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Characterization of calcium bentonite to use as a natural barrier in a surface repository

Teixeira[1]T. B. and de Tello[2] C. C. O.

[1,2] *Centro de Desenvolvimento da Tecnologia Nuclear (CDTN / CNEN – MG)/ Av. Presidente Antônio Carlos 6627*
Campus UFMG - Pampulha
31270-901- Belo Horizonte, MG, Brazil
[1].*thaisb@gmail.com;* [2] *tellocc@cdtn.br*

ABSTRACT

The wide use of nuclear technology in Brazil generates radioactive waste that, in general, have low and medium levels of radiation. This requires efficient management to keep the environment, humans and future generations safe. CNEN coordinates the CENTENA project which will consist of the implementation of the first national repository that will be a definitive solution for the storage of radioactive waste. It will be surface and multiple barriers, and bentonite will possibly compose the natural barrier, since it has good sorption capacity for several radionuclides and low hydraulic conductivity. This paper describes the practical work that followed the clay characterization protocol for use in a surface repository with calcium bentonite and proposes a future study to characterize the mixture of soil and bentonite with the addition of 8% and 15% clay in the soil in order to investigate what will be the best feasible combination to maintain the safety and economic viability of the project. XRD results confirmed the presence of montmorillonite, particle size analysis identified that 40% of the measured sample had an average particle size between 8.0 and 10.0 µm, the global average bentonite moisture was 14%, the high specific surface area value 82.741 m^2/g, the particle density value was 2.5287 ± 0.0057 g/cm^3 and the result of the cation exchange capacity by the methylene blue adsorption method was 750 ± 18.71 mmol.kg-1. All these results indicated that calcium bentonite is a good natural material to be used in the Brazilian repository.

Keywords: **CENTENA, surface repository, natural barrier, calcium bentonite, characterization.**

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1. INTRODUCTION

The nuclear technology used in Brazil in different areas generates radioactive waste that is mainly classified as low and intermediate level (class 2.1), which requires efficient management in order to maintain the safety of the environment, human beings and future generations [1]. There are Brazilian standards to establish how to properly manage and dispose of this waste, especially the standards CNEN NN 8.01[2] and CNEN NN 8.02 [3].

The CNEN (Brazilian National Nuclear Energy Commission) is responsible for implementing the repository for class 2.1 waste. The Nuclear and Environmental Technological Center - CENTENA- will be implemented to receive and dispose of these waste generated in the country. This disposal will be close to the surface using multi-barriers, considering that one is self-sufficient to prevent and delay the release of radionuclides [4]

Regarding to the natural barriers, the International Atomic Energy Agency (IAEA) reports that clays have good applicability in base, fill and cover layers for repositories [5]. Among the clays, bentonite was chosen for this research, for being internationally studied as a natural barrier to different deposits, for its good sorption capacity for several radionuclides and for its low hydraulic conductivity. At CDTN (Nuclear Technology Development Center), bentonite has already been studied as a reference to establish a clay characterization protocol [6], in order to use these materials as a natural barrier at CENTENA.

Generally, clays are incorporated into the soil of the repository site to improve the sorption and retention of radionuclides present in the radioactive waste. Since the CENTENA site is in the final selection phase, there were no samples from this site. Then mixtures of bentonite and soil was studied, using the CDTN site soil. Initially Barroso [7] performed the characterization of the soil, and after it was studied the mixture containing this soil with 30% sodium bentonite, in order to determine the influence of this mineral clay on the properties: particle size distribution, moisture content, specific surface, particle density, exchange capacity cationic, compaction curve and hydraulic conductivity. These evaluated properties of the soil were improved with the bentonite addition.

Based on these results, another research was carried out to characterize mineralogical and physicochemically a calcium bentonite. This paper summarizes the results of this study, and presents a proposition of a work to study other different addition of bentonite to the soil, in order to optimize economically and operational feasibility the use of bentonite in the natural barrier system of the repository.

2. MATERIALS AND METHODS

The methodology used for both studies, with calcium bentonite and with different mixtures of soil and sodium bentonite, follows the protocol for characterization of clays, which was also efficient for soils and mixtures [6,7]. Then, mineralogical analyzes and physicochemical characterization were carried out with calcium bentonite. The same methodology will be used to study another two mixtures of soil, with 8% and 15% of sodium bentonite, respectively.

2.1 X-ray diffraction (XRD)

The mineralogical analysis was performed using the X-Ray Diffraction (XRD) method. It aimed at to identify the phyllosilicates and iron oxides and to determine the type of clay, using the Rigaku D/Max diffractometer at SETEM X-ray Diffraction Laboratory - Mineral Technology Service/CDTN.

