STUDY OF STRONTIUM SORPTION IN BRAZILIAN CLAYS FOR THEIR USE AS A BARRIER IN REPOSITORY OF RADIOACTIVE WASTES

Carolina Braccini Freire[1], Clédola Cássia Oliveira de Tello[2]
Centro de Desenvolvimento da Tecnologia Nuclear – CDTN/CNEN
Avenida Presidente Antônio Carlos, 6.627, Campus da UFMG, Pampulha CEP 31270-901
Belo Horizonte, Minas Gerais, MG, Brasil
cbf@cdtn.br[1], tellocc@cdtn.br[2]

RESUMO

Todo e qualquer tipo de rejeito deve ser tratado e armazenado adequadamente. Portanto os rejeitos radioativos requerem gerenciamento apropriado e seguro, desde sua geração até seu armazenamento em repositório. O principal propósito da gerência de rejeitos radioativos é preservar a vida humana e o meio ambiente. O objetivo da pesquisa foi caracterizar algumas argilas brasileiras de modo a avaliar a viabilidade de seu uso na camada de recheio, uma das barreiras de um repositório de rejeitos radioativos. A principal função desta barreira é contribuir para retardar o movimento de radionuclídeos e prevenir sua liberação para o ambiente. Quatro argilas de fornecedores nacionais foram selecionadas para a pesquisa: montmorilonita cálcica (Dol 01), montmorilonita sódica (Dol 02), caulinita (Ind 01) e vermiculita (Ubm 04). Foram determinadas suas características físicas, químicas e mineralógicas e também seu potencial de sorção do cátion estrôncio. Foi confirmada por meio destes resultados relação direta entre a superfície específica (SE), a capacidade de troca catiônica (CTC) e o pH destas argilas, na seguinte ordem crescente: Ind 01, Dol 01 e Dol 02. De acordo com os modelos de Freundlich (K_f) e Langmuir (M), as argilas Dol 01 e Dol 02 foram melhores sorvedoras de Sr^{2+}. A variação de energia livre de Gibbs ($\Delta G°$) também foi calculada para as reações de sorção entre as argilas e os cátions e para todas as argilas, esta variação foi negativa, confirmando a espontaneidade das reações de sorção.

Descritores: rejeitos radioativos, sorção e argila.

ABSTRACT

Wastes in general should be properly treated and stored. Then the radioactive wastes also require suitable and safe management beginning in their generation until the storage in repository. The objective of this research was to characterize some Brazilian clays in order to evaluate the viability of their use in the backfill layer, one of the radioactive waste repository barriers. The main function of this barrier is to contribute in the delay of the radionuclides movement, and to prevent their release into the environment. Four clays provided by national suppliers were selected for the research: Ca-Bentonite (Dol 01), Na-Bentonite (Dol 02), Kaolinite (Ind 01) and Vermiculite (Ubm 04). Their physical, chemical and mineralogical characteristics were determined, and also their sorption potential of Strontium cation. It was confirmed through these results a direct relationship among their specific surface (SS), the capacity of cationic exchange (CCE) and pH. The CCE results followed this increasing order: Ind 01, Dol 01, and Dol 02. In accordance with the models of Freundlich (K_f) and Langmuir (M), the clays Dol 01 and Dol 02 were the best sorbers of Sr^{2+}. The Gibbs free energy change ($\Delta G°$) was calculated for the sorption reactions between the clays and the cations, and it was negative for all clays, confirming the sorption reaction spontaneity.

Key words: radioactive waste, sorption and clay.

INTRODUCTION

Radioactive wastes can be generated in several areas like nuclear plants, nuclear fuel cycle installations, hospital, colleges and institutes or research center. In the fuel cycle is

generated major waste amount, either solid or

liquid. The majority of these wastes are classified as low-level radioactivity wastes and their main contaminants are uranium and daughter [1].

Strontium-90 obtained of the uranium irradiation is an important source of radioactivity in the waste from the nuclear power industry. Its half-life is about 29.1 years and is potentially a very hazardous nuclide, because its very high solubility allows it to migrate through ground water to the biosphere. Furthermore because of its chemical similarity to Ca, Sr it is readily assimilated by terrestrial and aquatic organisms [2,3].

Based on these facts, this radionuclide must be confined in repository to prevent its release into the environment. Clays are often considered as buffer and backfill materials in the multi-barrier concept for both high-level and low/intermediate-level radioactive waste repository [4].

In the paper is explained the experiments about strontium sorption in four different kinds of clays to select the one, which sorbs more strontium, as a candidate to use as backfill.

