

Column tests of a compacted mixture of tropical soils for use in liners in Brazil

JULIANA BROGGIO BASSO¹ & ANTENOR BRAGA PARAGUASSU²

¹ *Geology, UNESP - Universidade Estadual Paulista. (e-mail: julibb@rc.unesp.br)*

² *Geology, USP - EESC - Universidade de São Paulo. (e-mail: nomus@sc.usp.br)*

Abstract: Transport and attenuation parameters for K^+ , Cl^- and Cu^{2+} obtained from column tests on a mixture of two compacted tropical soils found in the southern, mid-western and southeastern parts of Brazil are presented. The soils studied were derived from the sandstones of the Botucatu Formation (J-K) and the basaltic rocks of the Serra Geral Formation (J-K) which extend over an area of approximately 1.6×10^6 km². The soil of Botucatu origin was medium to fine-grained sand while that from the Serra Geral Formation was essentially clayey, composed of kaolinite, gibbsite, goethite, limonite, anatase, hematite and organic matter. The mixture studied comprised 60% dry mass of sandy soil and 40% of clay soil. Characterization experiments (grain size distribution, Atterberg limits, specific gravity, compaction and hydraulic conductivity), mineralogical analyses (X-ray diffractometry and differential thermal analyses) and physico-chemical analyses (pH in water and in KCl, cation exchange capacity and specific surface area) were carried out. The mixture was leached using 500 mg/L of KCl and $CuCl_2 \cdot H_2O$ solutions. The results obtained for K^+ , Cl^- and Cu^{2+} are presented in the form of breakthrough curves. The estimated retardation factor (R_d) and hydrodynamic dispersion (D_h) were found to range between 3.4 and 8.79, and 8×10^{-5} and 3×10^{-4} cm²/s respectively translating into acceptable values for cation exchange capacity and sorption of Cl^- . These values resulted from the presence of variable charge minerals, which is rare for soils located in cold or temperate climates. The estimated hydraulic conductivity (K) was 10^{-7} cm/s, a value considered satisfactory for the present study. Based on the results for hydraulic conductivity, cation exchange capacity, and sorption of Cl^- , it is concluded that the compacted mixture studied is suitable for application as a whole liner or as part of a composite liner.

Résumé: Les paramètres de transport et d'atténuation de K^+ , Cl^- et Cu^{2+} obtenu des essais de colonne d'une mélange de deux sols tropicaux compactés trouvés dans les régions sud, mi-ouest et sud-est du Brésil est présenté. Les sols étudiés sont de grès de la Formation Botucatu (J-K) et de roches basaltiques de la Formation Serra Geral (J-K) lesquels étendent sur une région d'approximativement $1,6 \times 10^6$ km². La granulométrie du sol d'origine Botucatu variait de sable moyen à fin portant celui de la Formation Serra Geral était essentiellement argileux, composé de kaolinite, gibbsite, goéthite, limonite, anatase, hématite et matériel organique. Le mélange étudié été composé de 60% masse sèche de sol sablonneux et 40% de sol en argile. Les essais de caractérisation (distribution granulométrique, limite d'Atterberg, gravité spécifique, compactage et conductivité hydraulique), analyses minéralogiques (diffractométrie de rayon-X et analyses thermiques différentielles) et analyses physique - chimiques (pH dans l'eau et dans KCl, la capacité échangeant de cation et surface spécifique) ont été réalisés. Prochainement, le mélange a été lessivé utilisant 500 mg/L des solutions KCl et $CuCl_2 \cdot H_2O$. Les résultats obtenus relatifs à K^+ , Cl^- et Cu^{2+} ont présenté en forme de courbes de percée. Les facteurs de retard (R_d) et dispersion hydrodynamique (D_h) estimés été entre 3,4 et 8,79, et 8×10^{-5} et 3×10^{-4} cm²/s ce qui traduisent en valeurs satisfaisantes de la capacité d'échange de cation et sorption de Cl^- respectivement causé par la présence de charge minéraux variables considérées rares pour les sols localisés dans les climats froids ou modérés. La conductivité hydraulique estimée (K) était de 10^{-7} cm/s, une valeur considéré satisfaisant pour la présente étude. Basé sur les résultats satisfaisants de conductivité hydraulique, la capacité d'échangeant de cation, et la sorption de Cl^- , il est conclu que le mélange compact étudié est convenable pour être employée comme *liner* entier ou comme partie d'un *liner* composé.

Keywords: clay minerals, laboratory tests, hydraulic conductivity, landfill, groundwater contamination, saturated materials

INTRODUCTION

Liners used in sanitary landfills are fundamental in the containment of leachate produced during the storage of domestic and industrial wastes. Liners constructed from both combinations of natural materials (loamy soils, compacted clays, compacted mixtures) and geosynthetics (GCL) are used to impermeabilize landfills, avoiding the contamination of soil and groundwater. These liners should have low hydraulic conductivity and retain contaminants. They can thus be employed to line the base for controlling the vertical migration of leachate, for surface covering, and as isolation walls for the control of lateral migration (Daniel, 1993; Rowe et al. 1995).

In Brazil, tropical soils are potentially suitable for the construction of barriers systems due to their geotechnical properties and wide occurrence. The objective of the present work was to evaluate the transport of pollutants by percolation with the aim of developing natural barriers composed of a compacted mixture of lateritic soils from the Botucatu and Serra Geral Formations. Solutions of KCl and $CuCl_2$ were used to represent contaminants since they are usually present in domestic refuse, and, in smaller quantities, in industrial waste.

LATERITIC SOILS AND THEIR APPLICATION IN LANDFILL LINERS

Lateritic soils are formed in regions with humid-tropical climates, as the result of the leaching of bases and silica with the consequent concentration of oxides and hydroxides of Fe and Al. In general, they are of red coloration, possess little organic matter and are slightly acidic.