2.2 Particle size analysis

The analysis was performed at LABCON/CDTN with Cilas® equipment with its own software. It has 3 lasers that measure the diameter of particles from specific wavelengths, in a humid environment. The equipment starts the analysis with a container of water to deagglomerate the particles and simultaneously there is the vibration from the ultrasound. There are also peristaltic pumps that allow the circulation of particles in the system. Finally, the lasers focus on the quartz window, through which the material passes and the wavelength reading is fulfilled. Figure 1 shows the software and equipment.

(a) (b) (c)

Figure 1. *Cilas® granulometric analysis (a) software command (b) opened equipment (c) closed equipment.*
Source: author

2.3 Moisture content

To determine the moisture content, the Technical Routine 0417 [8] was followed, with three aliquots (AM1, AM2 and AM3) and it was performed in triplicate (nine samples). Approximately 20 g of calcium bentonite were placed in nine porcelain crucibles that were placed in an oven at a constant temperature of (110 ± 5) °C for 16 hours. After that, it was put on the desiccator for one hour, and then it was weighted. This step was repeated twice until there was no variation in the mass. Then, if the mass remained constant, it was concluded that all the water had evaporated. After the tests, the moisture content was calculated in percentage.

2.4 Determination of specific surface and particle density

To determine the specific surface of calcium bentonite, the BET method, technique multipoint, Nova-2200 Quantachrome® equipment at LABCON/SENAN, was used. Samples containing 2 g of degassed clay minerals remained inside the equipment for 2 h at 100 ºC, so that their surfaces were free of volatile substances. The samples were kept at a temperature of -196 ºC while N_2 gas was added, in order to be absorbed on the surface and pores of the sample.

The experiment to determine the density of particles was carried out with the Ultrapycnometer Quantachrome®, Multipycnometer model, at LABCON/SENAN/CDTN. The sample was previously dried in an oven at 100 °C, after that it was cooled in a desiccator and then it was placed in the equipment, which makes sequential readings until in three consecutive times the error is less than 0.005. In the calcium bentonite tests, 20 readings were performed.

2.5 Cation exchange capacity (CEC)

The experiment to determine the cation exchange capacity (CEC) was performed in triplicate according to the method of methylene blue adsorption, described in NI-SEGRE-01 [9]. Exactly 2.0 g of the sample were dispersed in a beaker with 300 ml of deionized water under mechanical agitation. This addition was done slowly, in order to avoid formation of granules, resulting in a mud. The pH was adjusted to the range of 2.5 – 3.8 with sulfuric acid (H_2SO_4; 0.1 N) and this mixture was homogenized under stirring for ten minutes. Then increments of 1 ml of methylene blue are added to this mixture in intervals of one-minute. After each addition of methylene blue, a drop of the slurry was placed in a qualitative filter paper. The end of this test is when the image formed by the drop on the paper presents a blue halo. It means that there is an excess of the ions in the solution, called turning point.

3. RESULTS AND DISCUSSION

The results of the characterization of calcium bentonite are presented as follow.

3.1 X-ray diffraction analysis (XRD)

In Figure 2, the diffractogram shows that the sample presents 66.4% nontronite, 16.5% quartz and 8.1% montmorillonite, and 9% of amorphous material. Nontronite and montmorillonite present intense and very closes peaks, so from this analyses this result was not conclusive. As it is bentonite, the presence of montmorillonite was expected and nontronite also belongs to this group of clays. The well-defined peak of quartz occurs because it has a higher degree of crystallinity in relation to the other minerals present in the sample.

