# DIFFUSION OF URANIUM THROUGH COMPACTED LATERITIC CLAY

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## ABSTRACT

In Brazil lateritic clays are natural candidates for compacted clay liners of waste disposal sites, due to their availability and adequate geotechnical properties. However, little is yet known about the behaviour of such soils regarding pollutant migration. This paper presents a study of uranium diffusion through a compacted lateritic clay, with a view to conveying technical and scientific bases for environmentally safe design of waste disposal sites for uranium processing plants.

Diffusion tests were carried out with uranium solutions in nitric and sulphuric environments to evaluate diffusion and adsorption coefficients of uranium in the researched soil. Results show significant retention of uranium by the soil, whereas diffusion is slower and adsorption lower in sulphuric than in nitric medium.

## INTRODUCTION

Compacted clay layers have been used as liners in domestic and industrial waste disposal sites in order to protect subterranean waters from the pollution resulting from the seepage of the leachate through the subsoil. In Brazil, lateritic clays are the natural candidates for the construction of clay liners for waste disposal sites, due to their availability, their adequate geotechnical properties and the accumulated practice in their utilisation in dams, embankments and road bases. However, little is yet known about their behaviour regarding pollutant migration.

This paper presents a study of the transport of uranium natural radioactive isotope $^{238}U$ as a solute through a compacted lateritic clay in nitric and sulphuric media. The purpose is to convey technical and scientific bases for environmentally safe design of waste disposal sites for uranium processing plants.

The main mechanisms involved in the transport of a solute in a porous medium are: advection, mechanical dispersion, diffusion, chemical reactions among solute and soil solids, and chemical reactions of the solute in the solution. This study focuses water-flow independent mechanisms, i.e. only diffusion and chemical reactions were considered.

Diffusion tests as developed by Barone at al. (1985) were carried out with soil specimens compacted statically at the maximum dry unit weight and optimum water content determined at Proctor Energy. Diffusion tests comprehend both monitoring the concentration of a solution in contact with the probe with time and

determining the distribution of concentrations in the specimen with depth after some time. The determination of the concentrations of the liquid samples was arrived at by double-focusing sector field inductively coupled plasma mass spectrometry.

## TRANSPORT OF URANIUM AS A SOLUTE THROUGH THE SOIL

The main mechanisms of solute transport through a porous medium are: advection, mechanical dispersion, molecular diffusion, chemical reactions of the solute in the solution, such as radioactivity, and chemical reactions among solute and solids, such as adsorption.

Advection and mechanical dispersion are water-flow related phenomena, whereas diffusion and chemical reactions can occur even when there are no hydraulic gradients involved. This study focuses the mechanisms that are independent of water movement: only diffusion and the chemical reaction adsorption were researched. Radioactive decay, though considered, showed no significant effect on the variation of concentrations with time, since the half-life of uranium isotope $^{238}U$ is $4{,}51X10^{9}$ years.

The one-dimensional equation of solute transport in the interstitial water of a saturated, homogeneous and isotropic soil, without water flow and chemical reactions of adsorption and radioactive decay considered, can be expressed by:

$$n\frac{\partial c}{\partial t} = n D_d^* \frac{\partial^2 c}{\partial z^2} - \rho K_d \frac{\partial c}{\partial t} - \lambda c \qquad (1)$$

| | |
|---|---|
| z | depth |
| n | soil porosity at z |
| c | contaminant concentration at z at time t |
| $D^*_d$ | diffusion coefficient at z |
| $\rho$ | soil dry unit weight at z |
| $K_d$ | distribution coefficient (adsorption) at z |
| $\lambda$ | disintegration constant of the radioactive element |

## EXPERIMENTAL INVESTIGATION

### Geotechnical Characterization of the Lateritic Clay

The researched soil is a lateritic clay from the State of Bahia, in the northeast of Brazil. The particle size distribution curve of the soil, the Atterberg limits, specific gravity of the soil grains and compaction characteristics at Proctor Energy are presented in Figure 1.

