τ). In the dispersive part of transport, the phenomena are represented by the mechanical dispersion (α) and the percolation speed (v_s). The bio-physicochemical processes are related to the physical, chemical and biological interactions that may occur between the soil and the pollutant. In those processes, the interaction between the environmental conditions, the pollutant and the porous media may cause the delay, acceleration or degradation of pollution. In Eq. (1), among the parameters that govern these processes, are the distribution coefficient (k_d) and the retardation factor (R_d), which are directly co-related. The transport parameters can be determined through laboratory experiments such as column tests, diffusion tests and batch tests, or the transport parameters can be estimated according to literature data and by correlations or through retro-analysis with analytical or numeric solutions (Yong et al. 1992, Shackelford 1993, Sharma and Reddy 2004).

$$\frac{\partial C}{\partial t} = \frac{D_h}{R_d} \cdot \frac{\partial^2 C}{\partial x^2} - \frac{v_s}{R_d} \cdot \frac{\partial C}{\partial x} \Rightarrow em \quad que: \quad D_h = D^* + \alpha . v_s;$$

$$k_d = \frac{\partial S}{\partial C} \quad e \quad R_d = 1 + \frac{\rho_d}{n} . k_d \qquad (1)$$

The objective of this study was to determine and evaluate the transport parameters of Cd, Ni, Cr, Zn, Cu, Mn and Pb metals dissolved in a pH multispecies acid solution in a clayey residual with undisturbed and remolded structures. Both soil structures were evaluated with the objective of simulating, respectively, the condition of a natural barrier in the field as well as a remolded condition that represents the soil movement processes in mining, by percolation of an acidic and inorganic pollutant from acid mine drainage (AMD).

2 EXPERIMENTAL PROGRAM

2.1 Basaltic residual soil

The soil utilized in the present research was a basaltic residual soil sampled from the Geotechnical Experimental Site of the University of Passo Fundo, located in the city of Passo Fundo, in southern Brazil. The sample was obtained from the B horizon (1.2 m depth).

The mineral characterization was related to the specific superficial area (SSA), which was predominantly comprised of mineral clay kaolin. The SSA was 33.86 $m^2.g^{-1}$, and it enabled the soil to be characterized as a material close to the range suggested by Mitchell and Soga (2005) as well as Yong et al. (1992), who indicated that soils that predominantly contain kaolinite have an SSA within the range of 10 to 20 $m^2.g^{-1}$, and Meurer (2006), who indicated that the SSA was within the range of 7 $m^2.g^{-1}$ to 30 $m^2.g^{-1}$.

The chemical and geotechnical characterization of the physical indexes as well as the granulometry of this soil for the B horizon is shown in Table 1. The results include observations of low organic matter content, low CEC (cation exchange capacity), high clay content and an acidic pH.

Table 1. Geotechnical and chemical soil characterization of the studied area.

Parameter	Value
Clay (%)	67
Silt (%)	5
Sand (%)	28
Liquidity limit (%)	53
Plasticity limit (%)	42
Plasticity index	11
G	2.67
Natural moisture (%)	34.62
Natural specific weight (kN/m³)	16.30
Void ratio	1.19
Saturation degree (%)	75.70
Porosity (%)	54
pH (H_2O)	5.00
Organic matter (%)	0.80
CTC ($cmol_c/dm^3$)	12.50
Permeability (m/s)	1.39×10^{-5}
$SSA_{internal+external}$ (m^2/g)	33.86

2.2 Pollutant solution

The pollutant solution contained metals was dissolved in distilled water with a pH of 1.35. The concentration of metals in the pollutant solution (Table 2) was defined according to increasing of the reference value for underground water from CETESB (2005).

Table 2. Concentration of metals inserted in the columns.

Metal	CETESB (mg.L^{-1})	Increasing	Inserted Concentration (mg.L^{-1})
Ni	0.02	100	2
Cr	0.05	100	5
Pb	0.01	100	1
Cd	0.005	100	0.5
Zn	5	2	10
Cu	2	2.5	5
Mn	0.4	2	0.8

2.3 Molding of test samples

Each sample was taken from the field in its undisturbed form and in the shape of a cubic block with a 30 cm edge from the B horizon of the soil. In the laboratory, the cylindrical test samples (TS) were molded with an undisturbed and remolded structure. The remolded test samples had approximately the same density and natural moisture as the undisturbed samples. The diameter of the test samples was 5 cm, and the heights of the samples were variable. Tables 3 and 4 show the physical indexes for the test samples with undisturbed and remolded structures, respectively.

Table 3. Physical indexes of the test samples with an undisturbed structure.

TS	w (%)	H (cm)	D (cm)	ρ (g.cm^{-3})	e	n	Vv (cm³)
1	35.27	9.22	4.93	1.50	1.41	0.58	102.7
2	32.50	6.40	5.17	1.43	1.46	0.59	79.8
3	34.62	8.66	4.57	1.51	1.38	0.58	82.4

*w = moisture content; H – Height; D – Diameter; ρ- specific mass, e – void ratio; n – porosity; Vv – void volume.

