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Radium migration through clay liners at waste disposal sites

M. Eugenia G. Boscov[a,*], Ieda I.L. Cunha[b], Roberto T. Saito[b]

[a] *Escola Politécnica da USP, Caixa Postal 8174, CEP 05508900, São Paulo SP, Brazil*
[b] *Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049, CEP 05422970, São Paulo SP, Brazil*

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Abstract

The migration of ^{226}Ra through the bottom compacted clay liner of the wastewater disposal reservoirs of an industrial plant that processes uranium ore was evaluated. An instrumental method for ^{226}Ra analysis in soils, consisting of detector calibration, the determination of detector counting efficiency, cumulative counting of both background and soil samples in regular counting intervals, and photo-peak smoothing was developed. The ^{226}Ra was analyzed by means of its granddaughter ^{214}Bi, at a photo-peak of 609 keV. The results showed that most of the ^{226}Ra which diffused from the solution into the soil was retained in the upper layer of the sample, and that just a small percentage migrated to the subjacent layers. This methodology is adequate for the assessment of the migration of radionuclides through soil layers and for environmental impact studies related to contamination of soils by radionuclides.

Keywords: Pollutant migration; Radium; Clay liners; Lateritic clay; Diffusion test

* Corresponding author. Tel.: +5511-38185498; fax: +5511-38185181.
E-mail address: meboscov@usp.br (M.E.G. Boscov).

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1. Introduction

An industrial plant for processing uranium ore will be installed in a Brazilian rural area of low population density. Wastewaters resulting from this industrial process are composed of heavy metals, sulfates and radionuclides. The treatment of the wastewaters with lime in the disposal reservoirs causes the precipitation of heavy metals; however, part of the remaining liquid fraction is collected in a drainage system and re-utilized in the industrial process.

Environmental impact assessments often include the study of radionuclide migration through the subsoil and contamination of the subterranean water at waste disposal sites. Radium migration is a major concern because of its high concentrations and toxicity. Furthermore, radionuclides are easily detectable and have been successfully used as tracers for environmental studies. This paper has presented research that is being carried out to evaluate the migration of ^{226}Ra through the compacted clay liners that cover the bottom of the wastewater disposal reservoirs.

2. Transport of solutes 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, such as adsorption, between solute and solids.

This study has focused on solute migration mechanisms that are independent of water movement. Thus, only diffusion and the chemical reactions, adsorption and radioactive decay, were considered.

3. Experimental

3.1. Diffusion test

Tests to determine the migration by diffusion of ^{226}Ra through the soil to be utilized in the construction of the clay liner were carried out. The soil was a local red lateritic clay, forming a 6-m-thick superficial layer at the disposal site. The top of this layer will be excavated to the depth of 1 or 2 m, sieved, and compacted in order to achieve a more resistant, more homogeneous and less permeable layer.

Initially, an undisturbed sample was extracted from the depth of 3 m in order to represent the subsoil layers that will not be modified by excavation and compaction. From this sample, a specimen was trimmed to fit a 8.5-cm diameter PVC cylinder, maintaining the in situ characteristics. This specimen was permeated with a fluid similar to that to be deposited in the reservoirs, a synthetic effluent produced in a pilot plant and treated with lime. After the permeation, the soil sample was divided into three layers. The radium content was analyzed in each layer and also in the natural soil, in order to determine the background radium content of the soil (Table 3). The high radium concentration in the natural soil, compared to the soil which was permeated by the treated leachate, indicated the need to employ a more concentrated solution in the diffusion test to visualize the diffusion mechanism.

A diffusion test was then carried out with a soil sample compacted inside a diffusion cell in conditions similar to the soil to be compacted in the clay liner, i.e. at the maximum dry unit weight and optimum water content, as determined by a previous compaction test with Proctor Energy (see Table 1).

The diffusion test as described by Barone et al.

Table 1
Geotechnical characterization of the soil

Specific gravity, δ (kN/m^3)	26.9
Liquid limit, w_L (%)	34
Plastic limit, w_P (%)	9
USCS classification	ML
Clay fraction, C (%)	44
Silt fraction, M (%)	14
Sand fraction, S (%)	40
Gravel fraction, G (%)	2
Unit weight, γ (kN/m^3)	15.8
Water content, w (%)	10.9
Dry unit weight, γ_d (kN/m^3)	14.2
Porosity, n	0.47
Saturation degree, s (%)	33
Maximum dry unit weight, γ_{dmax} (kN/m^3)	17.7
Optimum water content, w_{opt} (%)	16.0

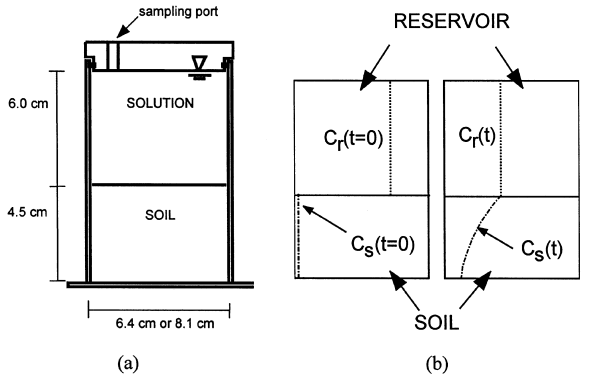

Fig. 1. Diffusion test: (a) diffusion cell; (b) typical concentration distributions.