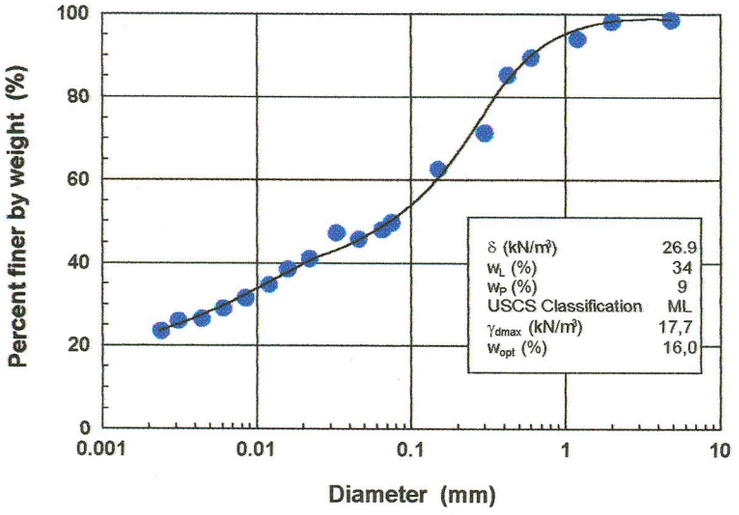



Figure 1 Geotechnical characterization of the lateritic clay

Diffusion Test

The diffusion test was presented by Barone et al. (1989) and adapted by Boscov (1997) for compacted specimens. Figure 2a shows an illustration of the equipment.

The specimen is compacted statically in the mould and saturated by capillarity. The superior part of the mould, referred to as reservoir, is filled with the solution, so as to form a liquid layer over the soil. Samples of the fluid in the reservoir are collected at regular intervals of time through the orifice in the mould cap, by means of a graduated pipette, in order to monitor the solution concentration. In the end of the test, the specimen is sliced in five to seven layers of equal thickness to determine the vertical distribution of pore water concentrations along the specimen depth. Pore water is extracted from each slice by the application of a 25 MPa pressure; it is assumed that under this pressure the double-layer water is not removed. Figure 2b presents typical curves of fluid concentration in the reservoir and along the specimen depth at the initial instant and at time t.

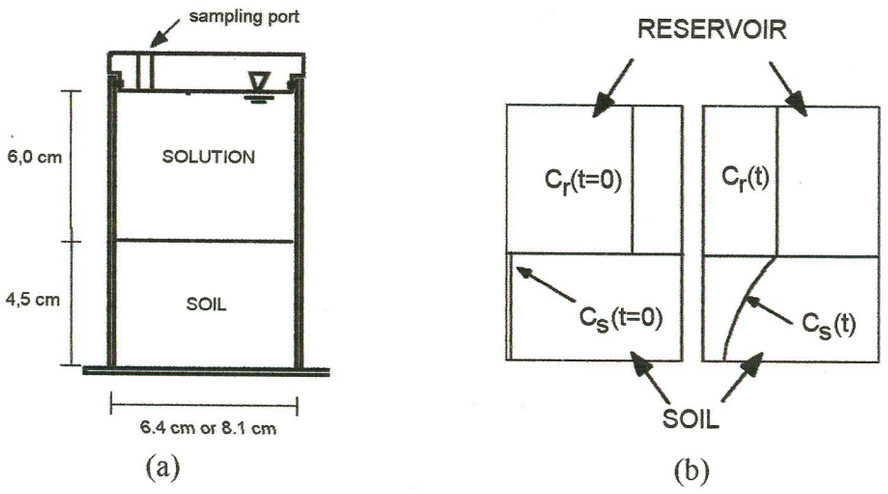



Figure 2 Diffusion test: (a) diffusion cell; (b) typical concentration curves

## Quantification of Uranium Concentration

In the late years, inductively coupled plasma mass spectrometry has been considered a powerful tool for the multielement analysis of metals at trace and sub-trace levels in environmental (Takaku et al 1994), biological (Kerl et al 1996), geological (Yamamoto et al 1995), nuclear (Gastel et al 1997) and other applications.