More than 60% of Brazil's surface area is covered with different types of lateritic soils, the most common of which is clayey-ferruginous and classified in pedology as a latosol. These soils are very well developed, friable, with fine grain size and characteristic of micro-aggregation (Melfi, 1994). The main mineralogical constituents in the sand and silt fraction are quartz and heavy minerals, while in the clay fraction the main constituents are clay minerals of the kaolinite group, oxides, hydroxides of iron and/or aluminum, and organic matter. Hydrated iron and aluminum oxides have cementing properties thus playing an important role in the formation of aggregates (peds) and laterite concretions.

Lateritic soils are comparable to soils found in temperate climates, with geotechnical characteristics, which can make them unsuitable for barrier construction projects. These properties include higher than expected compressive and shear strengths (due mainly to a low expansion capacity), reduced plasticity (due to the presence of oxides and hydroxides of Fe and Al), low cation exchange capacity and predominance of positive charges under natural pH conditions.

Interaction of lateritic soils and ionic solutions

The interaction of solutions in contact with solid soil particles is based on the competition of ions for the adsorbent surface. This competition takes place because of the presence of electric charges at the surface of the solid soil particles on organic matter, clay minerals and oxides. Such charges developed on the surface of clay minerals can be permanent in nature and originate during the genesis of the mineral. Isomorphic substitution of ions caused by structural imperfections inside crystals frequently results in a surface charge. Other causes are ion dissolution resulting from the adsorption of H^+ and OH^- forming hydrolyzed surfaces that can assume positive and negative charges, and ionization which is common in the organic fraction when it acquires positive and negative charges due to the dissolution of H^+ (Singh & Uehara, 1986). Surface charges can be modified by environmental factors such as pH and electrolyte concentration.

Kaolinite, $Al_2Si_2O_5(OH)_4$, an important clay mineral of the 1:1 class, possesses a structural configuration in which a large majority of the adsorption sites are located on the external surface with little or no adsorption in the internal surface. The appearance of electric charges results from broken Si–O–Si bonds and dissociation of the AlOH and SiOH groups. A consequence of a lack of isomorphic substitutions is a low permanent negative charge resulting in a low cation exchange capacity of about 3 to 15 meq/100g. The charges on kaolinite are pH dependent; when the pH is acidic, the broken surfaces of this mineral are positively charged while for an alkaline pH, they are negatively charged (Mitchell, 1993).

In a similar way, the presence of oxides and hydroxides of Fe–Al–Mn–Ti can result in negative surface charges due to the dissociation of H^+ on the lateral broken surfaces. Sorption reactions in oxides are restricted by the presence of variable electric charges which retain cations and anions depending on the pH of the environment, the ionic force and the oxidation state. Yu et al. (1997) confirm that for similar types of oxide, the ability to adsorb cations varies with the degree of crystallization of the oxide with amorphous substances showing high specific surfaces and high metal adsorption capacities.

The lateritic soils of the Botucatu (BOT), Serra Geral (SG) and mixtures of these two formations have been widely studied for their technological employment in liners. Zuquette et al. (1995) observed that for soils of the Botucatu Formation, the retention of K^+ under the experimental conditions used was high ($R_d > 5$) while that of Cl^- was less than 2 ($R_d < 2$). Percolation column tests using aqueous solutions containing K^+ , Cu^{2+} and Cl^- ions with associated concentrations in the mixture 75 BOT /25 SG indicated higher values of retention of Cu^{2+} followed by Cl^- and K^+ (Paraguassú et al, 2002). Diffusion column tests and batch equilibrium tests for studying the migration of K^+ , Cd^{2+} , Cl^- and F^- in soils and mixtures of soils of the same formations gave lower values of diffusion for samples of the Serra Geral Formation while for the batch equilibrium tests, Cl^- was found to be absorbed in the absence of F^- and low pH or pH close to pH_p , showing that chloride cannot be used as a conservative tracer. However, when associated with F^- in a multi-ion solution and for $pH > pH_p$, Cl^- is not absorbed (Leite et al, 2003).

Moreira (2004) obtained isotherms for the adsorption of Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} in competitive and non-competitive systems of lateritic soils found in the state of São Paulo. The most common sequence of metal affinity observed for non-competitive systems is given by $Cu > Zn > Ni > Cd$ while that for competitive was $Cu > Cd > Zn > Ni$. The author stressed the importance of manganese oxide in the sorption behavior of heavy metals present in soils.

A study of the effect of pH and ionic strength on the ion speciation and the distribution of Zn^{2+} , Cu^{2+} and Cd^{2+} in latosol samples containing residues from the treatment of domestic sewage, identified Cu^{2+} as the element least affected by variations in pH as compared to Zn^{2+} and Cd^{2+} , while at higher pHs, the quantity of metal in solution was found to reduce (Silveira, 2002). The increase in ionic strength relative to the original value of the soil solution was not found to affect the quantity or distribution of metals in latosols.

LOCATION AND CHARACTERIZATION OF THE SOILS STUDIED

The soils studied are found in São Carlos County, northeast São Paulo State. These soils are formed from unconsolidated material from the Botucatu and the Serra Geral Formations (Figure 1). These formations, of the Jurassic-Cretaceous Period, are situated in the Parana Sedimentary Basin and cover a vast area. The Botucatu

Formation consists predominantly of sandstone of aeolian origin and is an important aquifer. The soil is sandy with a fine to average grain size distribution. In contrast, the soil formed by the Serra Geral Formation results from the weathering of igneous rocks (basalts and diabases) and is essentially loamy in nature.

The samples were collected from a depth of approximately 3m below the surface layer in order to reduce the effects of organic matter and residues from anthropogenic activities. The soil samples were disaggregated in the laboratory, homogenized, dried in the shade and sieved.

A mixture consisting of 60% sandy soil (Botucatu) and 40% loamy soil (Serra Geral) by dry weight was prepared. This ratio was chosen based on the experimental study of Leite et al. (1998a). These authors obtained results from column tests for hydraulic conductivity of about 1×10^{-9} m/s, which is in very good agreement with international standards for liners. The homogenization of the mixture was carried out manually, to achieve a low loss of fines, using about 300 kg of the Botucatu soil and 215 kg of the Serra Geral soil.