(1989) and adapted by Boscov (1997) for compacted specimens was modified for the current radium analytical technique. The equipment consisted of a tight acrylic cell composed of a cylindrical body and detachable base and cap (Fig. 1a).

After compaction, the soil sample was saturated to prevent the formation of a hydraulic gradient during the diffusion test. A porous plate was immersed in a basin containing distilled water up to the top edge of the plate. The cell containing the soil sample was placed upon the porous plate. The soil sample, without any direct contact with the liquid, absorbed water by capillarity for 3 days, a sufficient time interval to achieve equilibrium saturation. After saturation, the cap and base were attached to the cell and the soil sample was topped with a solution of ^{226}Ra of higher activity (2.5 nCurie), filling the upper section of the cylindrical body, i.e. the reservoir. Other radionuclides were present at the industrial effluent at very low concentrations and did not demand further investigation according to environmental authorities.

The test was carried out for 15 days at a controlled temperature. As there was no hydraulic gradient, ions migrated from the solution in the reservoir into the soil by diffusion, caused by the concentration gradient. Diffusion tended to equalize concentrations; the concentration in the reservoir solution decreased with time, while an ionic front moved downwards through the soil, causing a gradual increase in the concentration in the soil interstitial fluid. An illustration of the concentrations in the reservoir (C_r) and in the soil pore fluid (C_s) at $t = 0$ and at time, t, is shown in Fig. 1b.

The test was interrupted when there was still a transient chemical flux. At the end of the test, the fluid in the reservoir was drained and the soil specimen was divided into four slices of equal thickness. Those were oven-dried at 105–110°C for 24 h. ^{226}Ra concentrations were determined for a background sample, the four soil layers, the original solution and the solution after 15 days in contact with the soil sample.

3.2. Methodology for ^{226}Ra analysis

An instrumental method for ^{226}Ra analysis in soils was developed. ^{226}Ra was analyzed by means of its granddaughter ^{214}Bi, at a photo-peak of 609 keV. The method consisted of detector calibration, the determination of detector counting efficiency, cumulative counts of both background and soil samples at regular time intervals, and photo-peak smoothing.

Counting measurements were carried out by means of a hyperpure Ge detector (ORTEC, GEM 60120P Model), with resolution of 1.9 keV at the 1332.40-keV photopeak of ^{60}Co. The data acquisition software was MAESTRO II. Detector calibration was performed by means of several gamma ray emitting nuclides. The IAEA reference materials were employed to determine the detector counting efficiency in the ^{214}Bi photopeak region.

Since the standard methodology was not sensitive enough for the analysis of radionuclides at low concentrations, it was necessary to establish a new methodology for radium analysis.

A study of background radiation variation in the region of ^{214}Bi photopeak as a function of time was performed by means of MAESTRO II software. Background counting was carried out for 250 000 s, at intervals of 10 000 s. A linear regression was fitted through data ranging from 70 000 to 250 000 s only, because statistical errors were very high for the data, relative to total counting times, below the lower limit of 70 000 s.

The same process was repeated for the soil

sample. Comparisons between the linear regression curves for the background and soil samples allowed for the determination of soil sample activity, correcting for background activity at each time. The gamma spectrum was smoothed according to a binomial algorithm, which replaced original data by smoothed data.

^{226}Ra was assayed by gamma counting: standard plastic pots containing the sample were counted in the Ge detector; cumulative counts were recorded at intervals of 10 000 s, whereas the total counting time ranged from 25 000 to 150 000 s.

^{226}Ra activity was calculated according to the following equation:

$$(A_{Cs} \pm \sigma_{Cs}) = \frac{(C_S \pm \sigma_S) - (C_{BG} \pm \sigma_{BG})}{m_A \cdot t \cdot (\varepsilon \pm \sigma_\varepsilon)} \cdot 1000 \quad (1)$$

where:

- A_{Cs} = ^{226}Ra activity in the sample (Bq. kg^{-1});
- σ_{Cs} = S.D. of ^{226}Ra activity in the sample (Bq.kg^{-1});
- C_S = gross ^{226}Ra counts in the sample;
- σ_s = S.D. of ^{226}Ra counts in the sample;
- C_{BG} = background counts;
- σ_{BG} = S.D. of background counts;
- m_A = sample mass (g);
- t = counting time (s);
- ε = counting efficiency of the ^{226}Ra photopeak (609 keV);
- σ_ε = S.D. of counting efficiency.