EXPERIMENTAL

Materials: For this study four clays from Brazilian suppliers were used: Ca-Bentonite (Dol 01), Na-Bentonite (Dol 02), Kaolinite (Ind 01), and Vermiculite – (Ubm 04).

Clays Characterization: The physical properties like granulometry [5] and humidity [6] for the selected clays were determined. Their specific surface was measured by sorption of N_2 using the equipment Autosorb - NEW Quantachrome 2000. For some clays the cationic exchange capacity (CEC) was determined by using the method of the blue methylene described in ASTM Standards [7]. The analysis of X-rays diffraction (XRD) was carried out to identify the main argilominerals and some impurities present in all samples. The diffractometer used to acquire the diffractograms is a half-automatic Geigerflex model with Cu-K α.radiation, produced by Rigaku industry. The analysis was carried out by varying 2θ from 0 to 70° in the samples.

Sorption Experiments [8]: Sorption experiments were performed using the bath method. Firstly was determined the ideal clay:solution ratio. The second step was to determinate the equilibrium time. These two parameters establish the system for the bath sorption assay. After this, the selected mass of clays were put in contact with 08 (eight) diluted solutions of Sr^{2+} with concentrations in a range from 8,600 until 239,000 $\mu g.L^{-1}$, in selected equilibrium time. The mixtures were filtrated and the liquid phases were analyzed by Atomic Emission Spectroscopy (ICP/AES). The amount of Sr sorbed (x/m), $\mu g.kg^{-1}$, was calculated by equation 1 [3, 4, 9]:

$$x/m = \frac{C_o - C}{m}(V) \qquad (1)$$

where C_0 is the initial concentration ($\mu g.L^{-1}$), C is the final concentration ($\mu g.L^{-1}$) after the contact with the sorbent, V is the volume of solution (L) and m is the mass of sorbent oven-dried basis (kg).

Sorption equation models: The Freundlich model is represented by equation 2:

$$\frac{x}{m} = K_f \, C^n \qquad (2)$$

where K_f can be defined as the sorbent capacity or affinity for solute [8] and the exponential term n indicate, qualitatively, the reactivity of energy sites of soil or the intensity of sorption [10].

The equation 3 represents the Langmuir model:

$$\frac{x}{m} = \frac{K_L MC}{1 + K_L C} \qquad (3)$$

The coefficient K_L ($L.\mu g^{-1}$) is somehow related to the bonding energy between the sorbed ion and the sorbent. The parameter M ($\mu g.kg^{-1}$) is usually accepted as the maximum sorbent sorption regarding to the specific solute and it is understood as the maximum amount that a sorbent could retain [8]. The linearized form of the equation 3 is the equation 4:

The values of K_L and M can be obtained thought of the linear ($1/K_L$) and angular ($1/M$) coefficients of the straight line.

RESULTS AND DISCUSSIONS

The results of the physical properties of the four clays (Ca-Bentonite– Dol 01, Na-Bentonite – Dol 02, Kaolinite – Ind 01 and Vermiculite – Ubm 04) are showed in Table 1. Note that the specific surface (SS), the cationic exchange capacity (CEC) and the pH presented the same tendency. The mineralogical properties, obtained by X ray diffraction, are also shown in Table 1. The two samples of bentonites (Dol 01 and Dol 02) present the montmorillonite and quartz as predominant minerals. The sample Ind 01 has the kaolinite as predominant mineral, and the sample Ubm 04 the major constituent is vermiculite in accordance with their suppliers.

The sorption experiment was performed during 24 hours in controlled temperature. The selection rate for the Dol 01, Dol 02, Ind 01 and Ubm were: 1:200, 1:500, 1:20, and 1:500, respectively. The Freundlich model isotherms are exemplified in Fig. 1. The coefficient, parameter and constant values calculated for the isotherms from Freundlich and Langmuir models are summarized in Table 2.

In accordance with the isotherms, Dol 02 the Na-bentonite was the clay that presented the higher sorption capacity for Sr^{2+} or higher K_f

followed by Ubm 04, Dol 01 and Ind 01. The parameter M of the Langmuir equation was used to estimate the maximum sorption capacity of the sorbent. The results show that Ubm 04 presented the highest M value, i.e. the highest capacity of sorbing a Sr^{2+} monolayer in its surface. The coefficient K_L, related with the bond energy, also follows the same tendency of sorption capacity (K_f) being the highest for the Na-bentonite. Therefore the Sr^{2+} was more strongly sorbed in sodic montmorillonite (Dol 02) and less sorbed in kaolinita (Ind 01), although this clay also presents high sorption capacity.