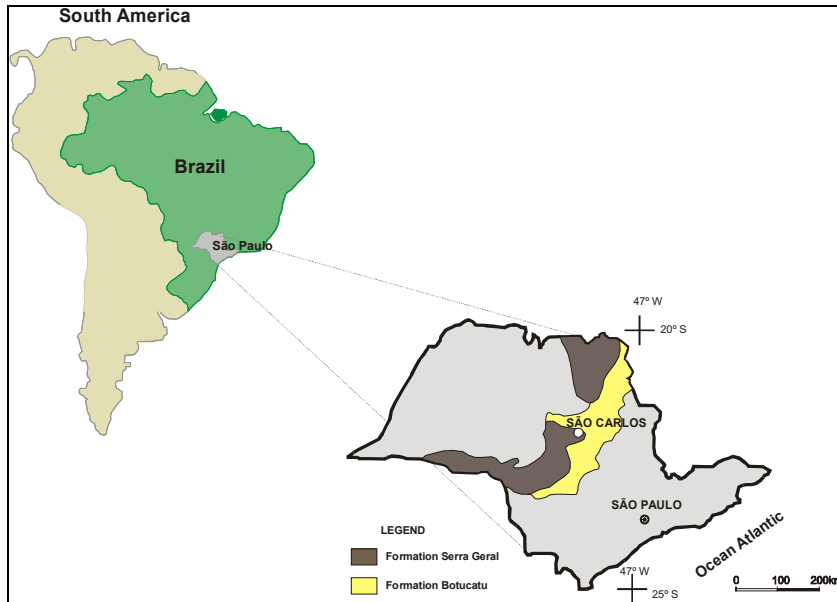


Figure 1. Location map of the soils studied.

GEOTECHNICAL, MINERALOGICAL AND PHYSICO-CHEMICAL CHARACTERIZATION

Geotechnical characterization aimed at determining the composition of the soils and mixture (60/40) studied and hence their physical applicability as liner material was carried out. The combined physical and chemical analyses permit us estimate the quantity of soluble salts in the soil, its capacity to retain exchangeable cations, and the prevalence of surface charges (in sign and magnitude). Table 1 shows the geotechnical properties together with the principal physico-chemical and mineralogical characteristics of the silt and clay fractions of the soils.

COLUMN TESTS

Experimental stages and setup

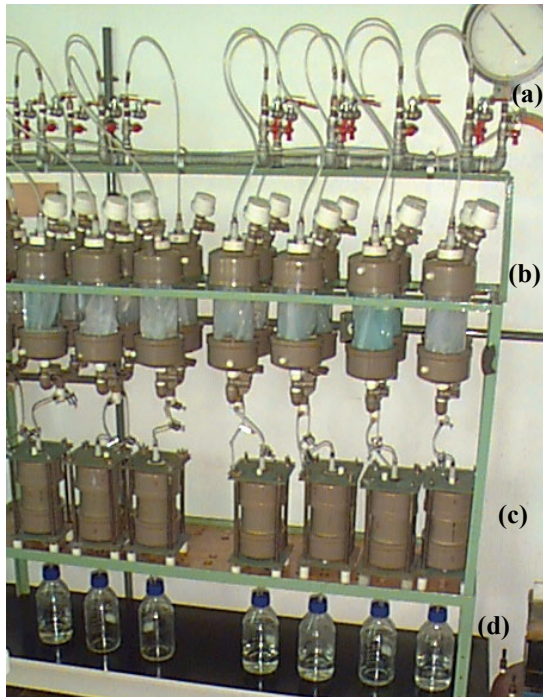
Percolation tests were simultaneously conducted in two soil columns with a hydraulic head of 76 kPa applied to each column, the same head as used by Paraguassú et al. (2002) and Leite et al. (1998a). This pressure was chosen to be in the interval of 50 to 100 kPa, a range common in barriers used in sanitary landfill (Peirce et al., 1986). The temperature was maintained at $22 \pm 2^\circ\text{C}$. The specimens were kept under saturation for a period of approximately 2 months in distilled/deionized water and during a period of 3 months for percolation of contaminated solution.

The experiment was carried out in a series of steps: (a) compaction of the column mixture of soils (60/40) of Botucatu and Serra Geral Formations, (b) saturation with distilled/deionized water and (c) percolation with solutions of potassium and copper chloride. The column test was concluded when the relative concentration (C/C_0) was equal to 1, in other words, when the concentration of the effluent solution was equal to that of the initial influent solution, characterizing an advective flow of the solute. With the obtained concentrations and the number of percolated voids volume (T), Breakthrough Curves were constructed. From the curves, the retardation factor (R_d) and the coefficient of hydrodynamic dispersion (D_h) were obtained.

The equipment used for this experimental study was first designed and built by Leite et al. (1998b). However, some modifications, as described in Basso (2003), were made in order to increase the precision in the results obtained. Figure 2 shows the equipment used in carrying out the percolation columns test.

