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Characterization of bentonite, vermiculite and soil as potential materials to compose the natural barriers in a near-surface repository

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ABSTRACT

The use of nuclear technology is growing in Brazil, where it is possible to carry out the entire nuclear fuel cycle. This technology generates radioactive waste that must be treated before being released into the environment or stored in suitable facilities. Then, the first national repository - CENTENA - will be implemented, where all low and intermediate level radioactive waste generated in Brazilian territory will be safely stored. One of the barriers that will compose the repository will be formed of natural materials such as soils and clays, the latter for having a high adsorption and cation exchange capacities and swelling potential. The purpose of the article is to show the research carried out in Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) with natural materials aiming their use in natural barriers. Four materials were characterized: CDTN soil, this soil with bentonite, expanded vermiculite and bentonite, using the clay characterization protocol. Primary mineralogical, physical and chemical analyzes were performed, such as X-ray diffraction, scanning electron microscopy, particle size distribution, specific surface area and cation exchange capacity. The results showed that these clays are potentially candidates for composing CENTENA's natural barriers.

Keywords: **bentonite, soil, expanded vermiculite, repository, radioactive waste.**

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1. INTRODUCTION

The use of nuclear technology is growing in Brazil. It applies to the optimization of industrial processes, in the medical field when, for example, important tests are performed that are essential for assertive diagnostics, in the generation of more energy with less environmental impact, when compared to traditional hydroelectric and thermoelectric plants, among other areas and performances.

Currently, Brazil has the seventh biggest uranium reserve in the world. It is able to carry out the entire nuclear fuel cycle and through Brazilian Multipurpose Reactor will become self-sufficient in the production of radioisotopes and radioactive sources. The Brazilian uranium production capacity will assure the supply of the current and future power plants. In addition, if it will be interesting to the Brazilian Government in the long term, this capacity enables it to take part of the international market [1].

The 2050 Brazil National Energy Plan has three main strategic objectives for the nuclear sector. The first one is to consolidate the country as an important nuclear fuel manufacture; the second is to participate competitively in the supply of electricity. The third one is to develop and ensure know-how of all steps for the nuclear power plant commissioning, including its equipment manufacturing and the production of fuel elements.

This technology generates radioactive waste, defined as any material resulting from human activities which contains amounts of radionuclides exceeding the exemption limits established by the Comissão Nacional de Energia Nuclear (CNEN, Brazil). It must be treated before being released into the environment or stored in appropriate facilities. Then, to ensure the absence of environmental impacts, to preserve the health of human beings and also to protect future generations, it is essential to manage this waste. The final step of this management is to permanently store the treated waste in the repository. The repository of Abadia de Goiás - GO, was built for the wastes generated from the radiological accident with cesium source occurred in Goiânia in 1987. In Brazil, the CENTENA will be the first national repository in Latin America, which implementation is coordinated by CNEN. This repository will receive all the low and intermediate level radioactive waste generated in the country. Therefore it will be near surface one, using multiple barriers, natural and engineering and each one capable of containing the release of radionuclides [2-4]. These natural barriers can be composed of clays and soils. The clays are largely studied for this purpose, especially the bentonite for being composed mainly of clay mineral from the montmorillonite group and having high capacity of the adsorption, high cation exchange capacity and swelling potential.

As the first national repository project, it must follow all stages of design and construction, including all studies of possible processes and materials to be used, as well as their characterization and selection methodology. The project uses the application of characterization methods for regional natural materials and contributes to the security of the repository barriers, ensuring the maintenance of the integrity of the environment and human beings, including future generations. In it, radioactive wastes generated in Brazilian territory will be safely and centrally stored.

The purpose of the article is to show the research performed with the clays for use in natural barriers, beginning with the creation of a characterization Protocol [5] using a sodium bentonite as reference material. Then it was applied to characterize an expanded vermiculite [6], a soil sample collected in the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) and a mixture of this soil with sodium bentonite [7].

For the characterization of these four materials were carried out the primary mineralogical, physical and chemical analyses, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size distribution (PSD), specific surface area (SSA) and cation exchange capacity (CEC). The results showed that these clays are potentially candidates for composing CENTENA's natural barriers.