The Gibbs free energy change in equilibrium ($\Delta G°$) was calculated through the Van't Hoff equation ($\Delta G° = - RT \ln K$) [11]. The equilibrium constant values (K) were evaluated from the $C_s C^{-1}$ versus C (Cs is the concentration of Sr^{2+} on the sorbent at equilibrium) plot. K and $\Delta G°$ values are shown in Table 2. The Gibbs free energy indicates the spontaneity of the sorption process and as higher negative is the value more energetically favorable is the sorption [12]. All clays presented $\Delta G°$ negative value confirming the feasibility of the process and the spontaneous nature of sorption with a high preference of strontium on the clays.

Table 1. Predominant mineral, granulometry, humidity, specific surface (SS) and cationic exchange capacity (CEC) of the studied clays.

Clays	Predominant mineral (~ 60%)	Granulometry (μm)	Humidity ± 0,2%	SS (m² g⁻¹)	CEC±0,25 (mmol$_c$ kg⁻¹)	pH ± 0,02
Dol 01	Montmorillonite Quartz	95% < 297 5% < 38	11.5	65.4	685	8.80
Dol 02	Montmorillonite Quartz	95% < 297 4% < 38	14.6	78.7	925	10.37
Ind 01	Kaolinite	85.2% < 297 30% < 38	11.2	15.3	55	5.13
Ubm 04	Vermiculite	6.3% < 297 0.1% < 38	8.8	2.5	ND	6.18

Table 2. Coefficients and constants of Freundlich and Langmuir Models for the strontium sorption on the studied clays.

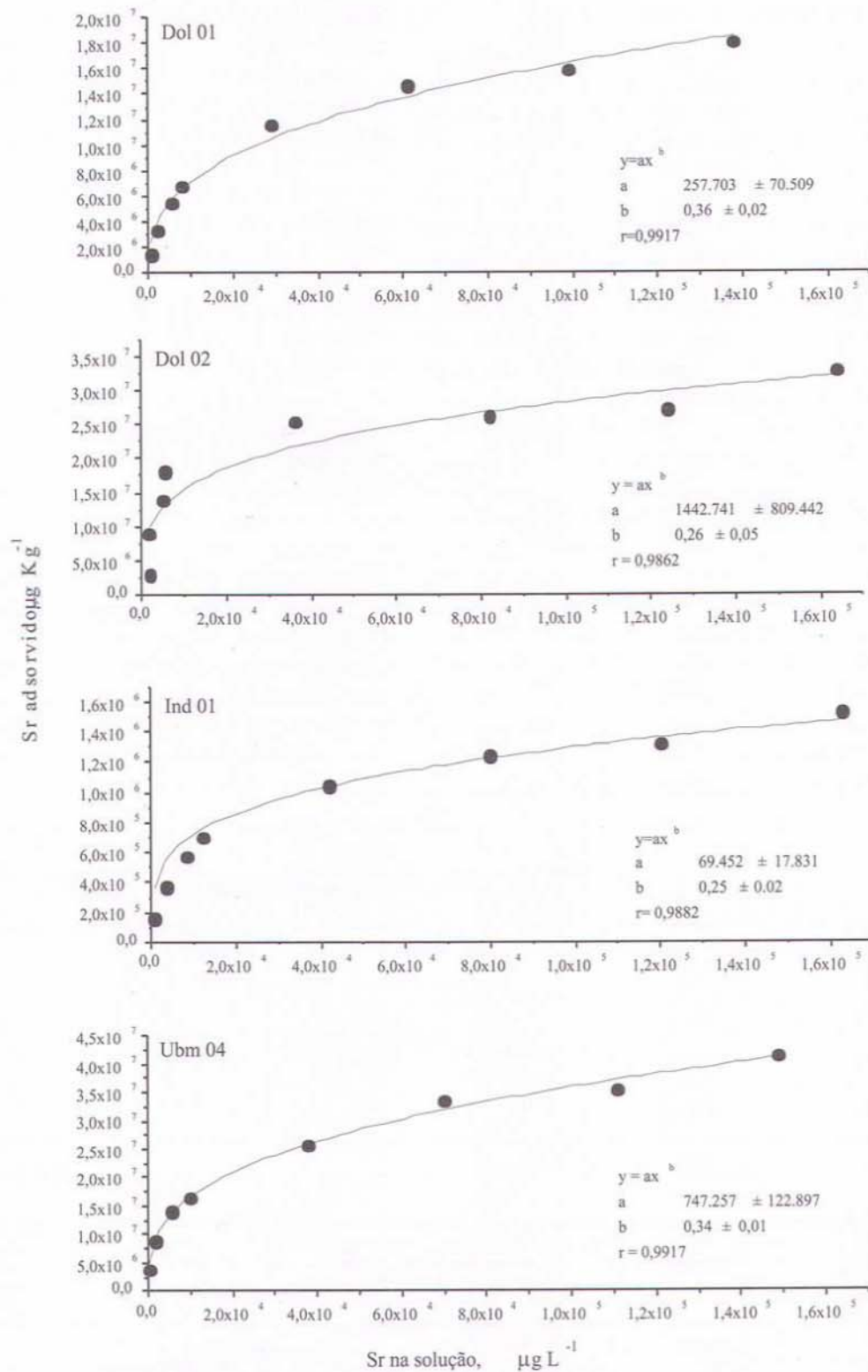| Clay	Freundlich Model			Langmuir Model			K	- ΔG (kJ mol⁻¹)
	K_f	n	r²	K_L (L g⁻¹)	M (g kg⁻¹)	r²		
Dol 01	257,703	0.36	0.9834	79.92	18.80	0.9902	301	14.14
Dol 02	1,442,741	0.26	0.9725	101.42	32.02	0.9806	380	14.65
Ind 01	69,451	0.25	0.9765	70.13	1.56	0.9880	334	14.36
Ubm 04	747,256	0.34	0.9835	83.66	41.65	0.9793	1,310	17.54

