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# Impact of alkaline alterations to a Brazilian soil on cesium retention under low temperature conditions

Jaqueline Alves de Almeida Calábria [a, *], Stela Dalva Santos Cota [b], Gustavo Ferrari de Morais [a], Ana Cláudia Queiroz Ladeira [b]

[a] Radioprotection and Safety Division / Brazilian National Commission for Nuclear Energy, Rua General Severiano 90, Rio de Janeiro, RJ CEP: 22290-901, Brazil

[b] Center for Development of Nuclear Technology / Research and Development Division/ Brazilian National Commission for Nuclear Energy, Av. Presidente Antônio Carlos 6627, Belo Horizonte, MG CEP: 31270-901, Brazil

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ABSTRACT

To be used as backfilling materials in radioactive waste disposal facilities, a natural material must have a suitable permeability, mechanical properties and a high sorption capacity for radionuclides. Also important when considering a material as a backfill is the effect of its interaction with the alkaline solution generated from concrete degradation. This solution promotes mineralogical alterations that result in significant changes in the material key properties influencing its performance as a safety component of the repository. This paper presents results of an investigation on the effect of alkaline interaction under a low temperature on cesium retention properties of a local soil being considered suitable as a backfill for the Brazilian near surface disposal facility. A sample of the Brazilian soil was mixed with an alkaline solution, simulating the pore water leached in the first stage of cement degradation, during 1, 7, 14 and 28 days. The experiments were conducted under low temperature (25 °C) aiming to evaluate similar conditions found on a low and intermediate level radioactive waste disposal installation. A non-classical isotherm sorption model was fitted to sorption data obtained from batch experiments, for unaltered and altered samples, providing parameters that allowed us to assess the effect of the interaction on material quality as Cs sorbent. The sorption parameters obtained from the data-fitted isotherm were used then to estimate the corresponding retardation factor ($R$). Alkaline interaction significantly modified the soil sorption properties for Cs. The parameter $Q$, related to the maximum sorption capacity, as well as the affinity parameter ($K$) and the retardation coefficients became significantly smaller (about 1000 times for the $R$ coefficient) after pretreatment with the simulated alkaline solutions. Moreover, the increase in $n$-values, which is related with the energy distribution width and heterogeneity of surface site energies, demonstrated that the adsorbent surface became more homogenous as a consequence of the alkaline alteration. Together these results suggest that cementitious leachate has a profound effect on Cs retention and should be accounted for estimating radionuclide retention in radioactive waste disposal systems containing cementitious materials.



## 1. Introduction

A near surface repository is being designed by the Brazilian Commission for Nuclear Energy (CNEN) in order to dispose of the low and intermediate level radioactive waste generated in the country. According to the Brazilian disposal concept, the waste package and other engineered barriers are responsible for isolating the radioactive wastes until they reach natural levels of radioactivity (Tello, 2008). One of the most important barriers is the backfill, which can consist of clay, soil, rock, mortar or a combination of these materials. Besides void filling between the packages to promote mechanical stability, backfilling materials are used to control water infiltration and gas liberation, to facilitate waste retrieval if necessary, and to retard radionuclide migration by precipitation or sorption. In this context, the properties that make a

* Corresponding author.
*E-mail addresses:* jaqueline.calabria@cnen.gov.br (J.A.A. Calábria), sdsc@cdtn.br (S.D.S. Cota), gustavo.morais@cnen.gov.br (G.F. de Morais), acql@cdtn.br (A.C.Q. Ladeira).

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material suitable for backfilling are the permeability (or hydraulic conductivity), the mechanical properties and the sorption capacity (IAEA, 2001a; 2001b).

In a near surface facility, large amounts of cement are used, mainly in the structures and installations that comprise the multi-barrier system. This cement, when hydrated, will generate a high pH plume that will change the properties in the near field and engineering barriers in the long term. Several studies concerning this phenomenon have been conducted, aiming to investigate the effect of alkaline interaction on the mineralogy of materials (Bauer and Berger, 1998; Bérubé et al., 1990; Fernández et al., 2006; Honty et al., 2010; Moyce et al., 2014; Ramírez et al., 2005b, 2002; Sakamoto et al., 2007; Savage et al., 2007, 1992), or related to kinetic (Fernández et al., 2006; Rozalén et al., 2008, 2009) and geochemical modelling of alteration mineral phases (Fernández et al., 2009; Gaucher et al., 2004; Ramírez et al., 2005a; Savage et al., 2002; Yamaguchi et al., 2007), or even to diffusion of both the alkaline plume and radionuclides in the geosphere and other barriers (Kozaki et al., 1999; Nakayama et al., 2004; Sato, 2005; Wang and Liu, 2004).

Most of these studies have focused on the effects under high temperatures, which tend to accelerate and intensify the mineralogical changes. Few studies have been carried under relatively low temperatures, the condition expected in a disposal facility for low and intermediated level radioactive waste. The few studies performed in low temperatures, have generally focused on the effect of temperature on the kinetics of alteration product formation (Bauer and Berger, 1998; Fernández et al., 2006; Nakayama et al., 2004; Rozalén et al., 2008, 2009; Sánchez et al., 2006). Other authors, however, claim that the morphology of the new formed phases is a function of the temperature applied in the experiments. Fernández et al., 2010 for example, finding that bentonite altered at a high temperature (120 °C) leads to the formation of secondary Mg-clays, zeolites and the precipitation of crystalline calcium silicate hydrates (CSH) of tobermorite-type, but, on the other hand, at a low temperature (25 °C), the formation of non-crystalline CSH gels was observed.