2. MATERIALS AND METHODS

In this research a sodium bentonite (BN), expanded vermiculite (VM), soil (SL) and a soil/bentonite mixture (SBN) (70/30 by mass) were studied. The bentonite used in the mixture and the bentonite characterized in this research was the same, a Brazilian one. The soil/bentonite ratio of the mixture was arbitrarily defined, since the definition of an optimal value for this ratio will be established in a future time, for the CENTENA site. The objective was to analyze the influence of the addition of bentonite on the soil properties [7]. Studies of the mineralogical, physical and chemical properties of BN, VM, SL and SBN have been carried out to provide a database for CENTENA and optimize the choice of natural materials to be used as backfill and coverage layers in the surface repository.

The bentonite used was an activated sodium bentonite, named Brasgel™ Bentonite, produced and supplied by Bentonit União Nordeste Ltd., sited in Boa Vista, PB. The term “activated” means that this material was processed to substitute the calcium, predominantly present in the natural Brazilian bentonite, for sodium [8]. The vermiculite used was an expanded vermiculite produced and supplied by Vermiculita Isolantes Termo-Acústicos Ltd., sited in Belo Horizonte, MG. The expanded vermiculite has low thermal conductivity and high liquid retention capacity [9].

As the local, where the CENTENA will be built, was not selected yet, and due to the impossibility of studying the large variety of soils scattered throughout the Brazilian territory, it was decided to collect the soil sample in the CDTN site. This decision also took into account technical and logistic needs to sampling the material any time (Figure 1) [7].

Figure 1: *Sample collection locations in the CDTN.*
Source: Barroso, 2021.

After sampled, the soil was dried at room temperature and then it was physically disaggregated and sieved to 2 mm. Subsequently it was homogenized, it was made a longitudinal pile of this material and after it was separated in 1 kg fractions. For the preparation of the soil/bentonite mixture an additional step was made, after the disaggregation, the soil was mixed with the bentonite, and the samples of 1 kg were prepared as previously. This preparation was made to obtain the bulk samples (lab samples) [7].

The properties studied in this research were mineralogical composition and morphology (XRD and SEM), PSD, SSA and CEC. All characterization was conducted using bulk samples of BN, VM, SL and SBN. The exception was the PSD of the SL, in which the soil in natura was used [5-7].

2.1. Characterization techniques

Qualitative and quantitative analysis were carried out in studied materials in order to identify the main clay minerals. SL and SBN samples for mineralogical analysis were prepared following the procedure proposed by Albers et al. [10]. X-ray diffractograms were recorded on a Rigaku D|MAX Ultima Plus™ diffractometer equipped with CuKα radiation over 2θ scan range of 2-30°. The counting interval and step size were 60 s and 0.02°, respectively.

SEM provided the surface morphology of samples using the Carl Zeiss field-emission scanning electron microscope (FEGMEV™), Sigma VP model. An acceleration voltage of 40 kV was applied and it was used an Al-holder, which was laminated with a double-sided adhesive carbon tape. Very diminutive amounts of the powdered samples were dispensed onto the tape.

The PSD was determined with the mechanical method and performed in triplicate [11]. This grain size analysis was to determine the relative proportions of the different grain sizes that make up a given material mass.

The SSA was measured by nitrogen adsorption, multiple point technique, Nova-2200 Quantachrome™. The samples were outgassed and then maintained at a constant temperature of -196°C, while the addition of N_2 gas happened, it was adsorbed on the surface and pores of samples. The specific surface area of the samples was calculated using the equation developed by Brunauer-Emmett-Teller (BET), for N_2 adsorption data in the range of relative pressure values between 0.05 and 0.35 [12].

The CEC was determined with the methylene blue adsorption method [13]. This test consists of dispersing 2 g of each sample in 300 mL of deionized water under mechanical agitation, so that slurry is produced and adjusting the pH between 2.5 and 3.8 with sulfuric acid. Sequentially, methylene blue solution was added in 0.5 mL increments to the slurry, stirring for 1 to 2 min. Drops of this slurry are put in a filter paper. The appearance of each drop was observed until a clear halo around the blue drop emerged.

3. RESULTS AND DISCUSSION

3.1. Mineralogical characterization

The mineralogical composition and the diffractograms, which were determined by XRD of the four materials studied (BN, VM, SL, SBN) are showed in Table 1 and Figure 2, respectively.

Table 1: Mineralogical composition of the materials by X-ray diffraction (XRD).