Mass spectrometry is a technique based in the measurement of the mass/charge ratio. A mass spectrometer is basically composed of four parts: a sample introduction system, an optical system for ions transfer, a mass analyser and a detection system. The sample is introduced in argon plasma at a temperature of approximately 8000K, where the molecules are dissociated and ionised. The generated ions are taken out of the interface region. This interface works as a beam collimator and separator between the plasma and the lenses system, where the ions are focalised. The ionic beam is hurled into a magnetic field, where each ion is separated by its mass/charge ratio. Subsequently, these ions are once more separated by their mass/charge ratio as they are hurled into an electrostatic field. After the separation, the ions are detected by an electron-multiplier detector.

A double-focusing sector field inductively coupled plasma mass spectrometer (ICP-MS; ELEMENT Finnigan MAT, Bremen, Germany) with a reverse Nier-Johnson geometry was employed in the present work. Sensibility levels, matrix effect, isobaric interference, ionic transmission with low, medium and high resolution, memory effect, medium influence and physical parameters were studied (Pedreira et al 1999).

## Experimental Procedure

Lateritic clay specimens compacted statically at the optimum compaction point at Normal Proctor Energy were submitted to uranium $^{238}U$ diffusion tests. After moulding, the specimens were submitted to saturation by capillarity for three days, reaching saturation degrees of at least 93%.

Tests lasted 21 days, with collection of 1 mL samples of the reservoir fluid at intervals of 48 hours. Collected samples were diluted till concentrations of the order of ppb (ng/L) before the measurement in the spectrometer

It was considered necessary to test uranium solutions in nitric and sulphuric media, since the environment can influence diffusion and adsorption mechanisms. Furthermore, specimens moulded in similar conditions were tested for diffusion with solutions of different concentrations, in order to verify experimentally the assumption that the diffusion coefficient of an element in a given soil is a constant independently of solution concentration.

Diffusion tests in nitric environment were carried out at concentrations varying from 1 mg/L to 15 mg/L, with three repetitions for the concentration of 1 mg/L, besides a blank test, i.e. nitric environment and same pH value without uranium. The repetitions were considered necessary to observe the consistency of the experimental procedure and to evaluate diffusion and adsorption coefficients. Two additional specimens were tested with solutions in concentrations of 100 mg/L and 2000 mg/L, to complete the study of diffusion behaviour with solution concentration; these concentrations were not further researched, since they are very unlikely to occur in real leachates.

Likewise, diffusion tests in sulphuric environment were carried out at

concentrations varying from 0.5 mg/L to 10 mg/L, with two repetitions for the concentrations of 0.5 mg/L, 1 mg/L and 10 mg/L, besides a blank test, and two additional specimens tested at concentrations of 100 mg/L and 1500 mg/L.

All tested solutions presented pH value approximately equal to 1, corresponding to very acidic environment, usually regarded as unsuitable to sorption phenomena.

Air temperature and relative humidity during the experiments were 25°C and 75%, respectively.