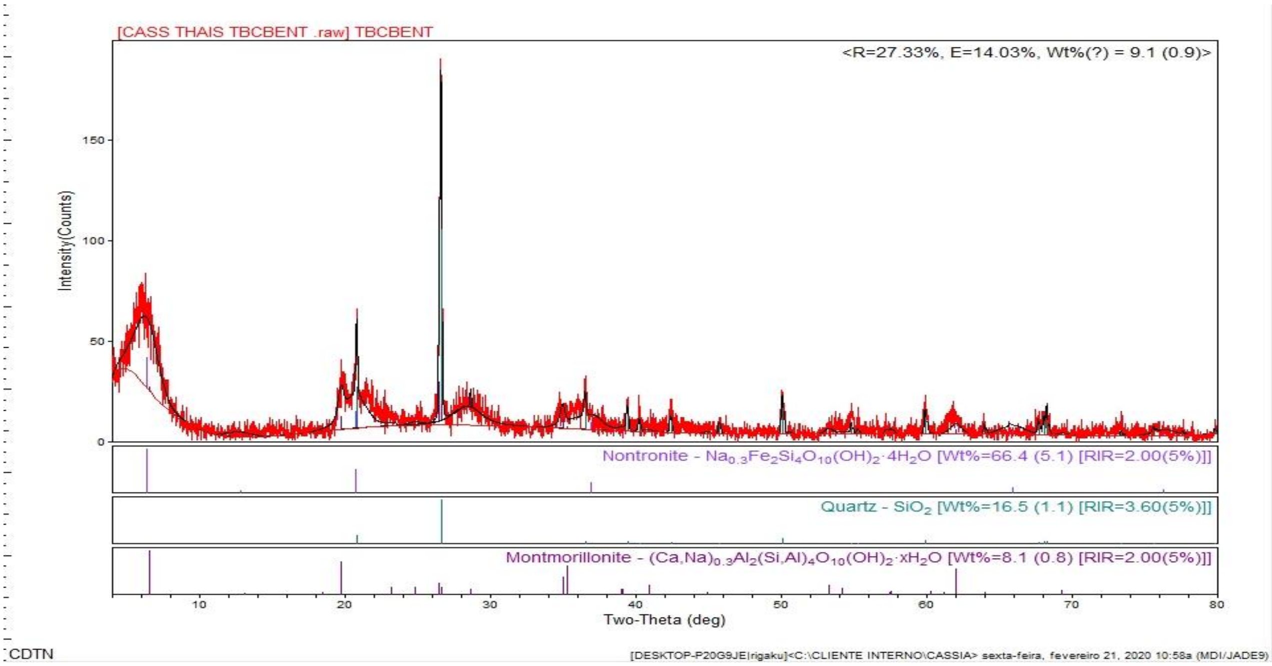

Figure 2: *Diffractogram of Ca-bentonite.*
Source: author

3.2 Particle size analysis

The results of the laser difctometric-Cilas- with the given diameters were shown in Table 1. It was identified that 40% of the measured sample had an average particle size between 8.0 and 10.0 µm, as shown in the Figure 3. According to the limits of soil fractions by granulometry defined by ABNT [10] this is the clay fraction, which was expected, since bentonite is predominantly composed of clay minerals.

Table 1: Diameter percentages and the average diameter

Diameter	**Result**
Diameter at 10%	2.26 µm
Diameter at 50%	8.47 µm
Diameter at 90%	19.09 µm