Sample	**Clay minerals* X-ray laser diffraction****							
	(N)	**(Mo)**	**(Q)**	**(B)**	**(Mu)**	**(V)**	**(K)**	**(G)**
BN	VH	M	M	ND	ND	ND	ND	ND
VM	ND	ND	ND	VH	H	L	ND	ND
SL	ND	ND	M	ND	ND	ND	VH	ND
SJ/BN	ND	H	L	ND	ND	ND	M	H

*Nontronite (N) ; Montmorillonite (Mo) ; Quartz (Q) ; Biotite (B) ; Muscovite (Mu) ; Vermiculite (V) ; Kaolinite (K) ; Goethite (G).

**Semi-quantification of clay minerals based of X-ray diffraction analysis - Low (L) = <10%; Medium (M) = 10-30%; High (H) = 30-50%; Very High (VH) = 50-100%; Not Detected (ND).

The BN contains the larger concentrations (mass %) of nontronite and montmorillonite, while in other materials (VM and SL) these clay minerals were not detected. For the SBN material, the montmorillonite appeared in high concentration, as expected, due to the addition of bentonite to the soil. For SL, the predominant clay minerals were kaolinite and quartz.

The VM material is predominantly composed by biotite and muscovite, both clay minerals of the mica group. This occurred because the VM is an expanded material, i.e., has different characteristics from those observed in vermiculites in natura, including changes in the mineralogical composition.

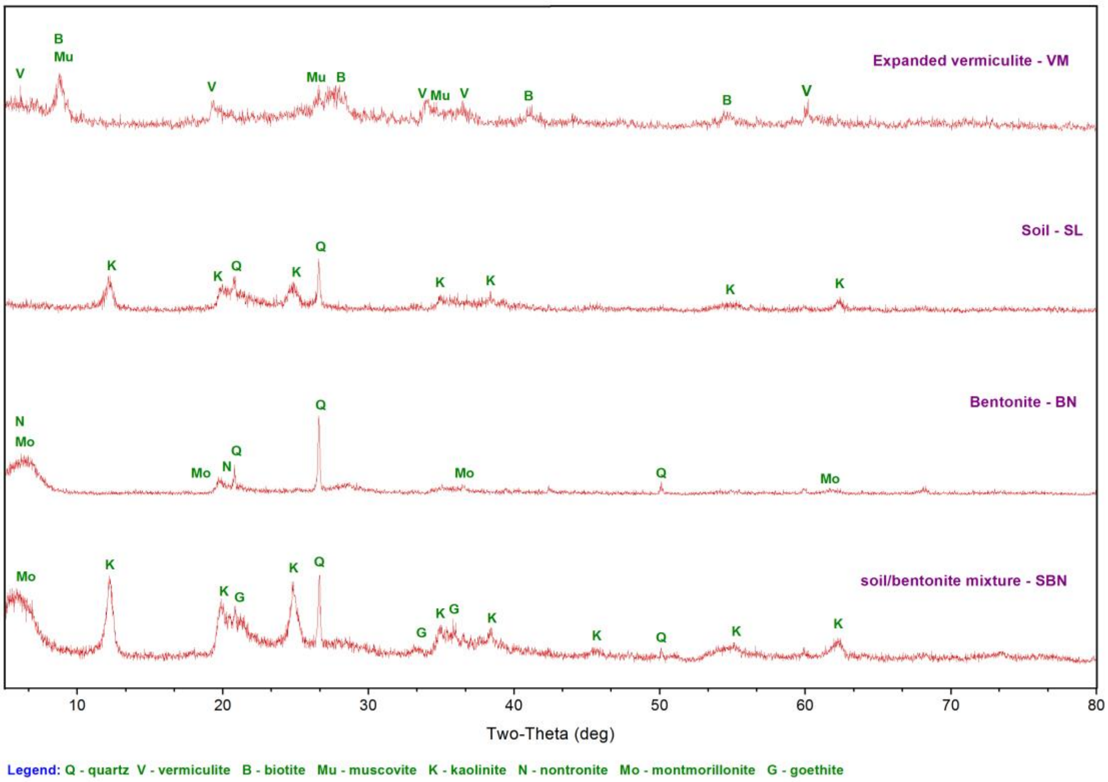

Figure 2: *Diffractograms of the materials: (a) VM; (b) SL; (c) BN; (d) SBN.*

SEM was used as a complementary analysis for the mineralogical characterization and it is presented in Figure 3. In different scales (Figure 3a and 3b), the structure of SL material is presented. This structure is grouped and stacked in pilasters and crystals organized in booklet, i.e., in lamellar form. These individual crystals are presented as flakes of pseudo-hexagonal morphology, most of them with defined corners and angles close to 90 and 120º, characteristic of the kaolinite structure [14].

