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# Solubilization and diffusion of metallic cations from a tropical residual soil in a acidic environment

## Solubilization et diffusion de cations métalliques d'un sol résiduel tropical dans un environnement acide

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### ABSTRACT

This paper presents a study of solubilization and reverse diffusion of metallic cations in a tropical residual soil caused by contact with acidic solutions, aiming to assess the influence of these phenomena in the retention of heavy metals. Reverse diffusion tests were carried out to investigate the efficiency of the extractor i.e. solutions of HCl and HNO<sub>3</sub> in distilled water at pH 1, and the influence of the procedure of extractor application on the solubilization process ( $3V_v$  at once of in three steps of  $1V_v$ ,  $V_v$  = void volume of the soil specimen). Ten elements were investigated: Al, As, Ca, Cd, Cr, Cu, Fe, K, Na and Mg. Aluminum and cadmium were, respectively, most and least significantly extracted from the soil. Iron solubilization was lower than expected, considering that it is a major constituent of the soil. The extractor had no influence for all studied cations, except for Fe, which solubilized more intensely with HCl solutions. The solubilized mass of each element increases with the total applied volume of extractor, independently of the application procedure.

### RÉSUMÉ

Ce papier présente une étude de solubilization et la diffusion reverse de cations métalliques dans un sol résiduel tropical causé par le contact avec les solutions acides, visant à évaluer l'influence de ces phénomènes dans la rétention de métaux lourds. Les tests de diffusion reverse étaient des voiture-ried hors pour examiner l'efficacité de l'extracteur (solutions de HCl et HNO<sub>3</sub> dans l'eau distillée à pH 1), et l'influence de la procédure d'application d'extracteur sur le procédé de solubilization. Dix éléments ont été examinés : Al, As, Ca, Cd, Cr, Cu, la Fe, K, Na et Mg. L'aluminium et le cadmium étaient, respectivement, le plus et moins significativement extrait du sol. Solubilization en fer était plus bas que prévu, considérant que c'est un constituant majeur du sol. L'extracteur n'avait pas d'influences pour tous cations étudiés, sauf la Fe. La masse solubilized de chaque élément augmente avec volume total appliquée d'extracteur, d'une manière indépendante de la procédure d'application.

## 1 INTRODUCTION

Compacted clay liners for waste disposal sites have been constructed in Brazil with lateritic clays, which present good performance relative to retention of heavy metals.

The most important characteristics of lateritic soils are: advanced weathering, presence of resistant primary minerals and of chemically weathered secondary minerals, low cationic exchange capacity, slight differentiation among horizons i.e. homogeneous soil, thick layers, high in-situ porosity and permeability, abundance of micro-aggregates composed of clay minerals cemented by metal oxides, great variability in texture, and high chemical stability and shear strength when compacted (Nogami and Villibor, 1995; Embrapa, 1999; Oliveira, 1999).

Researches on metal migration through lateritic clays have shown that significant solubilization of metals from the soil grains takes place at acidic environments, affecting pollutant retention due to the interference among ions from the contaminant solutions and ions derived from the soil. This phenomenon should be considered in the analysis of laboratory tests results and in the evaluation of geo-environmental parameters.

Solubilization designates the process by which metal cations are released from the solid phase of the soil and enter the liquid phase due to the contact with an acidic solution. This definition comprises metal cations originated from the dissolution of soil grains by breakage of chemical bonds of minerals, or desorbed from the diffuse double layer of clay minerals (Tsugawa, 2004).

This chemical process is frequently employed in geochemistry to aid mineral prospection, ore processing and economic utilization of low-content ore. Solubilization has also been related to environmental contamination by toxic metals, as a consequence of inadequate disposal of mining effluents (Gray,

1998) or of application of sewage sludge as fertilizer (Roy and Couillard, 1998). A potential application of solubilization is the remediation of soils contaminated by toxic metals.

This paper presents a study of solubilization and diffusion of metallic cations in a tropical residual soil caused by contact with acidic solutions, aiming at a better understanding of the geo-environmental behavior of local soils for the construction of clay liners for waste disposal sites.

## 2 MATERIALS AND METHODS

### 2.1 Soil

The researched soil was a residual lateritic clay derived from diabase collected in the Experimental Center of the Agronomic Institute of Campinas, São Paulo.

The soil mineralogy determined by X-ray diffraction, consists mainly of quartz, kaolinite, gibbsite and hematite. The chemical composition determined by X-ray fluorescence indicated the predominance of silicon, aluminum and iron.