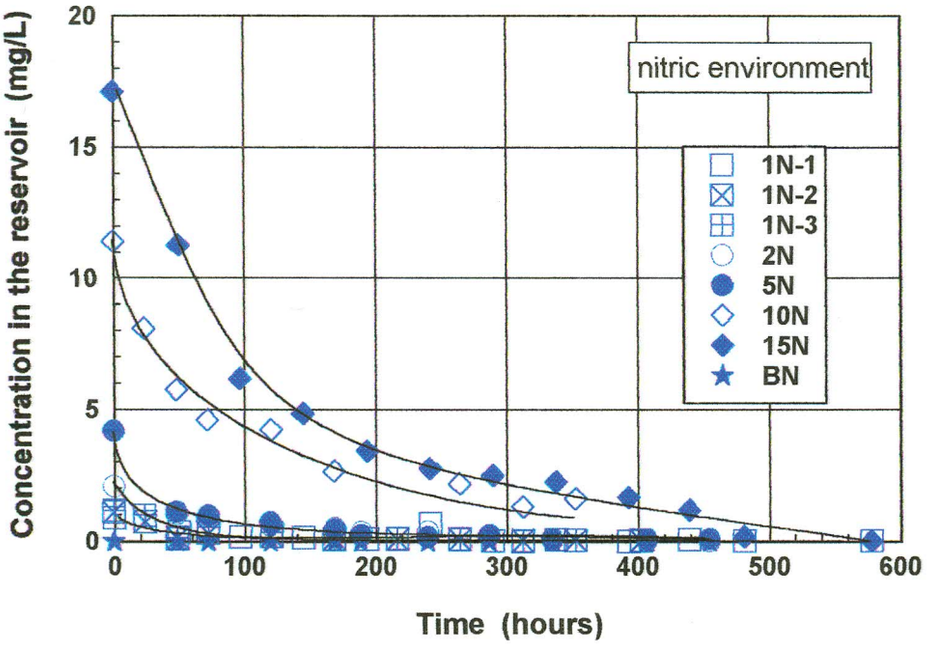
## RESULTS

Moulding characteristics of all tested specimens are presented in Table 1. Results from diffusion tests are presented as concentration curves of uranium in the reservoir fluid in function of time and uranium concentration in the soil pore water in function of specimen depth. Figures 3 and 4 show results of all diffusion tests in nitric and sulphuric environment, respectively.

Table 1 Moulding characteristics of the specimens

| Specimen | $c_0$ (mg/L) | $\gamma_d/\gamma_{dmax}$ (%) | $w-w_{opt}$ (%) | e | s | Environment |
|---|---|---|---|---|---|---|
| BN | - | 102,6 | 0,01 | 0,48 | 90 | Nitric |
| 1N-1 | 1 | 100,3 | 0,08 | 0,51 | 84 | Nitric |
| 1N-2 | 1 | 99,8 | 0,04 | 0,52 | 83 | Nitric |
| 1N-3 | 1 | 100,0 | 0,04 | 0,52 | 83 | Nitric |
| 2N | 2 | 101,0 | 0,01 | 0,50 | 86 | Nitric |
| 3N | 3 | 102,4 | 0,01 | 0,48 | 89 | Nitric |
| 5N | 5 | 103,8 | 0,01 | 0,46 | 93 | Nitric |
| 10N | 10 | 98,5 | 0,04 | 0,54 | 80 | Nitric |
| 15N | 15 | 100,4 | 0,08 | 0,51 | 85 | Nitric |
| 100N | 100 | 101,7 | 0,08 | 0,49 | 88 | Nitric |
| 2000N | 2000 | 101,6 | 0,08 | 0,49 | 88 | Nitric |
| BS | - | 101,0 | 0,01 | 0,50 | 86 | Sulphuric |
| 0.5S-1 | 0.5 | 100,1 | 0,01 | 0,52 | 84 | Sulphuric |
| 0.5S-2 | 0.5 | 101,6 | 0,01 | 0,49 | 87 | Sulphuric |
| 1S-1 | 0.5 | 99,3 | 0,04 | 0,53 | 82 | Sulphuric |
| 1S-2 | 1 | 102,7 | 0,04 | 0,48 | 90 | Sulphuric |
| 2S | 2 | 101,8 | -0,13 | 0,49 | 87 | Sulphuric |
| 5S | 5 | 100,7 | 0,01 | 0,51 | 85 | Sulphuric |
| 10S-1 | 10 | 102,8 | 0,04 | 0,48 | 91 | Sulphuric |
| 10S-2 | 10 | 99,8 | 0,04 | 0,52 | 83 | Sulphuric |
| 20S | 20 | 101,8 | -0,13 | 0,49 | 87 | Sulphuric |
| 150S | 150 | 101,8 | -0,13 | 0,49 | 87 | Sulphuric |
| 1500S | 1500 | 102,8 | -0,13 | 0,48 | 90 | Sulphuric |

$c_0$ initial concentration of the solution
$\gamma_d$ dry unit weight
$\gamma_{smax}$ maximum dry unit weight
w water content
$w_{opt}$ optimum water content
e void ratio
s saturation degree