According to the SEM for SBN material (Figure 3c and 3d) its structure presented crystals of heterogeneous aspect, irregular distribution and with different sizes. In addition, it presented a lamellar structure that is a characteristic of the montmorillonite. The high adsorption capacity of this material can be observed through the tactoids, formed by the stacking of these lamellar particles. Furthermore, the VM and BN materials also showed lamellar morphology (Figure 3e and 3f, respectively).

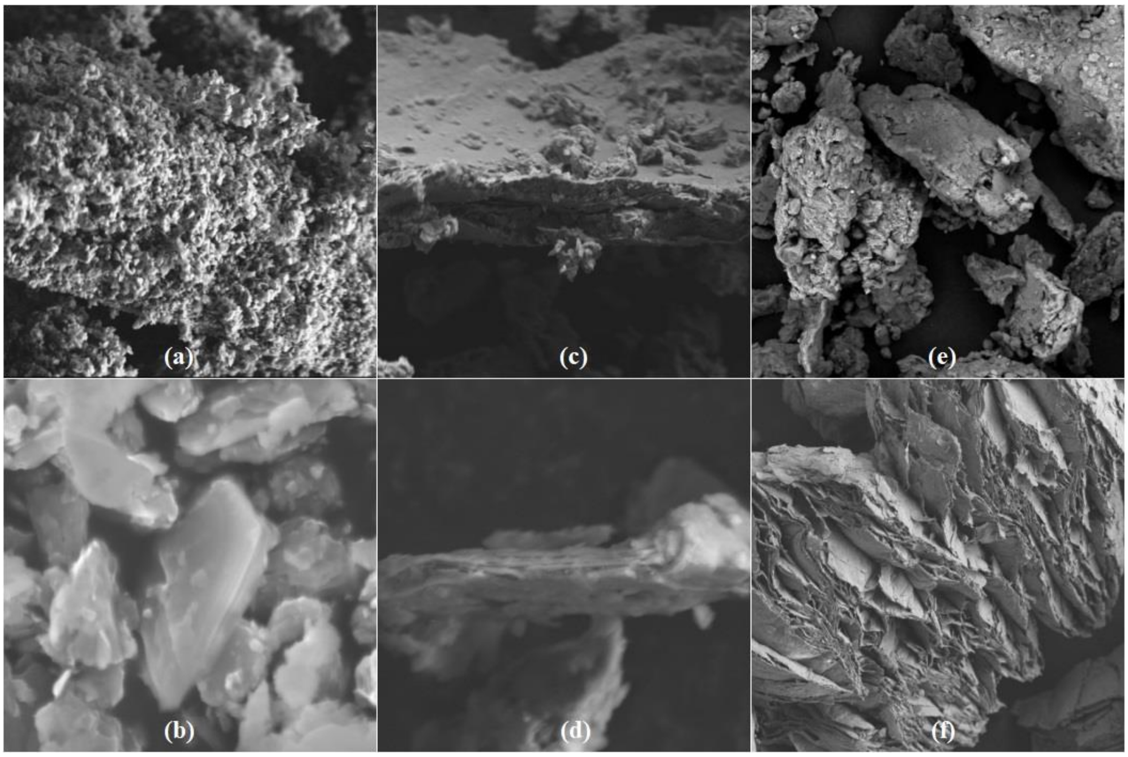

Figure 3: *SEM images of the materials: (a, b) SL; (c, d) SBN; (e) BN and (f) VM.*

3.2. Physical and chemical characterization

In Table 2, the results of the PSD, CEC and SSA of BN, VM, SL and SBN materials are presented.