Table 4. Physical indexes of test samples with a remolded structure.

TS	w (%)	H (cm)	D (cm)	ρ (g.cm^{-3})	e	n	Vv (cm³)
4		11.44	5	1.58	1.27	0.56	125.7
5	34.62[1]	9.64	5	1.56	1.29	0.56	106.7
6		7.96	5	1.55	1.32	0.57	88.8

[1]equivalent to the field values.

2.4 Processing the pollutant solution

A multispecies pollutant solution was made by diluting a A multispecies pollutant solution was made by diluting a standard solution of 1,000 mg.L-1 from each metal dissolved in distilled water. After the dilution, the pH was corrected with hydrochloride acid (HCl) until it reached 1.35, which was done to simulate the most critical acid mine drainage conditions.

2.5 Column test

The column test reproduces the transport of a pollutant through the soil and allowed for a determination of physical and biophysical-chemical transport parameters. The test was conducted with equipment produced according to the ASTM (1995). The test consisted of two steps, the first was the distilled water percolation until flow steady state, where the hydraulic conductivity was determined. In the second stage was carried out the percolation of the pollutant solution. For each structure, three test samples were tested simultaneously.

After percolating the pollutant solution through the soil, the liquid was collected in different percolated volume and tested times. The metal concentration in each collected samples was determined through analysis with an atomic absorption spectrophotometer at the UPF soil analysis laboratory.

After determining metal present in the percolated effluent from the test samples, it was possible to obtain the breakthrough curves for each test and pollutant. The breakthrough curve gives the number of percolated pores (percolated volume/void volume – V_{perc}/V_v) or the percolation time (t) along the x axis, and the pollutant relative concentration (percolated effluent concentration/initial concentration - C/C_o) is given along the y axis.

The mean hydraulic conductivity result of the samples was $3,7.10^{-4}$ cm/s.

2.6 Determination of transport parameters in the column test

Ogata and Banks(1961) developed a one-dimensional analytical solution (1D) for Eq. 2 by comparing the flow in homogenous and saturated soils (Shackelford, 1995) using both initial and boundary conditions: C(x,0) = 0 for x ≥ 0; C(0,t) = C_o for t ≥ 0; $\partial C(\infty,t)/\partial(t) = 0$ for t ≥ 0. Eq. (2) shows the analytical solution for a reactive solute for the occurrence of delay biophysical-chemical processes. In the equation, C/C_o is the ratio between measured percolated effluent concentration and the initial concentration, erfc is a function of the supplementary error, R_d is the delay factor, L is the one-dimensional flow distance given by the height of the test sample, v_s is the percolation speed, t is the time of the test, and D_h is the hydrodynamic dispersion coefficient.

To determine the D_h parameter, a theoretical curve was adjusted at experimental transport curve (breakthrough) from column test by the Ogata and Banks solution Eq. 2. To generate a theoretical curve, the C/C_o values were found by establishing different time ranges

(t), the height of the test sample (or the flow distance along x (L)), the percolation speed (v_s) and the parameters R_d. The R_d parameter was obtained from a method given by Shackelford (1995), which defines the area above the transport curve as a value corresponding to R_d.

$$\frac{C(x,t)}{C_0} = \frac{1}{2}\left[erfc\left(\frac{R_d L - v_s t}{2\sqrt{D_h R_d t}}\right) + \exp\left(\frac{v_s L}{D_h}\right) erfc\left(\frac{R_d L + v_s t}{2\sqrt{D_h R_d t}}\right) \right] \quad (2)$$

The k_d coefficient was obtained using a linear relationship between the mass absorbed by a unit of solid mass and the concentration of the substance in the solution when the soil is saturated, which was determined after equilibrium was reached. The parameter k_d was determined according to Equation 3, where: R_d is the delay factor, ρ_s is the specific soil dry mass, and n is the porosity of the test sample [30].

$$k_d = \frac{R_d - 1}{\rho_s} \times n \quad (3)$$

3 RESULTS AND DISCUSSION

Figure 1 show a example which was used for adjustments and determination of R_d. Tables 5, 6 and 7 show the parameters obtained for the tested metals with with undisturbed and remolded structures at a pH of 1.35.
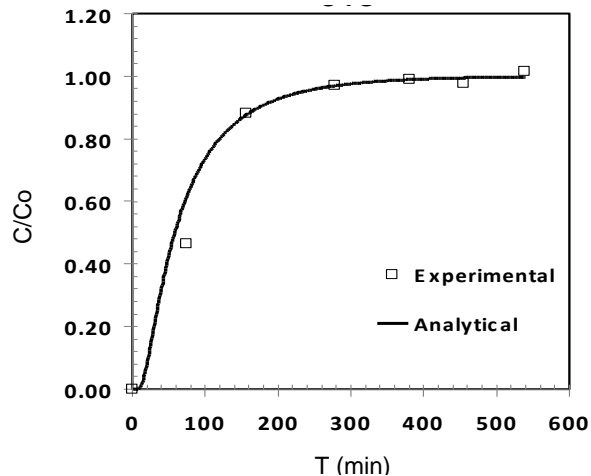

Figure 1. Example curve used for adjustment and determination of R_d.