The soil is composed by 15% medium sand, 12% fine sand, 14% silt and 59% clay. The specific gravity of the solids is 2.87. Liquid and plastic limits are 45% and 30%, respectively, and the organic matter content determined by 440°C heating is 13%.

The optimum water content and the maximum dry unit weight at standard Proctor energy are, respectively, 26.3% and 15.72 kN/m<sup>3</sup>. The hydraulic conductivity coefficient, determined by constant-head flexible-wall permeability tests, was measured as  $4 \times 10^{-10}$  m/s to  $1 \times 10^{-9}$  m/s at different stress levels.

The soil is classified as ML, a silt with low plasticity, by USSC, and as a lateritic clay (LG') by the MCT Classification

of Tropical Soils (Nogami and Villibor, 1995). Many lateritic soils present low plasticity even with high clay content, due to the low activity of kaolinite and to the cementation of clay particles by iron and aluminum oxides and hydroxides forming micro-aggregates.

## 2.2 Reverse diffusion test

Diffusion tests were carried out according to the procedure proposed by Barone et al. (1989). The diffusion cell consists of a cylindrical mould, attachable base, and cap with an orifice for sampling. The soil specimen was compacted inside the mould at the optimum water content and maximum dry unit weight determined at Proctor energy. After saturation by capillarity, the base was attached, the specimen topped with a solution, and the cap fixed. The upper part of the cell, where the solution is stored over the soil specimen, is named reservoir.

Solution samples were collected along time to monitor the reservoir concentration. After a predetermined time, the soil specimen was extruded from the mould and cut into slices of same thickness. Pore water was squeezed from each slice by the application of a 25-MPa pressure in order to determine the concentrations along the depth of the specimen.

Acidic solutions without metallic cations were utilized in this research, therefore diffusion of cations occurred from the soil to the solution i.e. reverse diffusion, similarly to previous researches by Barone et al. (1992) and Barbosa (1994).

Ten elements were investigated: Al, As, Ca, Cd, Cr, Cu, Fe, K, Na, and Mg.

Concentrations of liquid samples were determined by atomic emission spectrometry.

Two series of reverse diffusion tests were carried out to study, respectively, the influence of the extractor and of the solution application procedure on solubilization

In the first series of tests, solutions of HCl and HNO<sub>3</sub> in distilled water at pH 1 were used to investigate the efficiency of the extractor. The applied volume was equal three times the void volume of the soil specimen (3V<sub>v</sub>). Four specimens were tested with HCl (CP-1, 2, 5 and 6), and 5 with HNO<sub>3</sub> (CP-9, 10, 21, 22, 23). Additional tests were simultaneously carried out to monitor electric conductivity and pH along time.

In the second series of tests, the extractor (a HNO<sub>3</sub> solution at pH 1) was applied in three steps. At each step, a volume equal to the void volume of the soil specimen (1V<sub>v</sub>) was applied to the soil; when the concentrations of diffused metals reached a constant value, the solution was replaced with an equal volume of fresh solution, to restart the solubilization and diffusion processes. Thus, a total volume of 3V<sub>v</sub> was applied to each specimen in three steps of 1V<sub>v</sub> each. Reservoir samples were collected alternately from three replicate specimens in order to minimize the reduction of solution volume in the reservoir and maintain boundary conditions. Figure 1 illustrates the sampling process. Five specimens were used in these test (CP-28, 29, 30, 31 and 32), and an additional test was simultaneously carried out to monitor electric conductivity and pH along time.

Mass balances for each monitored element were calculated to assess the effect of the different procedures of applying solution to the soil: 3V<sub>v</sub> at one or through three steps of 1V<sub>v</sub> each.

## 3 RESULTS

Results are presented as reservoir concentration as a function of time and concentration in the soil pore water as a function of depth.

### 3.1 First Series of Reverse Diffusion

Figures 2 to 11 show results of the first series of tests for Al, Mg, K, As and Fe.

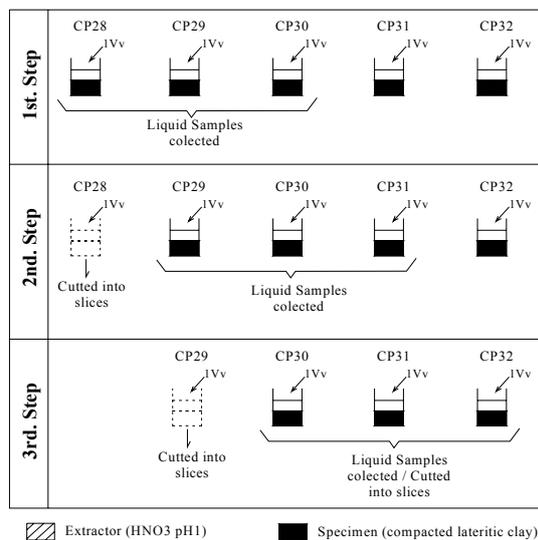


Figure 1 – Sampling process in the 2<sup>nd</sup> series of reverse diffusion tests.

