



## Brazilian clays for environmental solutions applied to radioactive waste management

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## ABSTRACT

Clayey materials have been adopted in most nuclear waste producing countries as a key constituent in engineered barrier systems for final disposal facilities at all levels of radioactive wastes (LILW-SL, LILW-LL, and HLW). The following study presents a thorough characterization upon five Brazilian clay-rich deposits, mostly smectite bearing clays, aiming to evaluate their expected performance as barrier under the conditions associated to a Low and Intermediate Level Waste Repository; being the former a matter of national strategic interest. Samples coming from the Brazilian states of Paraná, Bahia, Paraíba, and Maranhão were treated and analyzed by means of X-Ray diffraction as main technique. Other techniques such as FTIR, LALLS, XRF, and SEM-EDS, were performed in order to establish the mineralogical composition, particle size distribution, and chemical composition. Moreover, several standard clay treatments over the  $<1 \mu\text{m}$  size fraction were carried out to reveal information regarding layer charge, major interlayer cations, unit formula and other crystal features of smectite species present in a mineralogical assembly, aiming to provide information for the construction of a molecular model over which would be realistic to simulate the diffusion of radionuclides. Results obtained on  $^{133}\text{Cs}$  adsorption experiments indicate that mineralogical composition would probably be the single most influential factor controlling transport capacity of positively charged radionuclides in the current setup. The composition is especially expressed in terms of smectite contents, favoring montmorillonite rich materials containing majorly  $\text{Na}^+$  as compensating cation in interlayer position. All tested samples can be considered as suitable candidates to be used in the design of final destination storage for nuclear waste. Thus, efficiency on  $^{133}\text{Cs}$  adsorption trials also indicate that these materials could have potential uses as sorptive matrices (Sorbents) for water treatment of radionuclide polluted waters such as TENORM waste waters. However, these trends are yet to be contrasted against hydraulic conductivity measurements and swelling pressure in order to have a more comprehensive perspective of this clayey prospects as barrier enhanced layer; aligned to the multilayer barrier system approach for nuclear waste management.

**Keywords:** clays, smectites, TENORM, cesium, adsorption and EBS

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## 1. INTRODUCTION

A variety of activities generates radioactive wastes that need to be properly managed for the environment and human safeguard. Normally, these wastes need to be isolated for many years in a proper containment structure until they decay to safe levels for final disposal known as geologic disposal [1]. In this type of shelters, it is often found the use of smectite rich clays in order to embed waste fuel canisters as “clay buffer”, due to the following special properties: Low hydraulic conductivity, low anion diffusion capacity, low transport capacity, high swelling (and therefore enhance sealing capability if installed in a dry and highly compacted state), colloidal filtering properties, microbes filtering properties [2] and many other marvelous features of this naturally occurring nanoparticles.

In low and intermediate-level radioactive waste (LILW) disposal facilities, the standard containing infrastructures does not has to respond for such a long lifetime and consequently, other enhance applications of clay minerals apply such and clay liners, top cover bentonite/sand mix, filled or granulated smectite powder, etc.

The Brazilian nuclear waste legacy generated by Angra 1 and 2 power reactors are currently in interim storage on-site at Central Nuclear Almirante Álvaro Alberto in Itaorna (Angra dos Reis, RJ, Brazil). This storage’s capacity is expected to be exceeded between 2020 and 2025, raising concerns for a definitive repository construction. A preferred option for this question is the disposal in surface or near-surface facilities that would allow for long term storage of LILW. In these facilities, the radioactive waste would be placed in mineral or natural cavities some tens of meters below the surface [3]. The National Commission of Nuclear Energy (CNEN) is responsible for the regulation of radioactive waste storage and management. In 2009, they started a project called “Low and Intermediate Level Waste Repository” (RBMN) aiming at the construction of a repository for the Angra powerplants radioactive wastes [4, 5].

