

THE DETERMINATION OF THE CESIUM DISTRIBUTION COEFFICIENT OF
THE INTERIM STORAGE SOIL FROM ABADIA DE GOIÁS, GO, BRAZIL

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ABSTRACT

In September, 1987, an unauthorized removal of a cesium-therapy unit and its violation caused an accident, where several places of Goiânia's city, capital of Goiás, Brazil, were contaminated. The removal of the radioactive wastes generated from decontamination process, was made to Abadia de Goiás' city (near Goiânia), where an interim storage was constructed.

Soil samples collected from the 57th Street (Goiânia) and from the interim storage permitted to determine, through static method, the cesium distribution coefficient for different cesium solution concentrations. Those results allows for some migration/retention evaluations in disposal site selection.

Some soils parameters (water content, density, granulometric analysis etc) as well as clay minerals constituents were also determined.

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INTRODUCTION

Brief description of the accident

In September, 1987, a cesium-therapy unit was removed from the Instituto Goiano de Radioterapia (Radiotherapy Institute of Goiás) without authorization and was transported to a junk man's house, on 57th street, in central District of Goiânia's city, State of Goiás, Brazil. In the yard of the house the cesium 137 capsule (cesium chloride form), with about 50.9 TBq (≈ 1375 Ci), was violated. From this act on, the radioactive contamination spread out rapidly to other Goiânia's districts, due to commercial exchange of the pieces and the distribution of the radioactive material to some junk man relatives and friends because of its nice blue scintillation behavior.

There were seven contaminated areas with very high radiation levels. Several houses and some streets and squares of the city showed contamination. All the radioactive waste collected from the decontamination work were removed to a place specially selected for this purpose. This area is located out of downtown to avoid any risk to the population and the environment. It has approximately two hectares and is situated 20 km far away from the Goiânia's city. In this area, Figure 1, the entire amount of radioactive waste was deposited.

Soil characterization

To be able to assess the medium term storage of the selected area is important to investigate the migration of cesium in typical site soils. For this reason some experiments were realized in order to characterize the Goiânia and Abadia de Goiás soil's.

Soils are materials that result from mechanical wearing away derived from action of water, heat, wind, vegetation and also from alteration caused by chemical nature's mechanisms such as oxidation, hydration, carbonation etc(1). The joint action of all these factors produce gravel, sand, silt and clay.

Among the soil's mineral fractions, clay has the largest surface area and for this reason it has the main role in the physico-chemical processes, showing colloidal properties. So, clay undertakes the role of ion exchanger, fixing counter ions(*) because its electric charge(2,3,4)².

Clay is constituted by particles with diameter lower than 2 μm and is basically an octahedral and tetrahedral crystalline structure of hydrous aluminum (or magnesium, or iron) silicate(2,3,4). In tetrahedral structures, silicon or

(*)Retention is one of the properties of colloids, being explained by electrostatic adsorption. Colloid particles attract counter ions in order to keep neutrality, generating an electrostatic double layer around the colloid's surface.

aluminum atoms are linked with oxygen atoms or hydroxyl groups and in the octahedral structures the center is occupied by aluminum, magnesium, iron or titanium atoms.

Tetrahedral units share oxygen atoms by corner forming hexagonal sheets, likewise the octahedral units. A tetrahedral and an octahedral sheet stacking originate a 1:1 layer and a 2:1 layer is formed by stacking of two tetrahedral and one octahedral sheet. Three main aluminosilicate types can be distinguished, depending on the relation between the sheets: kaolinite (1:1), montmorillonite and illite (both 2:1).

Clay mineral structures described, have no electric charge but most of them show negative one. This can be resultant from isomorphic substitutions, happened during the octahedral and tetrahedral structures' formations. Broken bonds at the crystalline structure extremity are also another source of negative charges. Charge balance is kept through attraction of cations, being exchangeable because they are fixed on the structure's surface.

In this way, clay has an important function because it acts as an ion exchanger, and so, as a barrier that inhibit the radionuclide migration process.

Nowadays, determination of the distribution of radionuclide between two phases can be described by the distribution coefficient, K_d , defined as the ratio between the concentration of the radionuclide in the solid phase and the concentration in the liquid phase after equilibrium achievement.