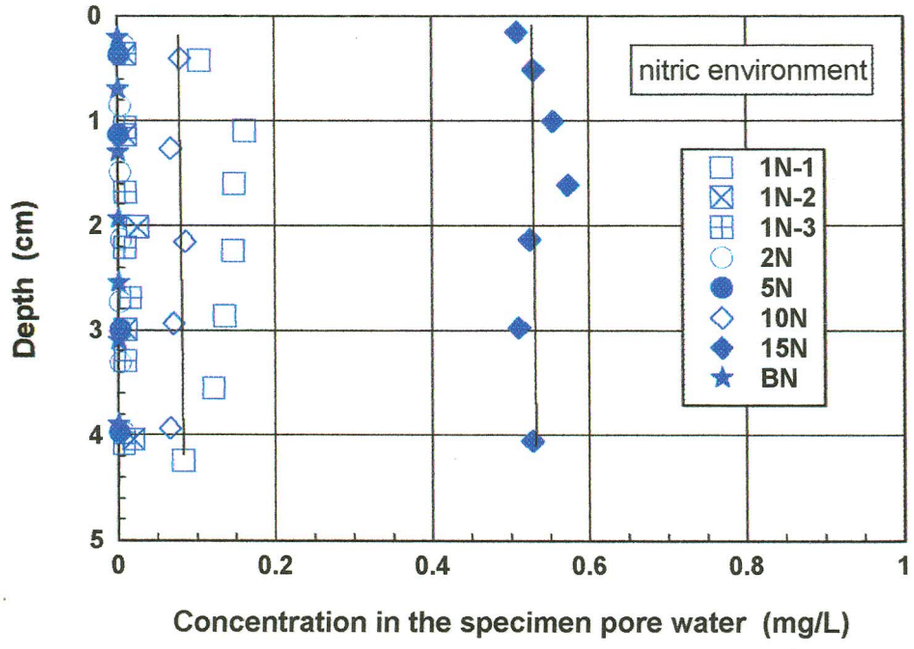




Figure 3 Diffusion tests results for nitric environment

Uranium concentration in the reservoir determined in the diffusion tests in nitric environment decreased significantly with time for all tested solutions. On the other hand, very low uranium concentrations were observed in the interstitial water of all soil specimens. The distribution of uranium concentrations along the depth of the specimens can be considered as a straight line, i.e. practically linear concentration profiles or constant uranium distribution in the soil.