Previous studies also demonstrated that the nature and extension of the modifications, caused by the interactions of the minerals with an alkaline solution, depend on the chemical/mineralogical composition of the solid material and the composition of the alkaline solution, besides other alteration conditions, such as the time of alteration and the size of the sample. Thus, the literature review shows us a broad range of results, sometimes diverging from each other, depending on the material under study, temperature, alkaline solution composition and contact duration (Gaucher and Blanc, 2006). As a result of these conflicting results, it is necessary to study site-specific conditions of interest when investigating the impact of the interaction on material properties. The specific conditions of temperature, types of barriers and materials applied, generally are related to the kind of disposal system and the type of radioactive waste to be disposed. The site location also influences the choice of backfill materials. Since large amounts of the backfilling material are required in a repository, the use of local natural materials instead of commercial ones is preferred.

Recently, aiming to find a suitable local material to be used as a backfill in the Brazilian repository, Calábria et al. (2017b) studied the Cs sorption capacity of some samples of soils from the southeastern region of Brazil. The typical rhodudult (according to soil taxonomy classification (USDA, 1999)) presented the best results exhibiting the highest value for the maximum sorption capacity, ($Q$) (18.4 mg.g$^{-1}$), distribution coefficient, $K_d$ (90.5 mL.g$^{-1}$), cation exchange capacity (CEC) (10.08 meq/100 g), iron (9.82%) and clay concentration (~50%).

In order to investigate the effect of alkaline alteration under low temperatures on Cs retention for this soil, a study based on the evaluation of isothermic parameters for the soil samples before and after the interaction with an alkaline solution for different periods was conducted. The isothermic parameters data were used for estimating the corresponding retardation factors ($R$) as a measure of the impact of the alkaline interaction on the migration velocity of the contaminant.

## 2. Methodology

### 2.1. Experimental

#### 2.1.1. Sampling and soil characterization

The sample site is located in the city of Conselheiro Pena, in the state of Minas Gerais in the southeastern region of Brazil and the geographic coordinates are 19° 07′ 57″ S, 41° 34' 21" W (WGS 84). The sampling point was georeferenced by a GPS (GPSmap 76CSx, Garmin) and the sampling procedure followed the Manual for Sampling Soil to Reference Values of Minas Gerais State (FEAM, 2013).

The sample was air-dried and passed through a 20# Tyler 0.841-mm sieve using a vibrating sifter (Mavi-Hude 6.12/M-03-4). The material that was <0.841 mm was crushed in a 10″ x 6" roll crusher (Denver 1076). The soil was thoroughly mixed to obtain homogeneous samples, which were properly characterized (Calábria, 2015).

According to the Brazilian System of Soil Classification (Sistema Brasileiro de Classificação de Solo – SiBCS), the sample is a typic rhodudult soil and its determined composition is kaolinite (>40%), quartz (>20%), halloysite (~15%), goethite (~9%), muscovite (~7%) and small quantities of feldspars.

#### 2.1.2. Alteration of the soil sample

The experimental alteration was carried out using an alkaline solution to simulate the young cement pore water (the pore water leached in the first stage of cement degradation). Prepared from analytical-grade reagents, the solution was composed of 0.11 mol.L$^{-1}$ NaOH and 0.25 mol.L$^{-1}$ KOH, and saturated with $Ca(OH)_2$, with a pH > 13.5 (Holgersson and Albinsson, 2002). The soil sample and the alkaline solution were mixed in polyethylene flasks in a 1/25 mass ratio. The flasks were kept under stirring for 1, 7, 14 and 28 days in a climatic chamber at 25 °C. At the end of each alteration period, the soil was separated from the solution by centrifugation using a fixed angle rotor, during 3 min at 3000 rpm. Then, the soil was washed with ethanol until the ionic conductivity of the washing solution reached a value between 55 and 40 μS.cm$^{-1}$.

#### 2.1.3. Sorption batch experiments

The sample soils – unaltered as well as altered for 1, 7, 14 and 28 days – had their sorption isotherms measured using the Soil Variable: Solute Ratio Method (EPA, 1992). The procedure consisted of mixing different amounts of the sorbent with 200 mL of solutions containing 100 mg.L$^{-1}$ of nonradioactive Cs prepared from analytical-grade CsCl. This high Cs concentration may not be representative of the expected concentration to be release into the environment from a disposal facility, but it was selected to provide ease in measuring the maximum sorption capacity ($Q$ parameter). Thus, the isotherm model (aqueous vs. solid phase Cs concentrations) generated from this study must be used with care to estimate Cs partitioning at lower aqueous Cs conditions. The solid:solution mass ratios were: 1:10, 1:20, 1:40, 1:60, 1:80 1:100, 1:150 and 1:200. Since we intend to investigate the Cs migration after long time scale, the pH of the suspension was adjusted to 5.5 ± 0.1 using 0.01 mol.L$^{-1}$ NaOH or HCl. This scenario is representative of the moment that the cement degradation is complete and the pH was