Table 5. Parameters obtained for tested metals Cd, Ni, Cr

TS	Cd		Ni		Cr	
	R_d	k_d[1]	R_d	k_d	R_d	k_d
TS1	5.00	2.09	6.70	2.98	6.50	2.87
TS2	5.50	2.45	9.00	4.36	6.00	2.72
TS3	7.00	3.10	15.00	7.23	-	-
Average	5.83	2.55	6.70	2.98	6.25	2.80
TS4	3.64	1.26	3.00	0.96	46.81	21.93
TS5	6.52	2.66	4.44	1.66	28.28	13.17
TS6	5.00	1.98	5.01	1.99	-	
Average	5.05	1.97	4.15	1.54	36.54	17.55

[1]cm³/g.

Table 6. Parameters obtained for tested metals Cu, Zn

TS	Cu		Zn	
	R_d	k_d	R_d	k_d
TS1	5.50	2.35	2.50	0.78
TS2	7.97	3.80	3.50	1.36
TS3	-	-	7.00	3.10
Average	6.49	3.07	4.33	1.74
TS4	6.52	2.64	3.11	1.01
TS5	8.49	3.62	4.47	1.68
TS6	7.29	3.12	4.29	1.63
Average	7.43	3.13	3.96	1.44

Table 7. Parameters obtained for tested metals Mn, Pb

TS	Mn		Pb	
	R_d	k_d	R_d	k_d
TS1	4.30	1.72	12.00	5.75
TS2	4.11	1.69	19.08	9.85
TS3	-	-	7.00	3.10
Average	4.20	1.70	12.69	6.23
TS4	1.50	0.24	7.00	2.87
TS5	1.50	0.24	-	-
TS6	1.46	0.23	5.00	1.98
Average	1.49	0.24	6	4.41

Concerning the magnitude of parameters k_d and R_d, similar values related to the changes in the tested structure were observed for the Cd, Ni, Cu and Zn metals. The Mn and Pb metals showed higher k_d and R_d values for the undisturbed structure, and only Cr had higher parameter values for the remolded structure.

For metals Mn, Pb and Cr, the behaviour between the k_d and R_d values related to the structure agrees with the finding of Reddi and Inyang (2000) and Daniel (1993), who have reported that the disturbance of a remolded structure influences the mobility of pollutants in soils. However, microstructural and chemical studies should be conducted for better understanding.

With respect to the metal retention sequence, which was observed through the parameters k_d and R_d, the following prevalence order was observed for the remolded structure: Cr>Pb>Cu>Cd>Ni>Zn>Mn. For the undisturbed structure, the following prevalence order was observed: Pb>Ni>Cu>Cr>Cd>Zn> Mn. The affinity order had a similar behavior for Zn and Pb metals, which agrees with the affinity order obtained by Soares (2004) from several soils in the state of São Paulo, Brazil. Nascentes et al.

(2007) claimed that Pb, Cr and Cu metals have reduced mobility in soil as compared to Zn, Mn, Ni and Cd metals, which was confirmed by the results of this study (except for Ni, which showed lower mobility undisturbed structure). Relative to the kaolinite clay mineral, which was predominant in the study soil, Yong et al. (1992) and Costa (2002) found the following preference series for pH values of 3.5 to 6: Pb>Ca>Cu>Mg>Zn>Cd. Similar results were obtained in the current study.

Vega (2006) simulated the concentration of a contaminating solution at 5 mg.L^{-1}, which is close to most of the concentrations employed in the present study, in soil with 90.6% kaolinite and 21% clay. The author obtained k_d values for Cd (4.9 cm^3.g^{-1}), Ni (9.5 cm^3.g^{-1}), Cr (17.3 cm^3.g^{-1}), Cu (15.0 cm^3.g^{-1}), Zn (6.5 cm^3.g^{-1}) and Pb (57.9 cm^3.g^{-1}). The values reported by Vega (2006) are similar to the ones found in the present study.

4 CONCLUSION

Concerning the comparison between the different structures, the results referring to k_d and R_d did not show a significant variation for Cd, Ni, Cu and Zn. For metals Mn, Pb and Cr there was a variation, but microstructural and chemical studies should be conducted for better understanding. The metal retention sequence for the remolded and undisturbed structure, respectively were Cr>Pb>Cu>Cd>Ni>Zn>Mn and Pb>Ni>Cu>Cr>Cd>Zn>Mn, which also agrees with several studies related to metal mobility in soils.

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