Cesium-137 is one of the radioactive fission products of most concern due to its high solubility, and can contaminate large volumes of water, being efficiently taken up by plants and absorbed by animals for its similarity to potassium, an essential nutrient [6, 7, 8, 9]. Therefore, an efficient containment is very important to prevent cesium transport to the environment and consequently

living organisms such as humans themselves. Cesium presents the tendency to bond to clay minerals in soils and sediments [10]. It is strongly adsorbed onto illites or hydroxyinterlayered vermiculite [11, 12].

## 2. MATERIALS AND METHODS

### 2.1. Clay sources

All clay sampling and characterization derive from the main author of this article [13, 14]. A set of five samples have been specifically selected from that set, representing most promising candidate clays for the purpose here being, and located within Brazil's national borders have been specifically selected, and listed in Table 1 as a function of their geological context. Most of them may be characterized as bentonites with the exception of the sample coming from Parana, with can be described as a clay-rich material with detrital amounts of smectite; and the rest may be considered low to mid-grade polycationic bentonites. Samples have been assigned with abbreviations of their respective origins, for instance, "BA" indicating the clay extracted in Bahia state, and so on.

**Table 1:** List of samples arranged by geological areas.

Sample	Location	Common name	Age	Parent rock	Formation Mode	Post-Events
PR	Paraná	Paraná Raw	Mid-Permian	Ryolite/Dacite	InSitu Alteration	Weathering/Illitization
BA	Bahia	Verde Duro	Tertiary	Basalt	In situ or Hydrothermal*	Uncertain
PB1	Paraíba	Chocolate	Tertiary	Basalt	Uncertain	Uncertain
PB2	Paraíba	Verde Macia	Tertiary	Basalt	In situ or Hydrothermal*	Uncertain
MA	Maranhão	Maranhao	Triassic	Basalt	Hydrothermal or whethering*	Weathering

### 2.2 Clay preparation

Clay preparation involved oven-drying of 1 kg/sample at 105 °C during 24 h, followed by grinding in a ceramic ball mill at 120 rpm and sieving till 100% passing 100 Mesh (100 % Wt < 149 µm). Afterwards, sub-sampling was carried out in a spinning riffler (Microscal Ltd.) to ensure representability. No Na activation was performed, neither acid attack nor H<sub>2</sub>O<sub>2</sub> was performed.

Observations over the <1 µm size fraction were proceeded by size fractioning via sedimentation, after drying the material was pulverized up to 100% Wt < 74 µm (200 Mesh) using a Herzog pneumatic mill (HERZOG Automation Corp., Cleveland, OH, USA) for XRF, SEM, and FTIR analysis. Smaller sample sizes (up to < 10 µm) were used in powder XRD for optimum setup [14, 15, 16].

### 2.3 Size distribution analysis

The size distribution of the clay samples will not only provide valuable information regarding mineral size populations, as also a frame or a sedimentation strategy. The analyses were performed for all bulk samples on a Malvern Mastersizer 2000 (Malvern Panalytical Ltd., Malvern). The tests were conducted without dispersant. The bulk samples were added in deionized water while applying a 1-minute intermittent ultrasonic treatment. The pumping speed was maintained at 2500 rpm.

### 2.4 Crystal structure analysis

X-ray diffraction (XRD) was carried out in a Bruker D8 Endeavour diffractometer (Bruker Corporation, Billerica, MA, USA) with a Cu anode using Co K $\alpha$  radiation (1.54 Å) at 40.0 kV and 40.0 mA over the range (2 $\theta$ ) of 2–75° with a scan time of 0.5° min<sup>-1</sup>, multilayer graphite monochromator and 2.3 mm soller slit for both incident and diffracted beam.

Bulk samples were prepared as “randomly oriented powder” (ROP) by backload on holders having 10 mm of the sample surface, and less than 1 µm size fraction as oriented slides (OS) on glass rounded slides of 25 mm. Most XRD protocols according to Moore and Reynolds [17] and Chipera and Bish [18].