Table 1. Measured values of the soil geotechnical and physical-chemical properties

Properties	Values		
	Botucatu	Serra Geral	Mixture(60/40)
Specific mass of solids, ρ_s (g/cm ³) ¹	2,727	2,955	2,761
Grain size fraction ²			
Clay (%) (<0,002mm)	8,7	52,2	26,7
Silt (%) (0,002-0,075mm)	1,9	17,3	6,6
Fine sand (%) (0,075-0,42mm)	31,7	14,5	23,7
Medium sand (%) (0,42-2mm)	51,6	15,0	37,7
Coarse sand (%) (2-4,8mm)	6,1	1,0	5,3
Optimum humidity - wot (%) ³	9,1	24,0	13,5
Dry specific mass ρ_d max (g/cm ³) ³	1,931	1,614	1,885
e	0,41	0,83	0,47
n (%)	29	45	32
Sr (%)	60,2	85,4	80,4
Atterberg limit ⁴			
LL	-	47	29
LP	NP	33	22
IP	-	14	7
Soil classification (USCS)	SC	CL	SM-SC
CEC (meq/100g) – Methylene blue ⁵	0,70	3,4	2,0
Specific surface area (m ² /g)	5,7	25,9	15,0
pH of soil in H ₂ O ⁶	4,78	6,08	5,72
pH of soil in KCl ⁶	4,34	6,34	5,89
Δ pH ⁶	-0,44	+0,26	+0,17
Electric conductivity of the aqueous extract (μ S/cm) ⁶	21	18	19
ZPC ⁷	3,9	6,6	6,0
Mineralogy of the fine fraction (<0,037mm) from X-ray diffractometry and differential thermal analyses	Kaolinite, gibbsite, quartzite	Kaolinite, gibbsite, hematite, magnetite, goethite	

¹ ASTM-D854 (Specific mass of solids);² ABNT-MB32 (Fraction of grain size);³ ABNT-MB33 (compaction);⁴ ABNT-MB30 & ABNT-MB31 (Atterberg limit)⁵ Pejon & Zuquette (1994)⁶ Camargo et al. (1986)⁷ Uehara (1984)**Figure 2.** A view of the percolation column test equipment comprising: (a) air distributor, (b) solution reservoirs, (c) percolation cells and (d) effluent collectors.

Compaction

For the column test, test specimens were directly compacted in 5 layers in PVC cylinders using a soil compactor working at the normal Proctor energy level. The humidity of the soil samples was based on the average optimum humidity (13.5%) obtained in three compaction test of the mixture under a normal Proctor energy, varying between a minimum of 13.4% and a maximum of 13.7%. The dimensions of the percolation cells used in the column test were approximately 14.5 cm in height and 9.7 cm in diameter. The data obtained from the compaction cells for the column test are shown in Table 2.

Saturation and percolation of contaminating solution

Distilled/deionized water was percolated through the columns initially to saturate the test specimen and obtain discharge of the effluent. This stage was carried out to satisfy three basic requirements: (a) reduction of the ion concentration of the pore liquid; (b) saturation close to 100% of the test specimen and (c) attain a condition of equilibrium flow during which the hydraulic conductivity remains constant.

The influent water used in saturating the soil columns had an average pH of 5.7 and a specific electrical conductivity of 1.4 μScm^{-1} . After saturating the columns with water, the reservoirs were emptied, aerated and then filled separately with aqueous solutions of potassium chloride and copper of approximate concentrations of 500 mg/L of K^+ and Cu^{2+} respectively. During the percolation of the solutions, the procedures used in monitoring the hydraulic conductivity and physico-chemical conditions were the same as those adopted in the percolation with distilled/deionized water.

The hydraulic conductivity and the pH and electric conductivity of the effluent and influent were monitored during the test and samples were collected in glass flasks whose volume was approximately the same as the void volume of the test specimen. The CuCl_2 and KCl test specimens were collected at intervals that varied between 2 and 3 days. After each equivalent void volume had percolated through, the effluent samples were collected for chemical analysis. For determination of the concentrations of the Cu^{2+} , K^+ and Cl^- ions, an inductively-coupled plasma spectrometer a flame photometer and an ion-selective potentiometer titrator were employed. The initial concentration of ions used in the test and the characteristics of the solutions are presented in Table 2.

Table 2. Compaction data of the test specimens and concentrations of contaminant solutions.

Properties	Column	
	KCl	CuCl_2
W for compaction (%)	13,4	13,0
Maximum specific dry mass (g/cm^3)	1,896	1,885
Void ration, e (%)	45,7	46,4
Porosity, n (%)	31,3	31,7
Void volume (cm^3)	343,8	342,1
Degree of saturation(%)	81,0	77,3
Ion concentration (mg/L)	$\text{K}^+ = 490$ $\text{Cl}^- = 417$	$\text{Cu}^{2+} = 575$ $\text{Cl}^- = 542$
pH	5,6	4,9
Specific electrical conductivity ($\mu\text{S}/\text{cm}$)	1720	1778

Calculation of contaminant parameters

The theoretical formula for the transport of contaminants through porous media is based on the principle of conservation of mass in one dimension. The system is assumed to be at a steady state, the medium to be homogeneous, isotropic and undeformable and the fluid non-compressible. This formula is known as the advection-dispersion equation. The basic equation (Ogata & Banks, 1961; Ogata, 1970), with the addition of the retardation factor (Freeze & Cherry, 1979) is as follows:

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

where erfc = the complementary error function, v_s = the seepage velocity, x = the distance, t = time, R_d = the retardation factor, D_h = the hydrodynamic dispersion coefficient, C = the final concentration, C_0 = the initial concentration.

The retardation factor (R_d) was determined by using the method described by Shackelford (1994). This method uses a mass balance approach and gives realistic results at low rates of flow. Experimental values were substituted into equation 1 and polynomial tendency curves obtained using nonlinear regression. This gave curves with values of R^2 around 0.9. These values correspond to the relative equilibrium concentration ($C/C_0 = 1$). The retardation factors (R_d) obtained for K^+ , Cu^{2+} and Cl^- are presented in Table 6.

The hydrodynamic dispersion coefficient (D_h) was calculated from the equation 1 by fitting the theoretical curve to the experimental data. All parameters obtained were kept constant and the corresponding value of D_h obtained by varying the time. The result adopted was from the curve that best fitted the experimental data.