In general, in the granulometric test studied, with the exception of the BN, the materials presented the sand fraction as predominant. The granulometric scale was established in ABNT [11]. For the BN material, from the PSD all the grains fit in the silt + clay fraction. The BN is predominantly constituted of the clay minerals, which are normally present in the clay fraction of clay materials (<0.06 mm). For vermiculite, between 0.500 and 0.297 mm is the greatest percentage passed, which indicates a predominance of grains in the sand fraction, according to the scale established in ABNT [11]. Nevertheless, this test associated with the results of X-ray diffraction confirmed the presence of vermiculite, it is a clay material.

Table 2: Physical and chemical characterization of materials.

Sample	**Physical characteristics**						**Chemical characteristic**
	Particle size analysis					**Specific surface area**	**Cationic exchange capacity**
	Silt + clay	**Fine sand**	**Medium sand**	**Coarse sand**	**Boulder**		
	%					**$m^2.g^{-1}$**	**$mmol.Kg^{-1}$**
BN	100	0	0	0	0	80.49	816.00
VM	11.19	20.98	48.22	19.22	0.39	6.22	ND
SL	12.02	11.85	25.34	21.12	29.67	11.56	14.89
SBN	44.85	10.78	25.98	18.39	0	26.19	228.00

As expected, the percentage of silt + clay in the SBN material increased due to the addition of bentonite compared with the SL material, since the BN material fit in the clay + silt fraction, the 30% of bentonite added to the soil, resulted in this effect.

The high specific surface area of clays enables high capacity for adsorption of water and other substances, since the pores between the particles are smaller, they are excellent materials for water retention, and they present a less drainage capacity [15]. The SSA of the BN material was 80.49 $m^2.g^{-1}$. This value implies that the material has a high adsorption capacity. Acevedo et al. [16] presented values of 128.5±0.3 $m^2.g^{-1}$ and 112.6±0.4 $m^2.g^{-1}$ of SSA for two bentonite samples, being very near to the value found for the BN. As the mass %-montmorillonite was not specified, it is not possible for further discussion. The larger is the specific surface area, the greater the amount of water that can be fixed to the available surface. Expanded vermiculite had the lowest value, 6.22 $m^2.g^{-1}$, lower than presented in the literature, 100 and 150 $m^2.g^{-1}$, for vermiculite in natura [17].

Comparing the results of SSA of SL and SBN material, an increase in the value was observed. Those results were expected, because bentonite has high values for this property, and it increased this value from 11.56 $m^2.g^{-1}$ to 26.19 $m^2.g^{-1}$. The results were in agreement with the PSD, as the sample with the highest SSA, SBN material, also presented the highest percentage of silt + clay fraction.

The SSA results showed a direct relationship with the CEC of the studied materials. The material with the largest specific surface area also presented the highest CEC. The CEC of the BN material was 816±9 mmol.kg^{-1}. According to Aguiar et al. [18] the CEC of the montmorillonite is between 800-2000 mmol.kg^{-1} of the clay. In addition, study using a bentonite with 46-49 mass %-montmorillonite presented 780 mmol.kg^{-1} of the CEC [19]. Both authors determined the CEC by extraction of NH_4^+. The BN has larger montmorillonite concentrations (mass %) in its composition (Table 1), so the value for CEC was near to that presented in the literature.

Comparing the results of CEC of SL and SBN material, it was observed an increase from 14.89 mmol.kg^{-1} to 228 mmol.kg^{-1}. Those results were expected because bentonite has high value for this property. It was not possible to determine the CEC of VM by the methylene blue method, because the methylene blue cation is not adsorbed in the interlayer vermiculite structure.

4. CONCLUSION

The results indicate that the materials under investigation (BN and VM) are potentially candidates for composing the backfill and coverage layers in the CENTENA. Other possible applications are the mixture of these materials with other adsorbents available at the CENTENA site, such as the SBN. The addition of bentonite to the soil was efficient to improve the required physical and chemical properties, for engineered barriers systems of repositories.

The materials presented different mineral compositions. The montmorillonite was detected originally on the BN and SBN material, and this clay mineral presents positive characteristics, which are very important for the repository, although this is not enough to classify the material as a candidate for use in natural barriers. Similar results for the CEC and SSA were found in the literature, confirming that BN material is an excellent choice for this purpose.

In the same way the results of VM indicated its use as a natural barrier for the repository. It is suggested for future work to carry out studies on the mixture of soil with vermiculite and also the determination of CEC.

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