Phase identification was performed using Bruker’s Software “Diffrac.Suite.Eva”(Version 4.1.1) and crystallographic information files PDF4 (2012) database. Semi-quantitative phase analyzes were performed by the total multiphase spectrum refinement method (Rietveld method) using Bruker’s Software “Diffrac.Topas” (Version 5.1). The diffraction patterns were recorded using

Bragg-Brentano geometry at room temperature over the angular range of 2° to 75° in the step of 0.02° with 2 second as step time.

## 2.5 Mineral quantitative analysis

Whole-rock and <1 μm size fraction chemical compositions were assessed by X-Ray fluorescence analysis (XRF) using a Bruker's S8 Tiger WDXRF spectrometer (Bruker Corporation, Billerica, MA, USA). Loss on ignition (LOI) was estimated for all samples and aleatory duplicates according to the following steps: (1) Porcelain crucibles were weighed after drying in an oven at 110°C; (2) Each crucible was labeled and filled with either whole-rock or <1μm particle size powders, dried for at least 3 hours at 105°C and weighed. Then the dry weight of the samples was recorded; (3) Subsequently, the powders were fired for 2 hours at 1020°C. Finally, from the difference of the weight after drying and after firing, the LOI was estimated. Fired powders after determination of LOI were mixed with lithium tetraborate (B<sub>4</sub>Li<sub>2</sub>O<sub>7</sub>) flux.

## 2.6 Adsorption Experiments

All solutions were prepared using analytical grade chemicals and ultrapure water (Milli-Q Gradient System > 18 MΩ.cm). The cesium solution was prepared in an initial concentration of 1 × 10<sup>-5</sup> mol L<sup>-1</sup> at pH 8. A dosage of 2.5 × 10<sup>3</sup> mg L<sup>-1</sup> of each clay was added in centrifuge tubes with 100 mL aliquots of the Cs solution. The tubes were then placed on an orbital shaker at a 60 rpm at room temperature. The samples were shaken continuously for a contact time of 4 days to allow sufficient time for Cs sorption onto the mineral. Mineral blanks were also tested to rule out any sorption onto container walls. After that, each tube was centrifuged for 30 minutes at 3,600 rpm in order to obtain a < 50 nm particle size cut off in the supernatant. An aliquot of the supernatant was taken from each sample and the <sup>133</sup>Cs was measured by TQ ICP-MS (Thermo Fisher Scientific™, Bremen, Germany). The distribution coefficient,  $K_d$  (L mg<sup>-1</sup>), for each sample was calculated according to Eq. (1).

$$K_d = \frac{[Cs]_i - [Cs]_{eq}}{[Cs]_{eq}} \times \frac{1}{[mineral]} \quad (1)$$

where  $[Cs]_i$  is the initial Cs concentration,  $[Cs]_{eq}$  is the equilibrium Cs concentration in the aqueous phase, and  $[mineral]$  is the solid-solution ratio in  $mg L^{-1}$ .