Figure 1. Sorption isotherms of strontium in clays studied: the points are the experimental results and the lines were fitted by Freundlich model.

CONCLUSIONS

The study of the strontium sorption in some clays showed that the specific surface (SS), the cationic exchange capacity (CEC) and the pH of the Dol 01, Dol 02 and Ind 01 presented a the same tendency, and all the clays. All clays presented some moisture content, even the air-dried samples.

The XRD results are agreed with the specification send by the clay suppliers, indicating a good quality control.

The Langmuir and Freundlich sorption models were used to represent the experimental equilibrium data, and these ones fitted very well to the two isotherm models. The results showed that the Dol 02 (Na-bentonite) presented the highest sorption capacity of Sr^{2+}, and the highest bond energy with this cation, respectively represented by K_f (1,442,741) and K_L (101.42 L g^{-1}) coefficients.

Finally for the tested clays the sorption behavior was spontaneous, confirmed by $\Delta G°$ negative value.

ACKNOWLEDGMENTS

REFERENCES

[1] C.C.O. Tello, Avaliação de bentonitas nacionais como aditivo na cimentação de rejeitos radioativos. Dissertação (Mestrado em Ciência e Técnicas Nucleares) - Universidade Federal de Minas Gerais, Belo Horizonte, 1988.

[2] K. Bunzl, W. Schultz, Distribution coefficients of ^{137}Cs and [85]Sr by mixtures of clay and humic material, Journal of Radioanalytical and Nuclear Chemistry, v. 90/1, pp. 23-37, 1985.

[3] K.M.A. El-Rahman, M.R. El-Sourougy, N.M. Abdel-Monem, I.M. Ismail, Modeling the sorption kinetics of cesium and strontium ions on zeolite A, Journal of Nuclear and Radiochemical Science, v. 07, pp. 21-27, 2006.

[4] J. Vejsada, E. Jelinek, Z. Randa, D. Hradil, R. Prikryl, Sorption of Cesium on smectite-rich clays from the Bohemian Massif (Czech Republic) and their mixtures with sand. Applied Radiation and Isotopes, v. 62, pp.91-96, 2005.

[5] CDTN, Análise granulométrica de minérios (RT(CT5)CDTN-0338), Belo Horizonte, 2001.

[6] CDTN, Determinação do teor de umidade em argilas (RT(SN1)CDTN-0417), Belo Horizonte, 2005.

[7] ASTM, Standard test method for methylene blue index of clay, C 837 – 81, Annual book of ASTM standards. Philadelphia, pp. 275-276, 1990.

[8] EPA, Batch-type procedures for estimating soil adsorption of chemical (EPA/530 SW-87-006-F). Washington, 1991.

[9] Z. Aksu,. Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto Chlorella vulgaris. Processes Biochemistry. v. 38, pp. 89-99, 2002.

[10] G. Sposito, The chemistry of soils, Oxford University Press, New York, 1989.

[11] Ozer, A.H., Ozer, D., Ozer A. The adsorption of copper(II) ions on the dehydrated wheat bran (DWB) determination of the equilibrium and thermodynamic parameters. Process Biochem. 39, 2183 – 2191, 2004.

[12] Aksu, Z. Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto Chlorella vulgaris. Process Biochem. 38, 89 – 99, 2002.