CHARACTERIZATION OF BENTONITE, VERMICULITE AND SOIL AS POTENTIAL MATERIALS TO COMPOSE THE NATURAL BARRIERS IN A NEAR-SURFACE REPOSITORY

SANTOS, Daisy M. M.[1], BARROSO, Samara A.[2],
TEIXEIRA, Thaís B.[3], and TELLO, Clédola C. O. de[4]

[1]*marymarchezini@gmail.com,*
[2]*samara.albarroso@gmail.com,*
[3]*teixeira.thaisb@gmail.com,*
[4]*tellocc@cdtn.br,*
[1,2,3,4]*Centro de Desenvolvimento da Tecnologia Nuclear –*
Comissão Nacional de Energia Nuclear – CDTN/CNEN, Av.
Presidente Antônio Carlos, 6627, Belo Horizonte, Brazil, 31270-
901

1. Introduction

The Brazil 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 [1]. This technology generates radioactive waste and it must be treated before being released into the environment or stored in appropriate facilities. The final step of the waste management is to permanently store this treated wastes in the repository. 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, 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.

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 CDTN and a mixture of this soil with sodium bentonite [7]. The results showed that these clays are potentially candidates for composing CENTENA's natural barriers.

2. Methodology

In this research a Brazilian sodium bentonite (BN), expanded vermiculite (VM), soil (SL) and a soil/bentonite mixture (SBN) (70/30 by mass) were studied. The objective was to analyze the influence of the addition of bentonite on the soil properties [7]. 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 [7]. SL and SBN samples for mineralogical analysis were prepared following the procedure proposed by Albers et al. [8].

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).

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. The PSD was determined with the mechanical method and performed in triplicate [9]. The SSA was measured by nitrogen adsorption, multiple point technique, Nova-2200 Quantachrome™ in the range of relative pressure values between 0.05 and 0.35 [10]. The CEC was determined with the methylene blue adsorption method [11].

3. Results and Discussion

The mineralogical composition (Table I) and the diffractograms (Fig. 2), of the four materials studied (BN, VM, SL, SBN), were determined by XRD.

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

Sample	Clay minerals*		Quartz (Q)	Biotite (B)	Muscovite (Mu)	Vermiculite (V)	Kaolinite (K)	Goethite (G)
	Nontronite (N)	Montmorillonite (Mo)						
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

*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 nontronita 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.

SEM was used as a complementary analysis for the mineralogical characterization and it is presented in Figure 3. In different scales (Fig. 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 [12].

According to the SEM for SBN material (Fig. 3 c and d) its structure presented crystals of heterogeneous aspect, irregular distribution and of 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 (Fig. 3, e and f, respectively).
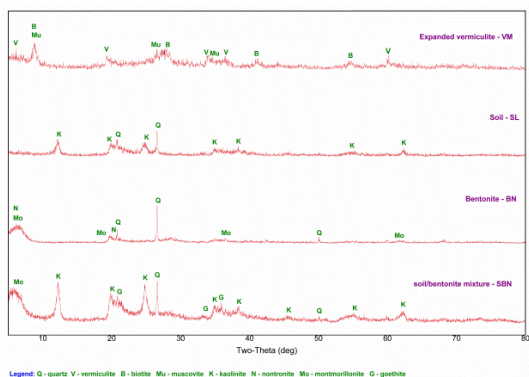

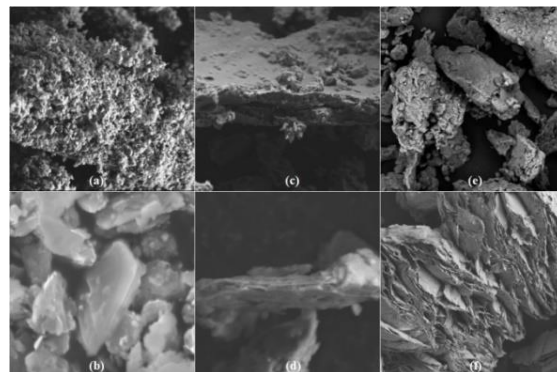Figure 2: Diffractograms of the materials: (a) VM; (b) SL; (c) BN; (d) SBN

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

In Table II, 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. Nevertheless, this test associated with the results of X-ray diffraction confirmed the presence of vermiculite, it is a clay material. 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.