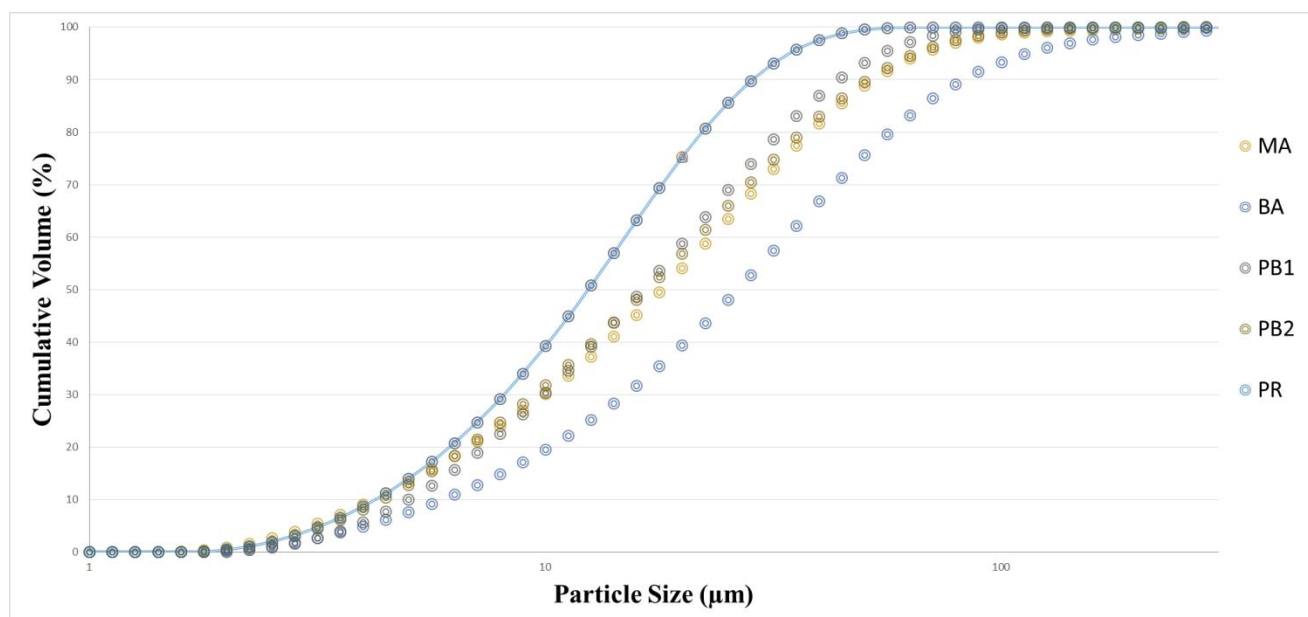
### 3. RESULTS AND DISCUSSION

#### 3.1 Size distribution analysis

Size distribution analysis for all bulk samples as presented (Figure 1), yielded mean size values ranging 75  $\mu m$  to 10  $\mu m$ .

High agglomeration, and sensibility for ultrasonic treatment were observed, along with a tendency for higher size values in association to higher quartz content and lower size particle mean value in correlation to may minerals overall content.

**Figure 1:** Size distribution analysis of all samples.



The graph above shows that the PR sample is composed in higher proportions (60 %) of particles of approximately 25  $\mu m$ , whereas 50 % of the BA studied sample has around 50  $\mu m$  representing the coarser distribution among all analyzed clays.

### 3.2 Geochemical information

Results from XRF chemical analysis on the whole-rock samples are presented in Table 3, and they offer a chemical composition in agreement with what can be expected from parent rock and genesis mode. Moreover, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents from bulk chemistry shown in Table 2, allowed deductions on the geochemical affinity with respect to the parent rock.

Smectites derived from basic rocks may have three times the iron content forming than those of intermediate to the basic volcanic source, and they tend to alter into Fe-Montmorillonites and Fe-beidellites, as it is the case for samples coming from Paraíba and particularly Maranhão.

Silica levels to a lesser extent may also indicate the acid to basic parent rock, tending towards intermediate to acidic in higher SiO<sub>2</sub> contents, and lower contents derived from basic composition extrusive rocks. Samples PB2 and MA showed higher Fe<sub>2</sub>O<sub>3</sub> values and relatively lower SiO<sub>2</sub>, which seems to be in agreement with they're basaltic precursors (Table 1 and 2).

**Table 2:** Whole rock chemical composition from XRF fused beads 10 major elements.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	Σ(Sum)
<b>PR</b>	66.1	16.08	5.74	0.05	1.667	0.51	0.68	2.02	0.855	0.05	6.26	99.97
<b>BA</b>	56.7	19.72	9.21	0.11	3.467	0.38	0.08	0.04	0.402	0.05	10.2	100.35
<b>PB1</b>	56.4	21.16	8.09	0.01	3.704	0.13	0.08	0.04	0.386	0.01	10.1	100.08
<b>PB2</b>	62.8	13.94	8.2	0.03	2.529	2.51	0.61	0.22	0.746	0.04	8.16	99.805
<b>MA</b>	46.9	20.62	17	0.19	2.942	0.51	0.01	0.97	1.716	0.03	10.02	100.86

Feldspar species and hematite appear to be the source of major concern for chemical interference with respect to the geo-barrier performance, in the sense that they offer higher solubility and via means of cation exchange with free K may induce lamellar collapse (illitization) as a function of time in a hydrothermal environment, as could be the case for samples PR & MA.