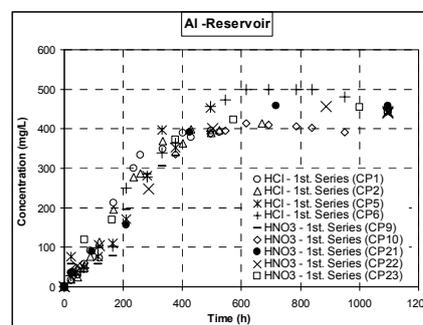


Figure 2 – Al concentration in the reservoir (1<sup>st</sup> series).

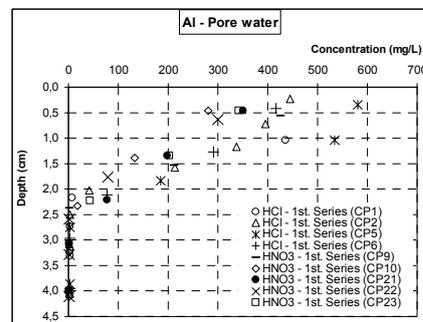


Figure 3 – Al concentration in the soil pore water (1<sup>st</sup> series).

Al and Fe are major constituents of the soil. Al was the most significantly solubilized among all monitored elements; reservoir concentrations were as high as 400 to 500 mg/L after 400 h of diffusion. The similarity of all experimental results ( 9 specimens and 2 different extractors) was remarkable.

Mg, Ca, K and Na were significantly solubilized, but less than Al. Ca concentrations in the reservoir and in the soil pore water were higher than the upper limit of the spectrometer calibration curve (120 mg/L). Maximum concentrations in the reservoir ranged from 40 to 60 mg/L for Mg, and from 8 to 13 mg/L for K. Na behavior was similar to K, but slightly less intense (6 mg/L). The results showed more dispersion than for Al. Solubilization of As, Cr, Cu e Cd was very low compared to the other studied metals, with a maximum value ranging from 0.4 to 0.6 mg/L for As, and lower for the other three metals. Cd was the less solubilized of all the monitored elements.

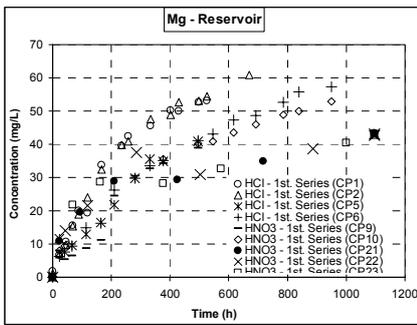


Figure 4 – Mg concentration in the reservoir (1<sup>st</sup> series).

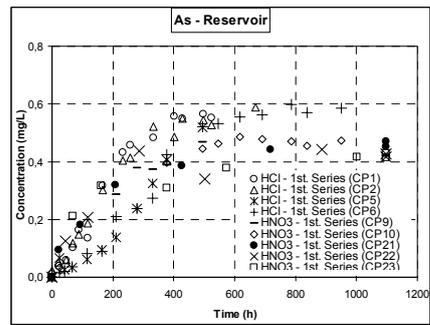


Figure 8 – As concentration in the reservoir (1<sup>st</sup> series).

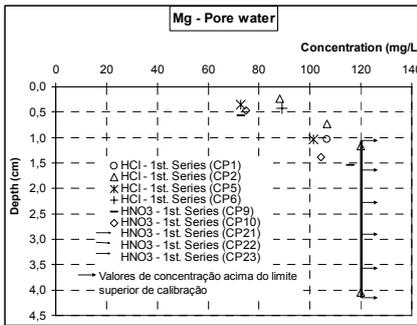


Figure 5 – Mg concentration in the soil pore water (1<sup>st</sup> series).

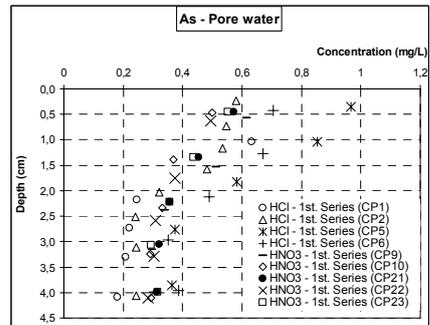


Figure 9 – As concentration in the soil pore water (1<sup>st</sup> series).