The seepage velocity (v_s) used in calculating the above parameters was determined from the average value of the seepage velocity of the contaminant solution during the percolation test and is presented in Table 5 together with other hydraulic parameters. For the determination of the distribution coefficient and the Peclet number (PI), equations 2 and 3 from Shackelford (1994) and Freeze & Cherry (1979) were used. The Peclet number (PI) determines the predominant transport mechanism in column tests based on the relative importance of advective transport, determined by the seepage velocity, and dispersive/diffusive transport, based on the values of D_h . For values of $PI \geq 50$, advective transport is dominant while for $PI \leq 1$, the dominant transport mechanism is molecular diffusion. The Peclet number and coefficient of distribution, K_d , of the absorbed chemical species were determined assuming a linear isotherm from the following equations:

$$Pl = \frac{Lv_s}{D_h} \quad (2)$$

where L = column length.

$$R_d = 1 + \frac{\rho_d}{n} K_d \quad (3)$$

where ρ_d = dry specific mass of the soil and n = porosity.

RESULTS AND DISCUSSION

Physico-chemical characterization of the soils studied

The values of CEC obtained indicate materials with low cation retention capacity as compared to soils from temperate climates. The results of pH in H_2O and in KCl tests show that the soils are slightly acid, the more acid soils being those from the Botucatu Formation with a pH of 4. The ΔpH values characterize soils composed of variable charges, predominantly positive, as in the case of soils from the Serra Geral origin and the soil mixture. The electric conductivity of aqueous extract indicates low concentrations of dissolved salts (Table 1).

Hydraulic and physico-chemical parameters of the test columns

Figures 3, 4 and 5 present the variation in hydraulic conductivity, pH and electric conductivity in the percolated columns using distilled/deionized water and solutions of KCl and $CuCl_2$ as a function of the number of void volume percolated (T). The hydraulic parameters of the columns percolated with distilled/deionized water and with contaminant solution are given in Table 5. Generally speaking, the hydraulic parameters did not show any significant variations during the experimental program even on addition of the ionic solution. Low values of K were observed in the beginning of percolation with water (Figure 3) suggesting an indication of the resistance imposed by gaseous phase present in the test specimen.

The pH of the KCl effluent solution varied between 7.1 and 6.4, and was higher than the pH of the influent solution which was 5.6, indicating that the soil liberated OH^- which made the effluent more alkaline. However the pH of the $CuCl_2$ effluent solution, observed to vary between 4.2 and 4.6, remained below the pH of the influent solution, indicating, in this case, the substitution of Cu^{2+} for H^+ and hence the acidification of the effluent. This effect of substitution and ion exchange, common for high concentrations and low pH, is reported in Shackelford & Redmond (1995) and other researchers on kaolinite soils. During the percolation test with distilled/deionized water, a neutral to slightly acid condition, which increased during the test, was observed.

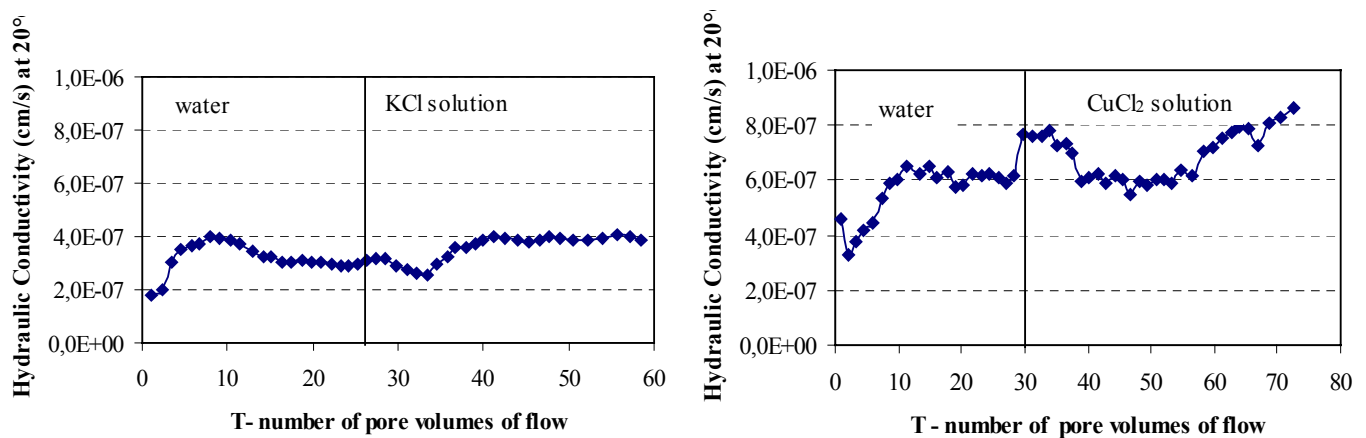


Figure 3. Curves showing the variation in hydraulic conductivity as a function of the number of void volume percolated with aqueous solutions of KCl and $CuCl_2$ during the saturation and percolation phases

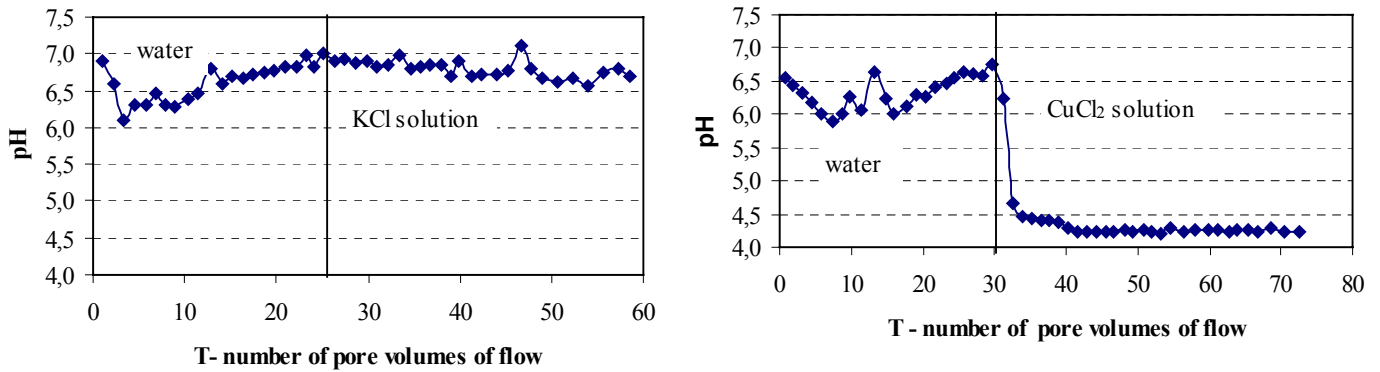


Figure 4. Curves showing the variation of pH as a function of the number of void volume percolated with aqueous solution of KCl and CuCl_2 during the saturation and of percolation phases