### 3.3 Mineral phase identification and quantification



Table 3 summarizes the mineralogical composition for all samples after crosschecking Rietveld-Topas results against XRF-XRF molar sum.

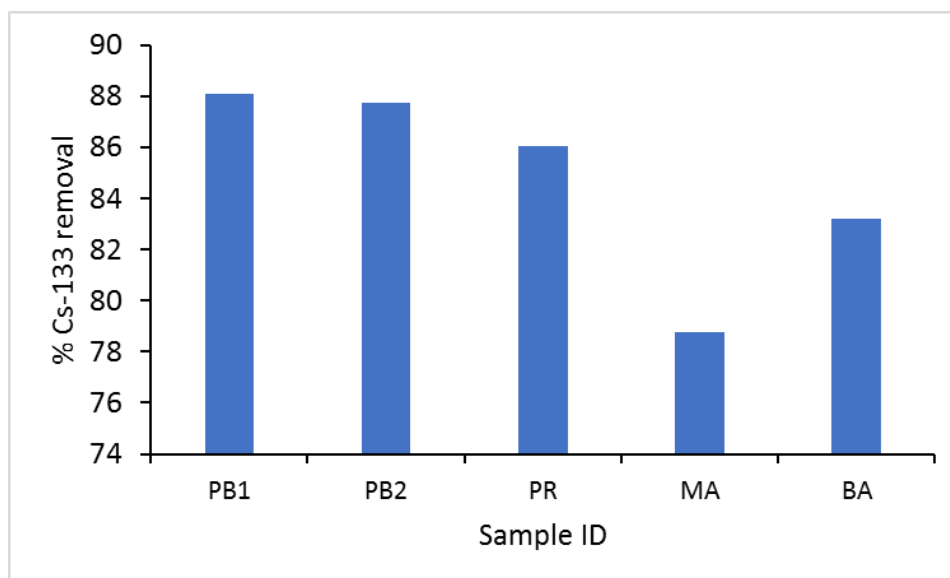
**Table 3:** Quantitative mineral analysis results.

Mineral	Sample	PR	MA	BA	PB1	PB2
<i>Montmorillonite</i>		29.4	64.5	83.0	55.0	50.0
<i>Quartz</i>		21.2		1.0	38.0	30.0
<i>Hematite</i>			6.8	1.0		
<i>Kaolinite</i>		6.9	23.3	13.0		19.0
<i>Illite</i>		19.3				
<i>Albite</i>		11.7	5.4			
<i>Cristobalite</i>						
<i>K-Felspar</i>		8.0		2.0		
<i>Anorthite</i>					3.0	1.0
<i>Graphite</i>		2.5			4.0	
<i>Olivine</i>		1.1				
	<b>SUM</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>

### 3.4 Cs Adsorption

All samples were tested for  $^{133}\text{Cs}$  adsorption capability in aqueous media. Results indicated that all adsorbents were effective in removing the target metal (Figure 2).