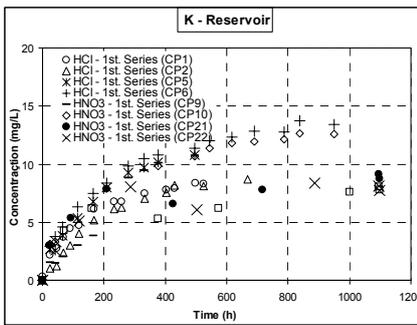


Figure 6 — K concentration in the reservoir (1<sup>st</sup> series).

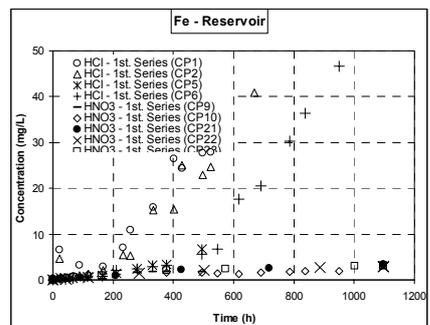


Figure 10 – Fe concentration in the reservoir (1<sup>st</sup> series).

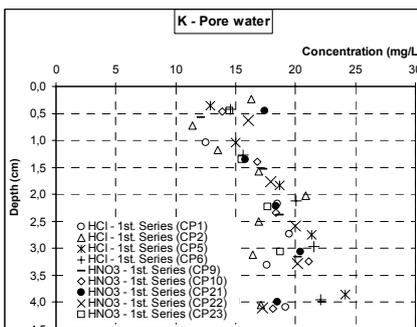


Figure 7 – K concentration in the soil pore water (1<sup>st</sup> series).

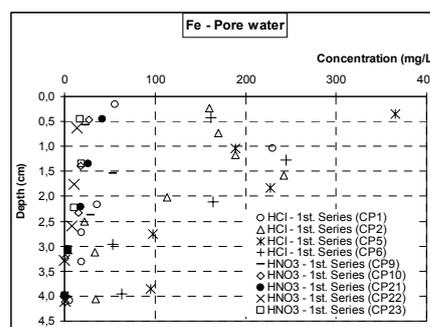


Figure 11 – Fe concentration in the soil pore water (1<sup>st</sup> series).

Despite being a major constituent of the soil, Fe was not remarkably solubilized, and was the only monitored element for which there was influence of the extractor on the solubilization process, indicating a preference for HCl. Concentrations in the reservoir still increased after 950 hours for HCl, whereas for HNO<sub>3</sub> concentrations stabilized around 1 mg/L in the first hours of the test. The concentration in the pore water of the specimen upper layer was higher than the concentration in the reservoir.

Concentrations in the soil decreased with depth for Al, Fe and As, and increased with depth for Mg and K.

### 3.2 Second Series of Reverse Diffusion

For all 10 monitored elements, concentration as a function of time presented a peak value for the first step of solution application. For the second and third steps, concentration generally increased as a function of time. Concentration profiles in the soil are very similar to those of the first series of tests.

Two different behaviors were noticed: for Al, Fe and As, solubilized concentrations were higher in the 3<sup>rd</sup> step than in the 2<sup>nd</sup> step, and these were higher than in the 1<sup>st</sup> step. For Mg and K, solubilized concentrations decreased from the 1<sup>st</sup> to the 3<sup>rd</sup> step. Figures 12 and 13 present concentrations of Al and Mg in the reservoir, respectively, as a function of time.

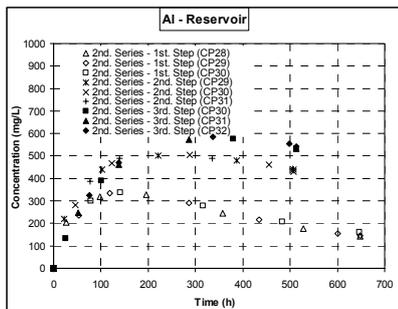


Figure 12 – Al concentration in the reservoir (2<sup>nd</sup> series).

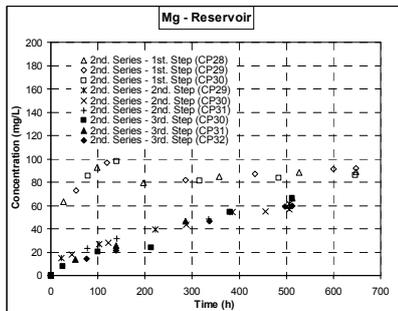


Figure 13 – Mg concentrations in the reservoir (2<sup>nd</sup> series).