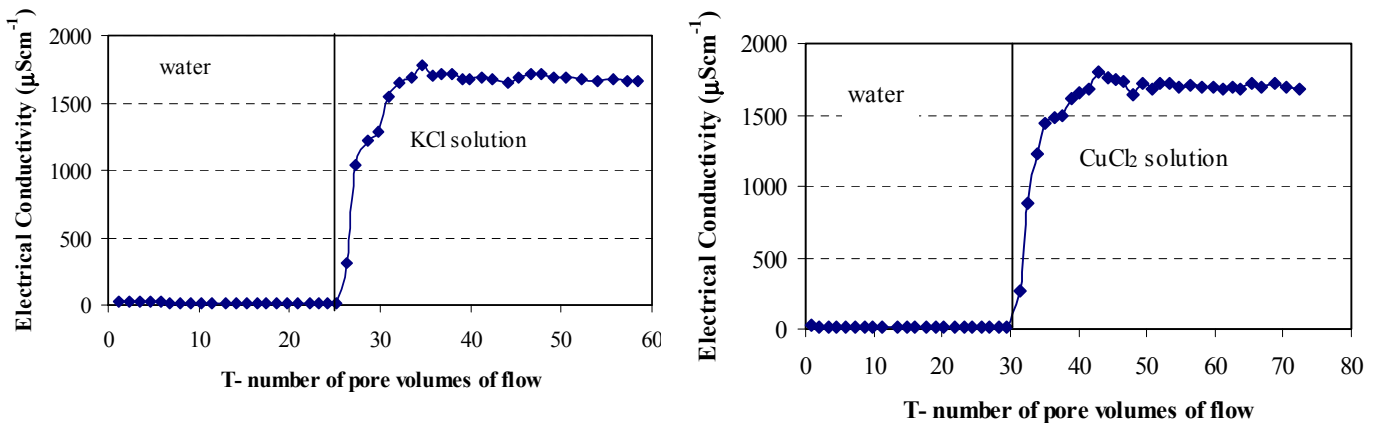


Figure 5. Curves showing the variation of electric conductivity as a function of the number of void volume percolated with aqueous solution of KCl and CuCl_2 during the saturation and of percolation phases

Table 5. Summary of average hydraulic parameters and their standard deviation for the percolation test columns

Solution	Q (flow rate) (cm^3/s)	K (Hydraulic conductivity) (cm/s)	Seepage velocity, v (cm/s)
H_2O	$1.3(\pm 0.21) \times 10^{-3}$	$3.2(\pm 0.57) \times 10^{-7}$	
KCl	$1.5(\pm 0.20) \times 10^{-3}$	$3.5(\pm 0.50) \times 10^{-7}$	6.4×10^{-5}
H_2O	$2.4(\pm 0.42) \times 10^{-3}$	$5.6(\pm 0.95) \times 10^{-7}$	
CuCl_2	$3.0(\pm 0.39) \times 10^{-3}$	$6.9(\pm 0.89) \times 10^{-7}$	1.3×10^{-4}

The electric conductivity of the effluent in the water-percolated columns was found to reduce until a stable value of between 5 and 10 $\mu\text{S}/\text{cm}$ was reached, considered as the maximum value of leaching of salts. When percolated with solutions, an increase in ion concentration up to a stable value close to that of the influent solutions was observed. The maximum concentration was found to be 1775 $\mu\text{S}/\text{cm}$ in the columns with KCl and in CuCl_2 ; the maximum concentration was 1798 $\mu\text{S}/\text{cm}$ indicating chemical saturation.

In the column percolated with CuCl_2 , chemical stability was observed to occur for about 10 more void volumes percolated than in the case of KCl. This explains the high values of R_d obtained from the CuCl_2 column, suggesting a reduction in the contamination front influenced by the absorption of the soil.

Breakthrough curves

The breakthrough curves of the K^+ , Cu^{2+} and Cl^- ions obtained from the column tests are presented in Figure 6. These curves were constructed from the number of void volumes percolated (T) and the relative concentration (C/C_0) obtained for the effluent. The results for the contaminant transport parameters for the columns percolated with solutions of KCl and CuCl_2 are presented in Table 6.