Average diameter	9.75 µm

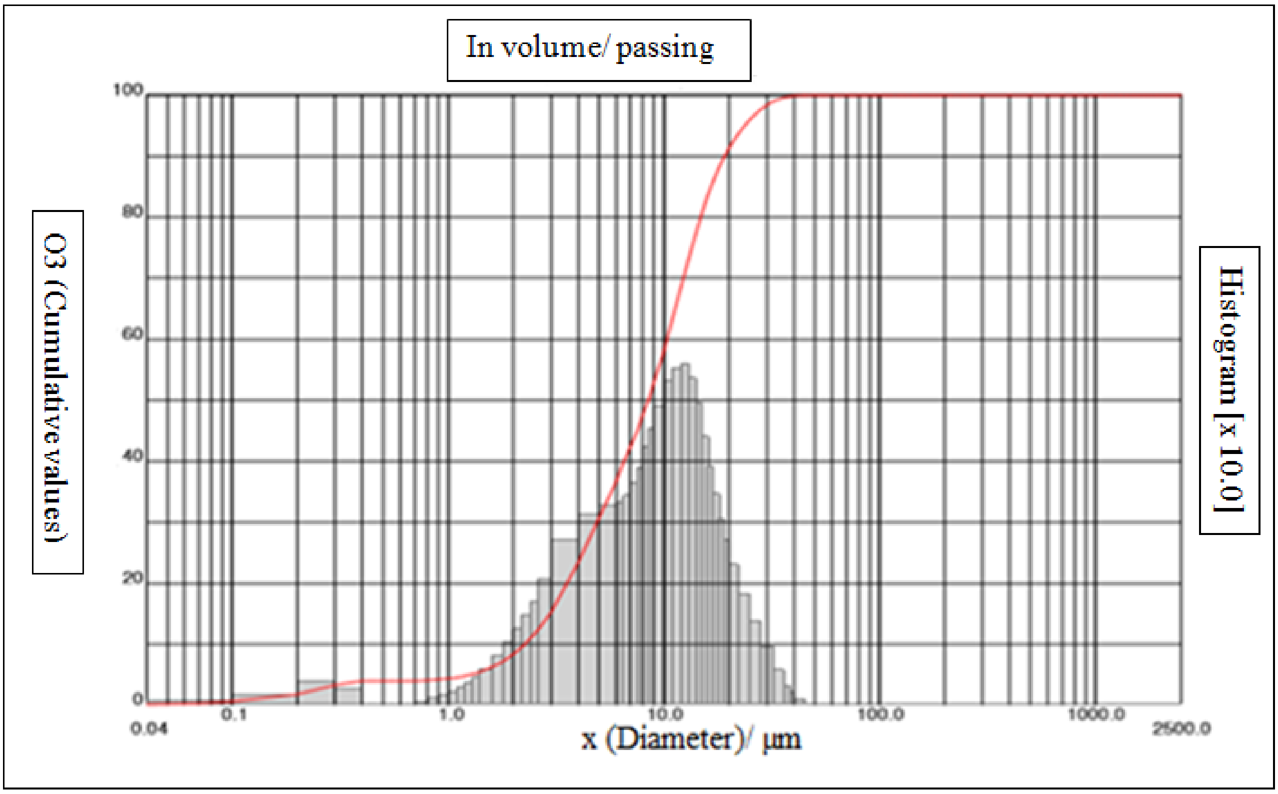

Figure 3: *Particle size analysis of bentonite by laser diffraction.*
Source: author

3.3 Moisture content

Equation 1 was used to calculate the individual moisture content (A), being M_{rau} the mass of the container with the wet sample; M_{ras} the mass of the container with the dry sample, and M_r the mass of the empty container.

$$A = \left[\frac{M_{rau} - M_{ras}}{M_{ras} - M_r}\right] x\ 100 \quad (1)$$

The global average of bentonite moisture was 14.0%, slightly higher than the protocol specification range (12.7% to 13.9%).

3.4 Determination of specific surface and particle density

The results of specific surface and particle density determination are presented in Table 2. The high value of the specific surface area confirms the great adsorption capacity of calcium bentonite, since the interaction processes directly depend on the specific surface of the sorbent material.

The value for the particle density, 2.5287 g/cm, is close to the one obtained by Barroso (2.6025 $g.cm^3$) [7].

Table 2: Specific surface and particle density results.

Test	Result
Specific surface (m^2/g)	82.741± 0.005
Particle density (g/cm^3)	2.5287 ± 0.0057

3.5 Cationic exchange capacity (CEC)

Fig. 4 shows the appearance of the droplet during the test for CEC determination. The drop identified as 104 is the end point, and the data of this point were used to calculate the CEC. For this calculation, in $mmol.kg^{-1}$, was used the Eq. 2, in which C_{AM} is the concentration of methylene blue, in mol. L^{-1}, V_{AM} is the spent volume of methylene blue, in L, and m_a is the dry mass of the sample, in kg. The result was 750 ± 18 $mmol.kg^{-1}$, within the expected range, since the clay mineral montmorillonite, which composes bentonite, has a CEC between 700 and 1,200 $mmol.kg^{-1}$[11].

$$CEC = C_{AM} \times V_{AM} \times \left(\frac{1000}{ma}\right) \tag{2}$$

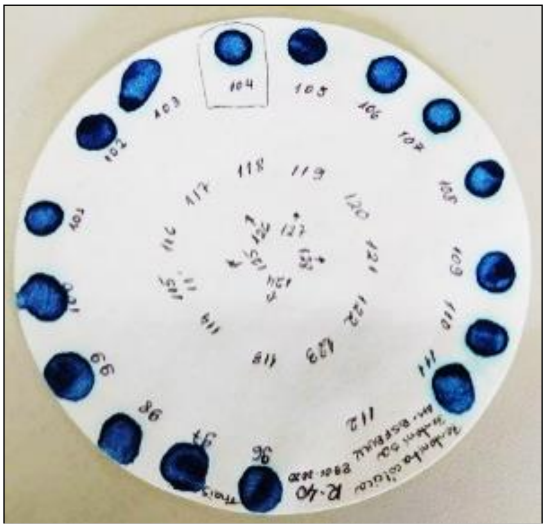

Figure 4: *Droplet appearance in the methylene blue adsorption process for CEC determination.*
Source: author

4. CONCLUSIONS

The calcium bentonite has good properties as natural barrier for the radioactive waste repository, mainly the particle size, high specific surface area and high cation exchange capacity.

The analyses demonstrated that this bentonite sample is predominantly composed of clay minerals. The high values of the specific surface area and the cationic exchange capacity evidence the potential of this material to be used in the repository.

The techniques and the tests developed will be used in the future work with mixtures of soil and clays to determine the optimum ratio to be used in CENTENA.

It is presented the results obtained in a preliminary study with calcium bentonite. As secondary objective of this study was also to verify the applicability of the protocol of clay characterization developed at CDTN.

In order to continue this research, it was started a project, which objectives are to evaluate and compare the efficiency of the different proportions of bentonite and soil (0 %, 8 %, 15 % and 30 %) as natural barriers, sustaining the viability technical and economical, always assuring the best performance for the repository.

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