Research paper

Comparison of two Algerian bentonites: Physico-chemical and retention capacity study

Fahd Arbaoui [a,b,*], Mohamed Nadir Boucherit [b]

[a] University Saad Dahlab of Blida, Street of Soumaa, BO 270, 9000 Blida, Algeria
[b] Nuclear Research Center of Birine, BO180, 17200 Ain Oussera, Djelfa, Algeria

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ABSTRACT

This paper presents the results of investigations on two Algerian bentonites (BentMag and BentMos), which may be considered for possible use in high level nuclear waste storage. The study concerns structural aspects and the chemical composition of the two bentonites (Bents). The effect of Na, Ca and K enrichment on cationic exchange capacity (CEC), specific surface area (SSA), dehydration and cation bonding selectivity has been examined. Results show that the BentMag contains more montmorillonite (Mt) and fewer impurities than BentMos. Ca and K treatments confer higher CEC and SSA to BentMag compared to BentMos. However, with Na treatment the two materials have similar CEC and SSA values. Nevertheless these values are higher compared to Ca and K treatments.

Thermodynamic investigation shows that the dehydration energy is more important with Ca-treated bentonites than Na and K-treated one. Unlike BentMos, BentMag possesses the ability to retain water beyond 200 °C. The results of hydration kinetics studies show that water absorption is faster with Ca treatment, whereas the Na treatment allows a higher retention capacity of water. Also, higher vertical compaction of Na treated BentMag reduces its ability to retain water compared to Na treated BentMos which has less Mt.

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1. Introduction

Deep geological repository for "high level nuclear waste" HLNW is based on a multi containment barrier principle in order both to ensure an integrity for several centuries (Rani and Sasidhar, 2011) and to store such materials for possible use that takes advantage of future nuclear technologies.

The engineered barrier system of nuclear waste has several configurations, materials and dimensions. Choices depend on the nature of the waste and on characteristics specific to the confinement site (Dohrmann et al., 2013; Wersin et al., 2007).

Natural swelling bentonite (Bent) is an important material in nuclear waste disposal. Its swelling property allows it to seal any void and crack. It restricts the intrusion of ground water and delays the eventual release of radionuclides (Lee et al., 2012; Zhang et al., 2012). Alternatively, the swelling Bent must also be sufficiently ductile to prevent critical high stress build-ups around canisters in the case of a seismic activity or cementation due to hydrothermal conditions (Pusch et al., 2010). Also, low permeability, low diffusion coefficient and the capacity to retain ions are other important and required properties (Anastácio et al., 2008).

Clay properties can be optimised through chemical treatment based on enrichment by a specific cation. In Sweden, Finland and Japan Na$^+$-Bent has been considered, and in France, Switzerland and Spain Ca^{++}-Bent has been considered (Lee et al., 2012).

All studies on clays for radioactive waste storage have been carried out on local materials: Opalinus clays for Switzerland, Kunigel V1 and Kunipia-F for Japan and MX-80 for France. Each clay mineral is characterised by specific properties. These properties are related to chemical and structural composition induced by geological processes specific to each region. The aim of this work is to study and compare some properties of Algerian Bents obtained from two sites. The study focuses on the chemical and phase composition, thermodynamic properties, the kinetics of hydration and cation bonding affinity.

2. Materials and methods

2.1. Samples

This study was carried out on two Bents obtained from the western part of Algeria and delivered by the National Company for Non-ferrous Mining Products ENOF. These materials are used in petroleum industry, cosmetic, construction materials and pharmaceutics.

The first sample designated as BentMos, was taken from the deposit of M'Zila in the Mostaganem region. A detailed description of the deposit was made by Grim and Guven (1978) who delimitate its origin to the Miocene age. They notice also that Bent beds are interlayed with ashy silts. The ash structure is preserved in the Bent indicating its origin.

* Corresponding author at: Nuclear Research Center of Birine, BO180, 17200 Ain Oussera, Djelfa, Algeria.

The other sample designated as BentMag was taken from the deposit of Hammam Boughrara in the Maghnia region. Its phase composition is reported in Table 1. This material was described by Sadran et al. (1955). The formation of the deposit was attributed to the hydrothermal alteration of rhyolite which occurred in a tertiary marine sequence. Their chemical analysis indicated a high magnesium amount and a low concentration of alkalies and silicon. This was related to the circulation of magnesium-bearing waters which added the magnesium and leached the alkalies and silicon.