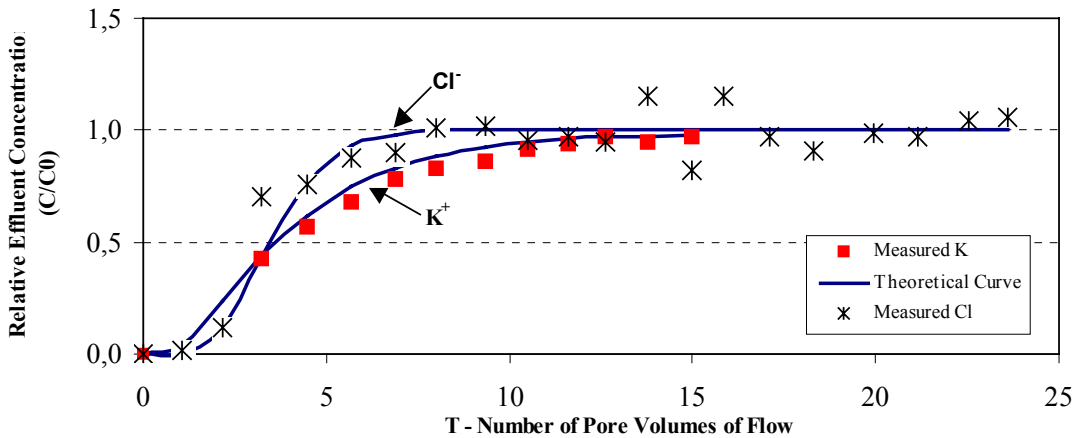


Figure 6. Breakthrough curves of K^+ and Cl^- ions

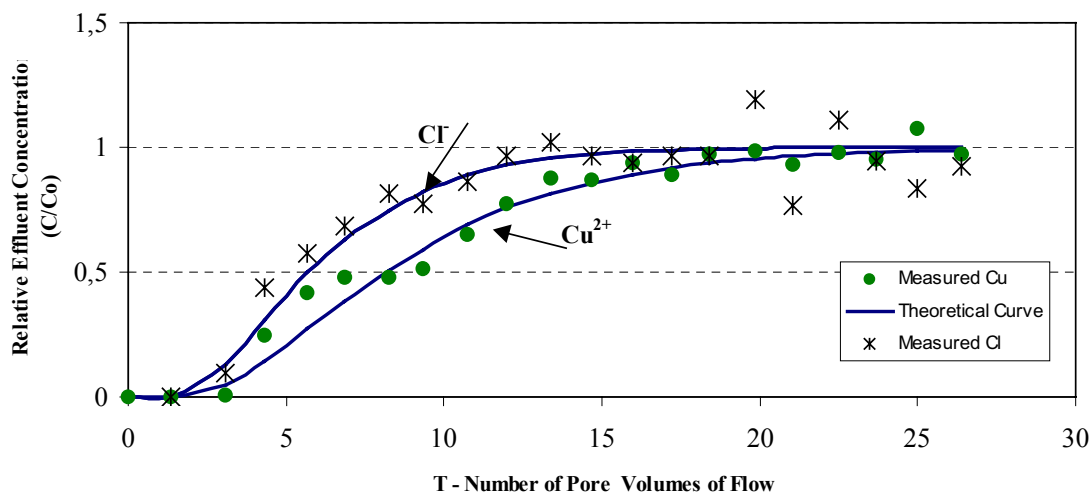


Figure 7. Breakthrough curves of Cu^{2+} and Cl^- ions

The shapes of the breakthrough curves for the columns percolated with KCl and with $CuCl_2$ are quite distinct. The elongated form of the breakthrough curves for $CuCl_2$ column indicates a higher attenuation of the element Cu^{2+} by the soil, confirmed by the values of R_d . The high sorption of Cu^{2+} is related to the higher ionic potential (higher valency) and ion exchange capacity as compared to the K^+ and Cl^- ions.

The Cl^- ion was the least retarded. However, when this ion accompanies Cu^{2+} , it acquires higher values of retardation ($R_d=5.85$) than K^+ . The conditions that favor anion retention are probably linked to the pH of the effluent solution of $CuCl_2$, between 4.2 and 4.6, which is below ZPC (6.0) and to the prevalence of positive electric charges (Table 1). The low retardation shown by Cl^- in the KCl must also be associated with the pH of the effluent ($\cong 6.5$), which is above ZPC, a much less favorable condition for anion retention.

The KCl column reached chemical saturation with a lower number of void volumes ($T=15 K^+$) than the $CuCl_2$ column ($T=25 Cu^{2+}$), confirming the tendency of the electric conductivity to stabilize after chemical saturation.

Values of the coefficient of hydrodynamic dispersion (D_h) were observed to be very similar for the two columns, generally in the order of $10^{-4} cm^2/s$. In the KCl column, the smallest value was obtained for D_h for Cl^- ($8.10^{-5} cm^2/s$), which is reflected in the vertical shape of the breakthrough curve. It is interesting to note that the elongated shape of the breakthrough curves for the other ions agrees with the high values of D_h ($3 - 4 \times 10^{-4} cm^2/s$). The K_d data are found to be close to those obtained by Rowe et al. (1995) for similar concentrations. However, these values should be treated with caution since they assume a linear isotherm model. Based on the Peclet number (PI), the pollutant transport mechanism was that of advection/dispersion.

Table 6. Summary of pollutant transport parameters obtained in this study

Chemical species	R_d	D_h (cm^2/s)	K_d (cm^3/g)	PI
K^+	5.09	3.0×10^{-4}	0.72	3.15
Cl^- (KCl)	3.40	8.0×10^{-5}	0.48	11.82
Cu^{2+}	8.79	4.0×10^{-4}	1.27	4.62
Cl^- ($CuCl_2$)	5.85	3.0×10^{-4}	0.84	6.16

CONCLUSIONS

The mixture of soils of the Botucatu and Serra Geral Formations was shown to give suitable results for hydraulic conductivity for their use in liners. The sorption capacity for the ions studied is considered to be low compared to those for soils in temperate climates. However, the capacity to retain anions, especially chlorides, is seen as an advantage when these soils are used in liners. The influence of pH of the solution and the surface charges ($\Delta\text{pH} = +$) on the adsorption of chlorides was investigated. It was shown that pH values below 6 (CuCl₂ column) favor the adsorption of chlorides while pH values above 6 (KCl column) are unfavorable to chloride adsorption.

Acknowledgements: The authors would like to thank the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) for financial help, without which this research would not have been carried out.

Corresponding author: Ms Juliana Broggio Basso, UNESP - Universidade Estadual Paulista, Av. 24A n° 1515 - Bela Vista, Rio Claro, São Paulo, 13506900, Brazil. Tel: 55(19) 35325119. Email: julibb@rc.unesp.br.