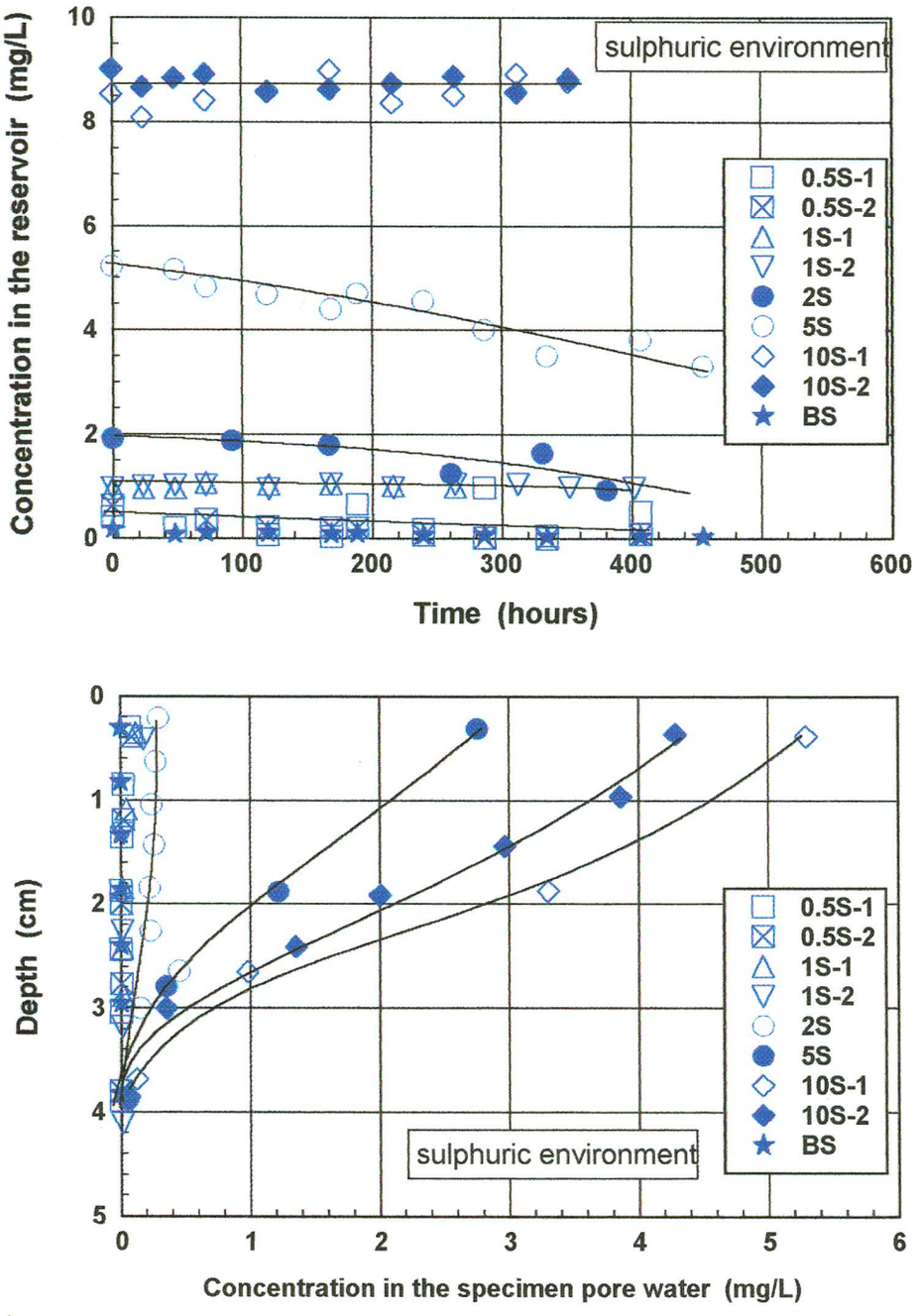



Figure 4 Diffusion tests results for sulphuric environment

Uranium concentration in the reservoir determined in the diffusion tests in sulphuric environment show a slight decrease with time for all tested solutions. The pattern of distribution of uranium concentrations along the depth of the specimens manifests a solute front entering and deepening in the soil.

Comparing Figures 3 and 4, the diffusion of uranium in a sulphuric environment seems to be slower than in a nitric environment.

It is important to notice that very low uranium concentrations in the reservoir fluid and in the soil pore water were observed in the blank tests in nitric and sulphuric environments, BN and BS respectively, indicating meaningless effects

due to uranium desorption or dissolution from the soil minerals on tests results. This consideration is relevant, inasmuch as some metals i.e. aluminum can be dissolved from soil particles of lateritic clays in acidic environments, affecting diffusion behaviour to a great extent (Boscov 1997).

Figure 5 show the tests results already presented in Figures 3 and 4 as percent values relative to the initial concentration of the solution, in order to assess qualitative trends in uranium diffusion.