Table II: Physical and chemical characterization of materials

Sample	Physical characteristics					Specific surface area	Chemical characteristic
	Particle size analysis						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

The high specific surface area of clays enable 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 [13]. 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. [14] 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 [15]. 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. [16] 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 [17]. 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. Conclusions

The clays under investigation 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.

Acknowledgements

References

[1] "PNE 2050: Potencial dos Recursos Energéticos no Horizonte 2050." https://www.epe.gov.br/sites-pt/publicacoes-dados-abertos/publicacoes/PublicacoesArquivos/publicacao-227/topico-416/NT04%20PR_RecursosEnergeticos%202050.pdf (2018).

[2] "CNEN-NN-8.01: Gerência de Rejeitos Radioativos de baixo e médio níveis de radiação." https://www.gov.br/cnen/pt-br/acesso-rapido/normas/grupo-8/grupo-8-rejeitos-radioativos (2014).

[3] "CNEN-NN-8.02: Licenciamento de depósitos de rejeitos radioativos de baixo e médio níveis de radiação."https://www.gov.br/cnen/pt-br/acesso-rapido/normas/grupo-8/grupo-8-rejeitos-radioativos(2014).

[4] "IAEA-TECDOC-1817: Selection of technical solutions for the management of radioactive waste." https://www-pub.iaea.org/MTCD/Publications/PDF/TE-1817_web.pdf (2017).

[5] SANTOS D. M. M., TELLO C. C. O. "Protocol for characterization of clay as a backfill and coverage layers for near surface repository", *Brazilian Journal of Radiation Sciences*, vol. 7, pp. 1–14 (2019).

[6] TEIXEIRA T. B., TELLO C. C. O. "Characterization of expanded vermiculite to use as natural barrier in repository", *Brazilian Journal of Radiation Sciences*, vol. 9, pp. 1–11 (2021).

[7] BARROSO S. A., TELLO C. C. O. "Study of a mixture of soil and brazilian bentonite using a protocol for clay characterization for near-surface radioactive waste repository", *Brazilian Journal of Radiation Sciences*, vol. 9, pp. 1–13 (2021).

[8] ALBERS A. P. F., MELCHIADES F. G., MACHADO R., BALDO J. B., BOSCHI A. O. "A simple method for the characterization of clay minerals by X-ray diffraction", *Cerâmica*, vol. 48, pp. 34–37 (2002).

[9] ABNT – Associação Brasileira de Normas Técnicas. *Soil: Grain size analysis - NBR 7181*. ABNT, Rio de Janeiro, Brazil (2016).

[10] GREGG, S., SING, K. S. W. *Adsorption, Surface Area and Porosity*. Academic Press, London, England (1982).

[11] CDTN – Centro de Desenvolvimento da Tecnologia Nuclear. *Determinação da capacidade de troca catiônica (CTC) de argilas utilizando o método da adsorção de adsorção de azul de metileno (AAM)*. CDTN, Belo Horizonte, Brazil (2012).

[12] MCBRIDE, M. B. *Environmental chemistry of soils*, Oxford University Press, New York, EUA (2014).

[13] BRADY, N. C., WEIL, R. R. *Elementos da natureza e propriedades dos solos*, Bookman, Porto Alegre, Brazil (2012).

[14] ACEVEDO N. I. A., ROCHA M. C. G., BERTOLINO L. C. "Mineralogical characterization of natural clays from Brazilian Southeast region for industrial applications", *Cerâmica*, vol. 63, pp. 253–262 (2017).

[15] LUZ, A. B., LINS F. A. *Rochas e minerais Industriais: usos e especificações*, CETEM/MCT, Rio de Janeiro, Brazil (2008).

[16] AGUIAR M. R. M. P., NOVAES A. C., GUARINO A. W. S. "Removal of heavy metals from wastewaters by aluminosilicate", *Química Nova*, vol. 25, pp.1145–1154 (2002).

[17] SUZUKI S., SAZARASHI M., AKIMOTO T., HAGINUMA M., SUZUKI K. "A study of the mineralogical alteration of bentonite in saline water", *Applied Clay Science*, vol. 41, pp. 190–198 (2008).