REFERENCES

- ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (1984) – Peneiras para ensaio EB22 (NBR 5734/80), Rio de Janeiro.
- ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (1984) – Solo – Análise Granulométrica MB 32 (NBR7181), Rio de Janeiro, 13p.
- ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (1984) – Solo – Determinação do Limite de Plasticidade. MB 31(NBR9180). Rio de Janeiro, 3p.
- ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (1984) – Solo – Determinação do Limite de Liquidez. MB 30 (NBR6459). Rio de Janeiro, 3p.
- ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (1984) – Solo – Ensaio de Compactação. MB33 (NBR7182) Rio de Janeiro, 10p.
- ASTM - AMERICAN SOCIETY FOR TESTING AND MATERIALS (1998) – Standard Method for Specific Gravity of Soils; (D854).
- BASSO, J.B. 2003. *Transport and Retention of K⁺, Cu²⁺ and Cl through compacted mixture of lateritic soils for use in liners: homogeneity procedures and columns test equipment adaptations*. São Carlos. Dissertação de Mestrado. Escola de Engenharia de São Carlos. Universidade de São Paulo. 168.
- CAMARGO, O.A., MONIZ, A.C., JORGE, J.A. & VALADARES, J.M.A.S.1986. *Métodos de Análise Química, Mineralógica e Física de Solos do Instituto Agronômico de Campinas*. Campinas, Instituto Agronômico, 94.
- DANIEL, D.E. 1993. Clay Liners. In: DANIEL, D.E. ed. *Geotechnical Practice for Waste Disposal*, London, Chapman & Hall, Chapter 1, 3-14.
- FREEZE & CHERRY 1979. *Groundwater*. Englewood Cliff. Prentice-Hall.
- LEITE, A.L., PARAGUASSÚ, A.B., ROWE, R.K. 2003. Sorption of Cd², K⁺, F⁻ and Cl⁻ on some tropical soils. *Canadian Geotechnical Journal/Rev. Can. Geotech.* 40(3): 629-642.
- LEITE, J.C., ZUQUETTE, L.V. & PARAGUASSU, A.B. 1998(a). Evaluation of compacted mixture of tropical soils for use as liners: potassium and copper ion percolation. In: *Proceedings of the 8th Congress of the International Association for Engineering Geology and the Environment, A.A. Balkema, Rotterdam*, 4, 2485-2490.
- LEITE, J.C. ZUQUETTE, L.V. & PARAGUASSU, A.B. 1998(b). An equipment for percolation tests in soil Columns. In: *Proceedings of the 4th International Congress on Environmental Geotechnics, Lisboa, SPG/LNEC*, 1, 211-215.
- MELFI, J.F. 1994. Lateritas e Processos de Laterização. Escola de Engenharia de São Carlos, Universidade de São Paulo, 29 pp.
- MITCHELL, J.K.1983. *Fundamentals of soil behavior*. NewYork, John Wiley & Sons.
- MOREIRA, C.S. 2004. Adsorção competitiva de cádmio, cobre, níquel e zinco em solos. Dissertação de Mestrado. Escola Superior de Agricultura Luiz de Queiroz. Universidade de São Paulo.108.
- OGATA, A. & BANKS, R.B.1961. A solution of the differential equation of longitudinal dispersion on porous media. US Geological Survey Professional Paper, 411-A, 7pp.
- OGATA, A. 1970. *Theory of dispersion in a granular medium*. US Geological Survey Professional Paper, 411-I
- PARAGUASSÚ A.B., BOFF F.E. & ZUQUETTE L.V. 2002. Laboratorial studies of lateritic residual soils to assess liner's behavior. *Geotecnia: Revista da Sociedade Portuguesa*, 94, 37-55.
- PEIRCE, J.J., SALLFORS, G. & MURRAY, L. 1986. Overburden Pressures Exerted on Clay. *Journal of Environmental Engineering, American Society of Civil Engineers*, 119, 5, 826-839.
- PEJON, O.J. & ZUQUETTE, L.V. 1994. Classification des sols de régions tropicales par la méthode du bleu de méthylène. In: *Proceedings of the 7th Congress of the International Association of Engineering Geology, Lisboa-Portugal, A.A. Balkema, Rotterdam*, 5, 3381-3389.
- ROWE, R.K., QUIKLEY, R.M., BOOKER, J.R. 1995. *Clayey barrier systems for waste disposal facilities*. London, E.&F.N. SPON.
- SHACKELFORD, C.D. 1994. Critical concepts for column testing. *Journal of Geotechnical Engineering Division, American Society of Civil Engineers*, 120, 10, 1804-1828.
- SHACKELFORD, C.D.& REDMOND, P. L.1995. Solute breakthrough curves for processed kaolin at low flow rates. *Journal of Geotechnical Engineering Division, American Society of Civil Engineers*, 121, 1, 17-32.
- SILVEIRA, M.L.A. 2002. Extração sequencial e especiação iônica de zinco, cobre e cádmio em latossolos tratados com Biossólidos. Tese de Doutorado. Escola Superior de Agricultura Luiz de Queiroz. Universidade de São Paulo.166p.
- SINGH, U. & UEHARA, G. 1986. Eletrochemistry of the double layer: principles and applications to soils. In: *Soil Physical Chemistry*, SPARKS, D.L. (Editor) Boca Raton, Florida, CRC Press.

- UEHARA, G. & GILLMAN, G.P. 1981. The mineralogy, chemistry and physics of tropical soils with variable charge clays. Westview Tropical Agriculture Series, n° 4, 170p.
- YU, T. R. 1997. Chemistry of variable charge soils. New York. Oxford University Press. 505.
- ZUQUETTE L.V., PEJON, O. J., PARAGUASSÚ, A.B., RODRIGUES, J.E., VILAR, O.M. 1995. O Comportamento dos Materiais Inconsolidados residuais da Formação Botucatu frente a Soluções Enriquecidas em Na, K e Cu. I: Simpósio Sobre Barragens e Rejeitos e Disposição de Resíduos, 3. Ouro Preto. Anais. Ouro Preto, ABGE/ABMS/CBGB. P.365-378.