### 3.3 Mass Balances

Mass balances for the reverse diffusion tests were carried out in order to analyze the influence of the procedure of solution application on the solubilization process. The percentage of solubilized mass of each investigated metal, referred to the dry mass of the soil specimen, was calculated as:

$$m_t = (m_f + m_{sam} + m_{sc}) - (m_i + m_{is}) \quad (1)$$

where:  $m_t$  = total solubilized mass;  $m_f$  = mass present in the reservoir in the end of the diffusion test;  $m_{sam}$  = mass extracted by reservoir sampling;  $m_{sc}$  = mass in the soil pore water in the end of the diffusion test;  $m_i$  = initial mass in the reservoir;  $m_{is}$  = initial mass in the soil pore water.

The initial or background mass of the metal in the soil pore water ( $m_{is}$ ) was determined by means of the chemical analysis of the pore water of a compacted and saturated soil specimen.

Mass balances for As, As, K and Mg, which correspond to the tests results with lower dispersion, are presented in Table 1.

Table 1 – Solubilized quantities -  $m_t/m_s$  (%)

Test	Al	As	K	Mg
1 <sup>st</sup> Series - 3V <sub>v</sub> HCl (CP-1, 2, 5, 6)	0.38	0.0005	0.011	0.06
1 <sup>st</sup> Series - 3V <sub>v</sub> HNO <sub>3</sub> (CP-9, 10)	0.35	0.0005	0.012	0.06
1 <sup>st</sup> Series - 3V <sub>v</sub> HNO <sub>3</sub> (CP-21, 22, 23)	0.41	0.0005	0.010	0.06
2 <sup>nd</sup> Series - 1V <sub>v</sub> , 1 <sup>st</sup> Step	0.05	0.0001	0.004	0.03
2 <sup>nd</sup> Series - 1V <sub>v</sub> , 2 <sup>nd</sup> Step	0.14	0.0002	0.004	0.02
2 <sup>nd</sup> Series - 1V <sub>v</sub> , 3 <sup>rd</sup> Step	0.20	0.0003	0.008	0.04
2 <sup>nd</sup> Series - 3V <sub>v</sub> (1 <sup>st</sup> + 2 <sup>nd</sup> + 3 <sup>rd</sup> Steps)	0.39	0.0005	0.016	0.09

$m_t$  = total solubilized mass of a determined metal;  
 $m_s$  = soil specimen dry mass.

The first series of tests with HNO<sub>3</sub> were carried out in two different occasions, with respective solubilized masses of Al equal to 0.35‰ and 0.41‰, with average of 0.38‰ for the five specimens. Solubilized mass was 0.38‰ for the tests with HCl, and the sum of the solubilized quantities in the three steps for the second series was 0.39‰. There is, therefore, no evidence of different efficiency of extractors, and no significant difference in applying the total volume of the extractor at once or in three steps. This observation is also valid for the other cations.

## 4 CONCLUSIONS

Comparison of results of the diffusion tests carried out in replicates shows that, despite a certain degree of dispersion, well-defined and consistent trends of solubilization and reverse diffusion behavior can be associated to each studied element.

Dispersion may be partially attributed to chemical and mineralogical heterogeneities of the soil, but actually these tests involve many different procedures (compaction, saturation, solution preparation, reservoir sampling, specimen separation in slices, pore water recovery, chemical analysis, among others), each subject to experimental errors, and a global experimental deviation is yet unknown. Parameters derived from these tests should be regarded as an indicative number rather than an absolute value, and sensitivity analyses should be the rule in design where these parameters are used.

There was no influence of the extractor on the solubilization process for all monitored elements, except for Fe, which has a great chemical affinity to HCl to form complexes.

Test duration of 600 h was considered adequate to achieve a constant concentration in the reservoir for all the monitored elements, except for Fe. Al was the most solubilized element, followed by Mg, Fe, K and Na, which solubilized approximately ten times less than Al. Solubilization of Cr, Cu, Cd and Pb was very low, which is consistent with the chemical analysis of the soil by X-ray fluorescence: these elements are not present in the soil, or contents are so low that could not be detected by the analytical technique.

The mass balance indicated that the solubilized mass of metals is directly related to the total applied volume of extractor, but that there is no significant influence of the procedure of extractor application on the solubilization process.

Results indicate the possibility of separating the solubilization process in two, desorption and dissolution of soil grains, based on the shape and values of the experimental curves from reverse diffusion tests. For example, Al and Fe could be easily differentiated from Mg and K.

## ACKNOWLEDGEMENTS

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