2.2. Sample preparation

The study was made on raw and chemically-treated materials. The aim of the chemical treatment is to saturate the clay mineral by Na^+, K^+ or Ca^{2+} exchangeable cation. Fifty gram of raw Bent was mixed with 1 L of 1 N NaCl, KCl or $CaCl_2$ solution. The dispersion was shaken for 6 h and the supernatant was decanted; this operation was repeated three times. The supernatant was then removed and the operation was repeated three times also. The excess salt was eliminated by washing the sample repeatedly with deionised water. The $AgNO_3$-Cl test was then performed to check that all salt has been eliminated. At the end the chemically-treated Bent was dried and pulverized. The chemically-treated samples are referred to as Na^+-BentMos, K^+-BentMos … etc.

2.3. X-ray diffraction

X-ray diffraction (XRD) was performed on a Philips PW1710 Diffractometer. The measures were performed between 3° and 80° using a 0.04° step, 40 kV voltage and 30 mA current.

2.4. Chemical analysis

The chemical composition of the samples was obtained by fluorescence spectrometry [Philips Magix-Pro]. The results are reported in mass% oxides for major elements.

2.5. Differential scanning calorimetry

A Setaran System Evolution 1500 calorimeter was used for thermodynamic investigations. An amount of a sample with a weight of 5 to 20 mg was loaded in a capsule. Then the capsule was subjected to a 10 mL/min nitrogen gas flow in an oven. A temperature scan between 25 °C and 750 °C with a 15 °C/min increment was performed and the heat consumed by the sample was registered.

2.6. CEC & SSA spot method

Cation exchange capacity (CEC) and specific surface area (SSA) are important properties that determine the reactivity of clay minerals. The spot test procedure for determining the SSA and CEC of treated samples was made following the procedure described by Yukselen and Kaya (2008).

Table 1
Phase composition of the two bentonites.

Bentonites	BentMos	BentMag
Phases (mass %)		
Montmorillonite	45–50	65–70
Illite	8–10	1–2
Illite/smectite	Minor	Minor
Quartz	15–20	15–20
Calcite	2	1–2
K-feldspar	3–5	5–10

The SSA is obtained by the relation (Santamarina et al., 2002; Yukselen and Kaya, 2008):

$$SSA = \frac{1}{10} \cdot \frac{1}{M.V}(0.5X)A_V A_{MB} \tag{1}$$

where M is the molar weight, V is the solution volume, and X is the solution volume increments of MB added to the clay mineral dispersion, Av is Avogadro's number and A_{MB} is the area covered by one MB molecule (typically assumed to be 130 $Å^2$).

The CEC is obtained by the relation (Santamarina et al., 2002; Yukselen and Kaya, 2008):

$$CEC = \frac{100}{m_s}V_{cc}N_{MB} \tag{2}$$

where m_s is the weight in g of the specimen, V_{cc} the volume in mL of the added MB, and N_{mb} its normality in meq/mL.

2.7. Hydration kinetics

The study of water retention by raw and treated Bents is made on compacted and uncompacted samples. A maximum of 10 tonne on a circular surface of 1.3 cm diameter is applied to make samples with a thickness of 3 mm.

Samples are weighed and then exposed to 100% humidity in a closed vessel. Every 3 days the weight increase is recorded.

3. Results and discussion

3.1. The chemical composition

Chemical composition of untreated and treated materials is presented in Table 2. The SiO_2/Al_2O_3 ratio was added to show free silica and to confirm an indication of the montmorillonite (Mt) amount in the material. The analysis results are coherent with those of Table 1 where the Mt proportion is important in BentMag than in BentMos. A high concentration of K_2O for BentMos compared to BentMag confirms the relatively higher proportion of illite phase in BentMos as reported in Table 1.

The analysis shows also more MgO in BentMag than in BentMos. Magnesium can occupy inter-sheet positions and at the same time it can replace Al^{3+} in the octahedral sheets. The substitution of Al by Mg in the octahedral sheets affects the layer charge which increases the CEC of the clay mineral (Churchman et al., 2002).

BentMos contains more Ca than BentMag. Ca^{++} can be a compensating cation and its presence may be due also to calcite ($CaCO_3$) or dolomite $MgCa(CO_3)_2$. The Fe_2O_3 and TiO_2 amounts are low which must explain the white colour of the Bents as suggested by Christidis and Scott (1997).

3.2. XRD pattern

The phase composition shown in Table 1 was provided by the supplier. To certify this composition, the two materials were analysed by XRD (Fig. 1). The presence of Mt which is a major phase in the two materials is confirmed by a series of intense peaks, particularly for the BentMag sample. This confirms the difference in composition indicated by Table 1. Furthermore, the illite phase is present only on the diffraction spectra of BentMos. Regarding the other nonclay phases, peak intensities are similar for both materials. A more detailed comparison of these spectra indicates some slight shifts between diffraction peaks of the two materials which can be attributed to the presence of defects and interlayer cations (Ferrage et al., 2005).