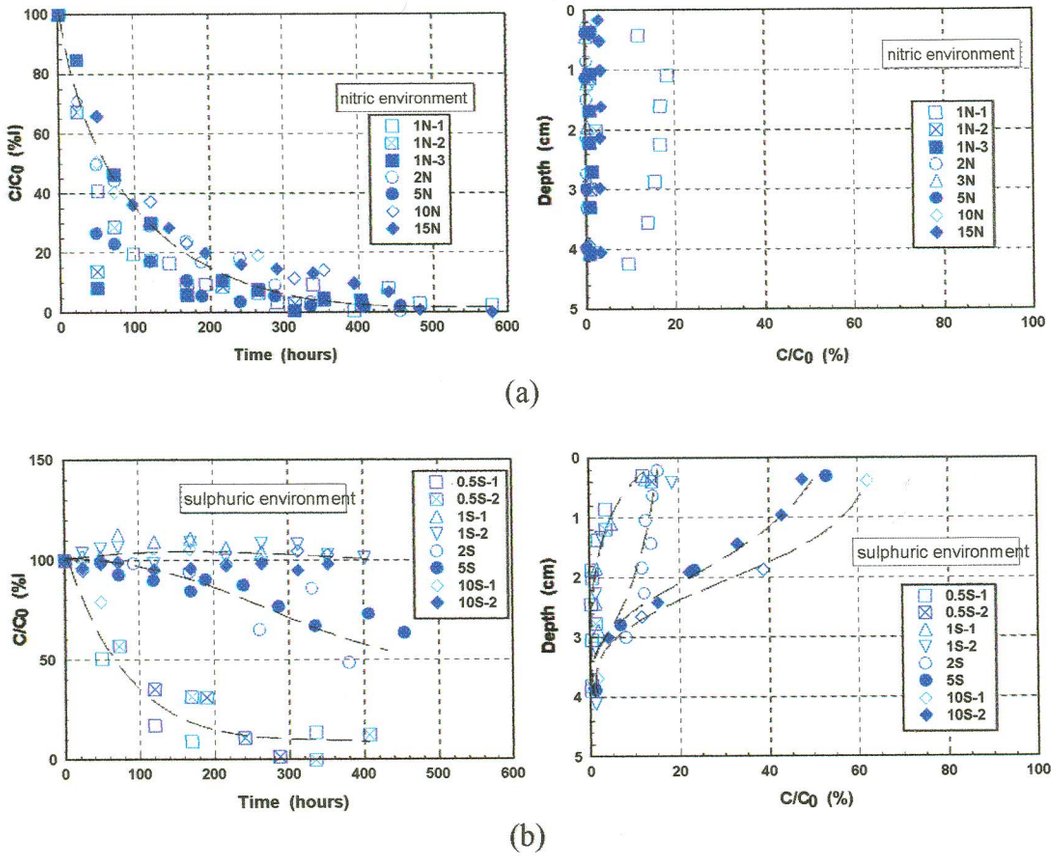



Figure 5 Diffusion tests results as percentage of initial concentration: (a) nitric environment; (b) sulphuric environment

The shapes of the curves of uranium concentration in the reservoir fluid in function of time and uranium concentration in the soil pore water in function of the depth in the specimen in terms of relative values seem to have lower dependence on the initial concentration of the solution in nitric than in sulphuric environment. In fact, tests in nitric environment could be roughly represented by two average curves when concentration values are expressed as percentage of initial concentration of the solution, for the range of concentrations of the tested solutions.

For much higher concentrations, i.e. 100 mg/L and 2000 mg/L in nitric environment, and 150 mg/L in sulphuric environment, different shapes of curves were observed (Boscov et al 1998, Boscov et al 1999). For the solution of 1500 mg/L in sulphuric environment, the soil was chemically attacked by the solution, forming an spongy material which swelled and remained in suspension in the

reservoir. Higher concentrations were not further researched, because they are hardly likely to occur in the field.

Figure 6 shows the tests which were repeated in order to assess the consistency of the experimental procedure.