It is usually expressed as:

$$K_d (\text{cm}^3/\text{g}) = \frac{\text{amount of radionuclide sorbed per gram of soil}}{\text{amount of radionuclide per cm}^3 \text{ of solution}}$$

There are two ways of K_d determination by means of laboratory tests: static (batch) and dynamic (column) method(2,3,5). To carry out this work the first method was chosen since it can offer more rapid data, through a simpler way. The method consists in shaking an amount of soil with a solution containing a certain radionuclide concentration, until attainment of the equilibrium in the liquid phase.

EXPERIMENTAL AND RESULTS

Soil's parameters as grain density, water content as well granulometry were measured using the standard procedures given by ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS(6,7,8). Bulk density was determined by the hydrostatic balance method. These results are presented in Table 1 and 2.

The identification of the mineralogical composition of the clay fraction was done by means of X-ray diffraction, using a RIGAKU diffractometer (model D-MAX 2) with copper target tube.

The soil's clay fraction was separated for determination of the existing minerals. In this way, 400 cm³ of distilled water was added to 50 g of air dried soil and 1 g of sodium hexametaphosphate, being dispersed during 15 minutes in one high rotation disperser. The resulting solution was transferred to a 1000 cm³ graduated cylinder and its volume completed with distilled water. An aliquot of 20 cm³, from a depth of 20 cm was collected, after a time interval (determined by the Stokes' law) and was centrifuged during 15 minutes at 3000 rpm. The obtained clay was deposited on a glass lamina and stove dried (for 24 hours at

20 °C). The minerals recognition, was made by the joint interpretation of three X-ray diffractograms:

- 1) natural form;
- 2) treated form (with ethylene glycol, for 24 h);
- 3) heated form (for 2 h at 500 °C).

The X-ray diffractograms are shown in Figures 2 and 3. Table 3 gives the main d-spacings of some clay minerals and Table 4 shows the identification of the minerals.

The distribution coefficient was determined using cesium chloride solutions prepared with distilled water and ^{137}Cs as a tracer, with concentrations ranging from 10^{-8} to 10^{-2} M. In a 100 cm^3 polyethylene flask 10 g of air dried soil were added (previously sieved; Tyler n29) together with 97 cm^3 of cesium chloride solution. The flask was closed with a cap and the mixture shaken for some hours.

In order to determine the activity concentration of the solution, a sample of 20 cm^3 was centrifuged for 15 minutes at 3000 rpm and a 3 cm^3 aliquot was pipetted from the supernatant solution and its activity measured using a scintillation detector, 3x3 in (well type) coupled to an ORTEC single channel spectrometer. This procedure was repeated after longer contact times till the measured

solution activity attained the equilibrium. The distribution coefficient, K_d , was then calculated from:

$$K_d = \frac{V(C_0 - C)}{mC} \quad \text{cm}^3/\text{g}$$

where C_0 = initial activity concentration of the cesium chloride solution

C = activity concentration of the sampled solution

V = volume of the initial cesium chloride solution

m = mass of the solid phase (soil)

The experimental results obtained for the K_d values are given in Table 5.

COMMENTS

The distribution coefficient, K_d , determined by batch procedure, for the interim storage and 57th street soils evidenced its dependence on the cesium concentration as shown in Figure 4. The K_d values increases as the concentration of cesium in the solution decreases.

Within the concentration range studied, the K_d value obtained for the interim storage was higher than that obtained for the 57th street although the clay content and pH values of the former were unfavorable. This happening can be explained as due to the higher content of silt in the interim storage which promotes some adsorption of cesium in the solid phase and mainly due to the higher content of organic matter in the 57th street soil which enhance the solubilization of cesium in the liquid phase.

The complexation with organic matter is one of the more important ways in which mobility of elements is increased. Several published works show that, in natural systems, radionuclides form complexes with organic matter and that these complexes are poorly sorbed(3).

The K_d values obtained for the interim storage indicate that its soil is acceptable for a temporary storage of the waste deposited there, since the average cesium concentration for each package is relatively low. Moreover the distribution coefficient achieved in this work corresponds to relatively higher concentrations than that possible by accidental release from the waste packages.

Considering, in a conservative way, a deposition area of only 2000 m², the average annual precipitation in Goiânia (about 1668.1 mm) and the cesium activity equal to 50.9 TBq

(1375 Ci) at the accident time, the molar concentration attained if all cesium were to be solubilized in the first year after deposition is 3.5×10^{-8} .

Even in such remote hypothesis the interim storage K_d value is higher than 800 which means that the retardation factor, R , expressed by :

$$R = u_n / u_w = 1 + K_d \rho \frac{(1 - \epsilon)}{\epsilon}$$

where

u_n is the nuclide transport velocity (m/s),
 u_w is the transport velocity of the water (m/s),
 ρ is the density of soil (g/cm^3) and
 ϵ is the porosity of the soil

is higher than 1000 !