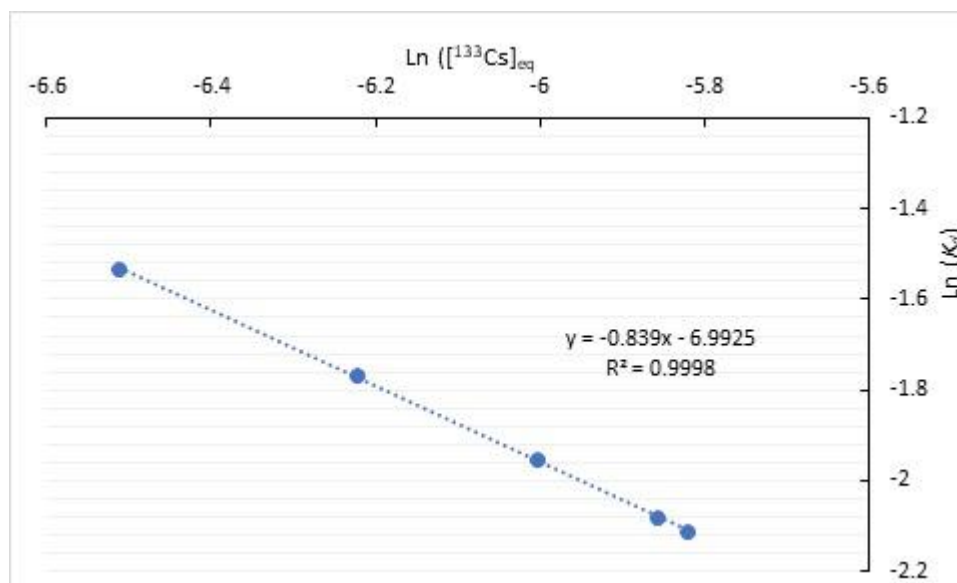
**Figure 2:** Adsorbents used in  $^{133}\text{Cs}$  sorption.  $[^{133}\text{Cs}]_0 = 1.02 \text{ mg L}^{-1}$ .



PB1 was the most effective adsorbent with 88% of cesium removal, and shares a similar performance with PB2, both being from the same region. Although smectite content for both of these samples is not the highest among in the set, it can be expected that the agglomeration presented as a smectite coating over quartz's large particles, in a low agitation energy system, may favor mesoporous interactions. Consequently, PB1 is presumably enhanced for containing higher  $\text{Na}^+$  cations in interlayer position, not containing kaolinite and possibly graphite is well known to be a sorptive media.

On the other hand, MA presented the lowest value, which was 79%, possibly due to very high layer charge  $\text{Fe}^+$  smectites and the presence of iron phases (mostly hematite), creating an electrostatic repulsive aqueous interaction in the experimental setup. Figure 3 presents the adsorption data in terms of the logarithm of the distribution coefficient ( $\ln(K_d)$ ) versus the logarithm of the equilibrium aqueous Cs concentration ( $\ln[{}^{133}\text{Cs}_{eq}]$ ).

**Figure 3:** Relationship between  $K_d$  and  ${}^{133}\text{Cs}_{eq}$ .



The relation between cesium concentration at equilibrium and the distribution coefficient was linear (inversely proportional), as indicated by Figure 3, with a correlation coefficient ( $R^2$ ) of 0.9998. The highest  $K_d$  value was obtained for PB1, with  $2.96 \times 10^{-3} \text{ L mg}^{-1}$ . This value is two-fold higher than that obtained by MA. These results indicate PB1 as the best option regarding cesium adsorption.

#### 4. CONCLUSION

This may be a first step aiming to fully develop a comparative perspective of local clay prospects having strategic interest for applied for radioactive waste management applications such as enhanced barrier properties and water treatment of radionuclide bearing wastewaters. Fundamental parameters are yet to be studied such as diffusion, geotechnical properties and compatibility, regularity of the mineral reserves, and state priorities and regulatory aspects concerning international nuclear energy establishments. Nevertheless, results thus far indicate that moderate grade bentonites could be a suitable material for a barrier in a LILW design, natural bentonite, and sand mix could in a certain type of constructive approaches constitute the most compressible materials and offering the possibility of controlled self-locking/sealing engineered

barrier after in situ hydraulic swelling. The crystal chemistry of smectite species showed to be a sensible parameter with respect to isomorphic substitutions, particularly in the case of  $\text{Fe}^{2/3}$  commonly located in octahedral positions regardless of oxidation state.

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