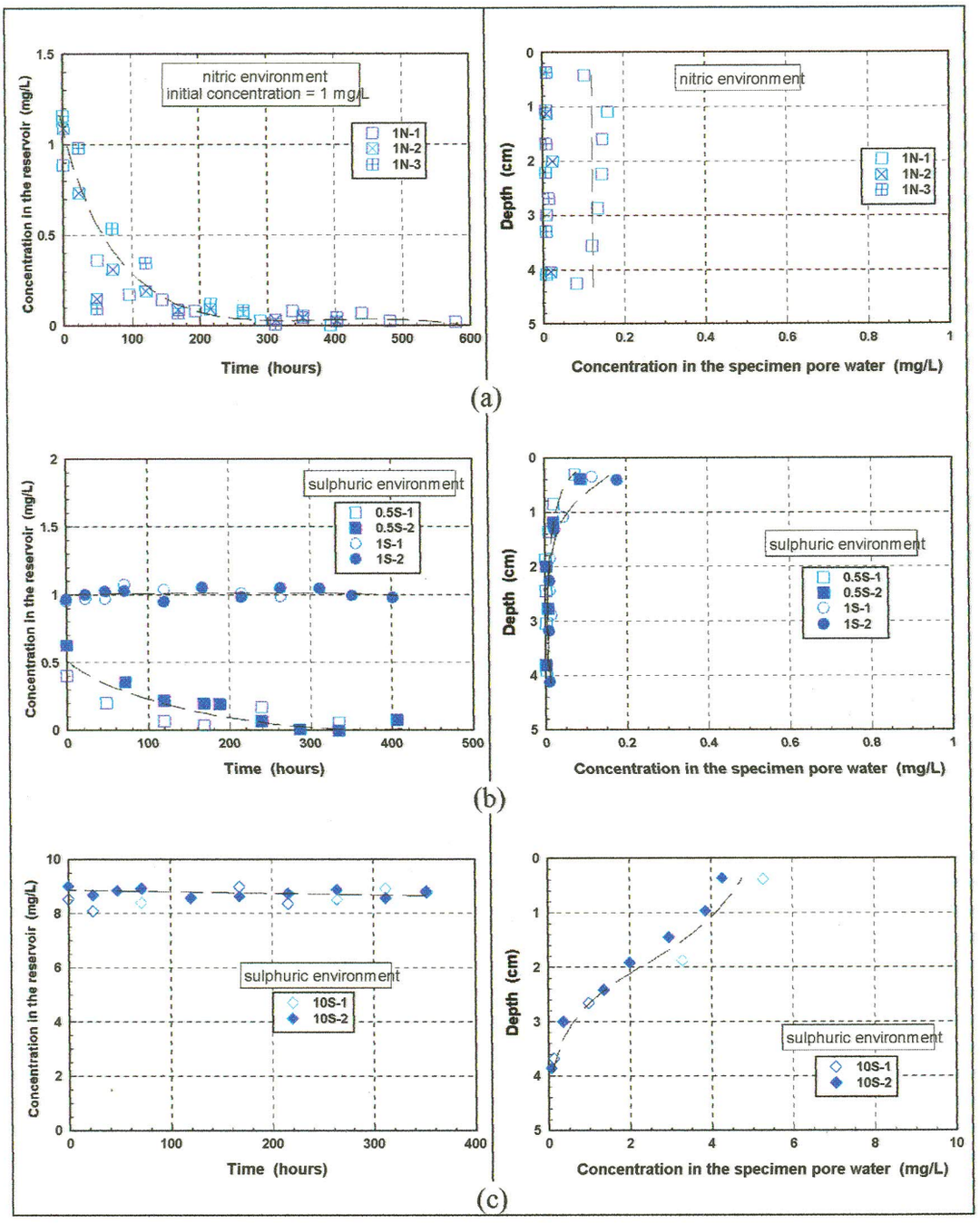



Figure 6 Repetitions of diffusion tests: (a) Nitric environment, $C_0$ = 1mg/L; (b) sulphuric environment, $C_0$ = 0.5 1mg/L and $C_0$ = 1mg/L; (c) sulphuric environment, $C_0$ = 10mg/L.

Repetitions indicate that the experimental procedure for diffusion tests conveys fairly reproducible results.

## CONCLUSIONS

The use of lateritic clays for the construction of clay liners in disposal sites for wastes of uranium processing industries is promising. Diffusion is an important mechanism of uranium transport, as can be seen by the curves of uranium concentration in the reservoir fluid in function of time. However, the soil apparently retains a great percentage of the uranium mass that migrates from the reservoir into the specimen, and only a minor fraction of the initial mass can be detected in the soil pore water.

Uranium diffusion in sulphuric environment is slower than in nitric environment, which was expected in function of ionic radii. On the other hand, more retention of uranium in the soil particles is observed in nitric than in sulphuric environment.

The continuation of the research must now focus on the influence of solution pH-values and flow on uranium adsorption and diffusion of uranium in the researched soil.

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