Thus, if one considers that the velocity of the water is around the maximum observable in nature ($\approx 315 \text{ m/a}$), the time to cesium reach the border of the trenches is about 257 years which means that the remaining cesium activity on that

time will correspond to a concentration of 0.8 nCi/g. This value is rather below the lower limit of concentration to consider matter as a solid waste.

The batch method utilized in this work is not as realistic as a column experiment, lysimeter or field measurement because it does not take into account irreversible processes. Nevertheless, it provides a sufficiently reliable basis to characterize the sorption property of a soil. Batch experiments allow studies of sorption kinetics as well as of the importance of chemical factors. The field experiments on the other hand are complicated and expensive and are not easily performed for higher sorbing elements that require long migration times, but they still constitute a necessary complement to laboratory measurements.

Although the interim storage area chosen at Abadia de Goiás presents favorable characteristics to sorption processes of cesium in the soil, the effects of the near field cannot be ignored in the hypothesis of waste burial.

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Table 1 - Properties of Abadia de Goiás' and Goiânia's soils

Site	Water content (wt %)	Bulk density wet (wt %)	Bulk density dry (wt %)	Grain density (g/cm ³)	Porosity (%)	pH (*)	Organic matter (**) (wt %)
Abadia de Goiás' Interior Storage	22.20	1.78	1.45	2.65	45	4.4	0.67
Goiânia's 57 th Street	17.67	1.70	1.44	2.68	46	4.9	2.55

(*) Determined with calcium chloride (CaCl₂)

(**) Determined by titration with ferrous sulphate (FeSO₄)

Table 2 - Granulometric characteristics of Abadia de Goiás' and Goiânia's Soils (*)

Site	Coarse sand (wt %)	Medium sand (wt %)	Fine sand (wt %)	Silt (wt %)	Clay (wt %)
Abadia de Goiás' Interior Storage	-	13	28	33	26
Goiânia's 57 th Street	5	5	46	7	37

(*) Soil granulometric characteristics: Coarse sand 4.8 - 2.0 mm;
Medium sand 2.0 - 0.42 mm; Fine sand 0.42 - 0.05 mm;
Silt 0.05 - 0.005 mm; Clay < 0.005 mm.

Table 3 - Main d-spacings for Cu(K_α) radiation

Clay minerals	Form of the clay used at diffraction		
	Natural	Treated	Heated
Kaolinite	7.15/3.57	7.15/3.57	-
Gibbsite	4.85/4.37	4.85/4.37	-
Goethite	4.18	4.18	-
Illite	10.1	10.1	10.0
Vermiculite	14.2	14.2	10-11

Table 4 - Composition of Abadia de Goiás' and Goiânia's soils obtained by X-ray diffraction

Site	Main clay minerals	Molecular formulas
Abadia de Goiás' Interior Storage	Kaolinite	$Al_4[Si_4O_{10}](OH)_8$
	Gibbsite	$Al(OH)_3$
	Goethite	$\alpha-FeO.OH$
	Illite	$K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$
Goiânia's 57 th street	Kaolinite	$Al_4[Si_4O_{10}](OH)_8$
	Gibbsite	$Al(OH)_3$
	Goethite	$\alpha-FeO.OH$
	Illite	$K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$
	Vermiculite	$(Mg,Ca)_{0.7}(Mg,Fe^{3+},Al)_{60}[(Al,Si)_8O_{20}](OH).8H_2O$

Table 5 - Distribution coefficient, K_d (cm³/g), obtained for the Abadia de Goiás' Interim Storage and the 57th Street (a)

Site	Concentration of cesium chloride solutions (M)						
	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸
Abadia de Goiás' Interim Storage	1.40±0.04	14.58±0.16	106±22	281±11	326±8	752±32	857±17
57 th street	1.28±0.04	6.80±0.03	22±0.2	47±1	298±8	398±26	458±7

(a) The results represents the average of three samples.

Figure Captions

1. Partial view of the interim storage platform
2. X-ray diffractogram of Goiânia's 57th Street soil (a) natural; (b) treated; (c) heated
3. X-ray diffractogram of Abadia de Goiás' Interim Storage. (a) natural; (b) treated; (c) heated
4. Distribution coefficient of cesium for variable molar concentration