4. Results

4.1. Geotechnical characterization of the lateritic clay

The soil analyzed was a local red lateritic clay. The results of geotechnical characterization tests and mineralogical tests are presented in Table 1. The soil is a sandy clay with low plasticity, classified as ML according to the Unified System of Soil Classification (USSC); other samples from the same layer may classify as CL, since the soil is practically over Casagrandes's A-line, which separates clays (C) from silts (M). The porosity of the soil is very high in natural conditions, near to or greater than 0.5, but when compacted it reduces to approximately 0.3. The permeability coefficient, 10^{-5} m/s for the natural soil, fell to 10^{-9} m/s for the compacted soil.

4.2. Diffusion test

Specimen characteristics for the undisturbed sample permeated with the lime-treated synthetic effluent, and the compacted sample submitted to the diffusion test are presented in Table 2.

Radium concentrations in the specimens layers and in the solutions at the end of the tests, for the undisturbed sample and the compacted sample, are shown in Table 3. It was observed that 50 g of material was enough for soil sample counting in order to statistically guarantee counts well above the detection limit of the applied methodology for ^{226}Ra analysis.

Mass balance considers the background activity of the natural soil, the activity of the four soil layers at the end of the test, and the initial and end (after 15 days in contact with the soil) activities of the solution in the diffusion cell reservoirs.

5. Discussion

The methodology was applied to IAEA reference samples (sediment samples) (IAEA-300, IAEA-315, IAEA-327, IAEA-368, IAEA/SD-N-2). The laboratory where this research was conducted had previously participated in an intercomparison analysis run by IAEA for the analysis of IAEA-384 sample (Fangataufa sediment sample). The analysis precision ranged from 2 to 7%. The methodology showed good precision and accuracy and could be considered satisfactory, especially as small photo-peaks appeared in the gamma spectrum.

The results showed that most of the ^{226}Ra which diffused from the solution into the soil was

Table 2
Characteristics of undisturbed and compacted specimens

Specimen	Undisturbed	Compacted
Height (cm)	4.8	4.5
Diameter (cm)	8.7	6.5
Mass (g)	553.05	298.23
Dry mass (g)	498.69	257.38
Soil volume, V (cm^3)	356.7	143.2
Unit weight, γ (kN/m^3)	15.5	20.8
Dry unit weight, γ_d (kN/m^3)	14.0	18.0
Water content, w (%)	10.9	15.9
Porosity, n	0.48	0.33
Saturation degree, s (%)	32	86
Relative compaction, $RC = \gamma_d/\gamma_{d\max}$ (%)	–	101.4
Water content deviation, $w - w_{opt}$ (%)	–	−0.1
End-of-test water content, w(%)	25.7	18.0
End-of-test saturation degree, s (%)	78	97

retained in the upper layers of the sample, and that just a small percentage of ^{226}Ra migrated to the subjacent layers: 99.7% of the initial mass of radium was retained in the upper 4.5 cm of the soil layer.

Frissel and Köster (1990), analyzing data from other authors, concluded that radium does not migrate through the soil, except for dispersed or dissolved ^{226}Ra. Even then, adsorption in the soil solid phase leads to a very low average migration, emphasizing the importance of decay. Jeffery et al. (1988) obtained radium concentration profiles in the subsoil, beneath an abandoned tailings dam, that highly resembled the distribution along the soil depth observed in the diffusion test. They attributed the relatively small increase in subsoil radium content to the low solubility of radium in the tailings, and to the absence of water movement through the tailings or down the subsoil.

Considering that the clay liner will have a low permeability coefficient when properly designed and constructed, the most important mechanisms for radium migration through the subsoil in the wastewaters reservoir will be diffusion and ad-

Table 3
Radium concentrations: undisturbed and compacted specimens

Sample	Sample dry mass (g)	Sample activity per mass[a] (Bq/kg)	Activity in the layer[a] (Bq)
Undisturbed specimen permeated with synthetic effluent			
Layer 1 — Top	196.66	56.19 ± 0.60	11.05 ± 0.12
Layer 2 —Middle	159.48	51.86 ± 1.56	8.27 ± 0.25
Layer 3 —Bottom	142.55	53.75 ± 0.23	7.66 ± 0.03
Total	498.69		26.98 ± 0.28
Soil (background)	498.69	53.43 ± 0.38	26.65 ± 0.19
Diffusion test with compacted specimen			
Layer 1 — Top	55.87	6259.35	349.71
Layer 2	58.67	13.87	0.81
Layer 3	57.11	3.35	0.19
Layer 4	56.10	3.35	0.19
Total	227.75		350.90
Soil (background)	227.75	53.43	12.17

[a]After deduction of the background activity of the soil

sorption. Diffusion test results showed a high retention of radium in the upper layers of the soil, surpassing the effects of migration by diffusion, even with ^{226}Ra dissolved in an extremely concentrated solution. The proposed soil seems to be a suitable material for the construction of the clay liner, since chemical reactions between solution and soil tend to limit the migration of the radionuclide by diffusion. Furthermore, the developed methodology seems to be adequate for the assessment of migration of radionuclides through soil layers and for environmental impact studies related to contamination of soils by radionuclides.

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