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Preliminary results on the material composition of Ca-bentonite from the Kardzhali deposit, Southern Bulgaria

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Предварителни резултати за материалния състав на Са-бентонит от находище Кърджали, Южна България

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Abstract. This paper presents a preliminary investigation of Ca-bentonite from the Propast-Dobrovolets deposit, Kardzhali (Bulgaria) with respect to its potential application in engineered barrier systems (EBS) for radioactive waste isolation. Three forms (raw, powdered and a fraction of 2 μm) of non-activated bentonite were analysed using geochemical analytical techniques and geotechnical testing.

The results indicate that the studied materials are dominated by dioctahedral montmorillonite (72–85%), with minor quantities of cristobalite, oligoclase, and calcite. The chemical composition confirms their classification as Ca-bentonites, with a SiO_2/Al_2O_3 ratio of 3.59.

The powdered bentonite, characterized by a higher clay fraction (59%), exhibits enhanced phisycal properties, including a higher liquid limit (267%), specific surface area (92 m^2/g), and water absorption capacity (391%) compared to the raw material. SEM observations reveal a characteristic honeycomb microstructure with edge-to-face contacts, indicative of a well-developed swelling matrix.

The analyzed Ca-bentonite shows properties that meet the requirements for EBS applications. It contains a high amount of swelling clay minerals, which provide high plasticity, swelling and strong sealing ability. Therefore, it could be considered potentially suitable for use as both a buffer and a sealing material in an engineered barrier system (EBS) for radioactive waste disposal.

Keywords: Ca-bentonite, montmorillonite, Kardzhali deposit, engineered barrier systems, radioactive waste disposal.

Резюме. Статията представя предварителни резултати от изследване на Са-бентонит от находище Пропаст – Доброволец, Кърджали (България) във връзка с потенциалното му приложение за инженерни бариерни системи (EBS) при погребване на радиоактивни отпадъци.

Анализирани са три форми на материала: необработен, прахообразен (смлян) и отделена фракция <2 μm посредством подходящи минераложки, геохимични и геотехнически методи.

Изследваните бентонитови материали са изградени предимно от диоктаедричен монтморилонит (72–85%), с незначителни количества кристобалит, олигоклаз и калцит. Химичният им състав потвърждава класифицирането им като калциеви (Ca^{-}) бентонити със съотношение SiO_2/Al_2O_3 = 3,59.

Прахообразният бентонит се характеризира с по-високо съдържание на глинеста фракция (59%). Той има по-добри физични свойства в сравнение с необработения бентонит, включително по-висока граница на протичане (267%), по-голяма специфична повърхност (92 m^2/g) и по-висок капацитет на водопоглъщане (391%). Електронномикроскопските (SEM) наблюдения разкриват характерна микроструктура тип „пчелна пита“ с контакти тип „ръб–повърхност“, което е показателно за добре развита набъбваща глинеста структура.

Като цяло изследваният Са-бентонит притежава минераложки и геотехнически характеристики, които потенциално биха удовлетворили изискванията за приложение в инженерни бариерни системи. Високото съдържание на набъбващи глинести минерали осигурява висока пластичност, значителна способност за набъбване и ефективни уплътняващи свойства, което дава основание изследваният Са-бентонит да се разглежда като потенциално подходящ, както за буферен, така и за уплътняващ материал в система от инженерни бариери при погребване на радиоактивни отпадъци.

Ключови думи: Са-бентонит, монтморилонит, находище Кърджали, инженерни бариерни системи, радиоактивни отпадъци.

Introduction

Bentonite is a naturally occurring clay material well known by its specific physical and chemical properties, including high water absorption, strong swelling pressure, high cation exchange capacity, self-sealing ability, low hydraulic conductivity, and thermal stability (Komine, Ogata, 1996; Karnland et al., 2006; Pusch, 2006; Sellin, Leupin, 2013; Ohazuruike, Lee, 2023). Altogether, these properties significantly reduce the risk of radionuclide migration and groundwater contamination while ensuring reliable mechanical stability (Pusch, 1979; Madsen, 1998; Chapman, McCombie, 2003). Due to this distinctive combination of characteristics, bentonite is widely recognized as a critical part of engineered barrier systems (EBS) for the safe isolation of radioactive waste (Wilson et al., 2011; Delage, 2019; Li et al. 2023; Li et al., 2025).

Contemporary radioactive waste disposal strategies are based on the multi-barrier containment concept (Takahashi et al., 1987; Chapman, McCombie, 2003). Within this approach, bentonite plays a critical role by providing both hydraulic and mechanical functions, including limiting water ingress, retarding radionuclide transport, and maintaining sealing performance under coupled thermo-hydro-mechanical-chemical (THMC) conditions (Sellin, Leupin, 2013, Ogata et al., 2020, Gens et al., 2021).

As a result, numerous countries—including Belgium, Canada, China, Finland, France, Germany, Japan, Spain, Sweden, Switzerland, and the United Kingdom—have adopted bentonite as a main EBS material in their radioactive waste repository programs (Karnland et al., 2006; IAEA, 2009; SKB, 2010; Pedersen et al., 2017; Li et al., 2025).

The bentonite performance is strongly dependent on mineralogical composition, geochemical characteristics, and exchangeable cation type. In particular, Ca-bentonites often exhibit different swelling behaviour and hydraulic properties compared to Na-bentonites, which are more commonly used in repository designs. Consequently, despite extensive global research on bentonites, site-specific characterization of bentonite deposits is essential to assess their suitability for use as engineered barrier materials.

The Kardzhali region in Bulgaria (Fig. 1) hosts important bentonite deposits that have been mined for industrial use. The main deposit (Propast-Dobrovolets), which is still being actively mined, is located about 3 km east of the centre of the town of

Kardzhali, on the north bank of the Arda River, near the village of Sedlovina. The bentonite clays are developed on the expense of intermediate volcanic glass hosted by the second Oligocene intermediate volcanic phase (Atanassov, Goranov, 1963; 1988; Bozhinov et al., 1984). In general, the bentonite clay unit consists of two layers: a dark grey-blue layer and a lighter yellow-green layer. (Atanassov, Goranov, 1963; Atanassov et al., 1965). The first layer mainly contains sodium bentonite (Na-bentonite), while the second layer contains calcium bentonite (Ca-bentonite). Trace element composition of these clays is reported in Ivanova et al. (2020).



Fig. 1. Location of the Kardzhali deposit.

Most likely due to the higher amount of Ca^{2+}, which causes a greater degree of aggregation of clay particles in water, Ca-bentonite is considered potentially useful for the isolation of radioactive waste. However, its mineralogical, geochemical and physical characteristics have not been investigated in this context. This lack of data limits the assessment of its potential use in radioactive waste management.

The present study aims to address this data gap by providing a characterization of representative Ca-bentonite samples from the Kardzhali deposit. The research focuses on the mineralogical and geochemical composition, as well as selected physical (geotechnical) properties of Ca-bentonite The results are expected to contribute to the evaluation of Ca-bentonite, especially in a powder form, as potential barrier materials and to support its consideration in future repository concepts and safety assessments.

Materials and Methods

Three forms of non-activated Ca-bentonite, extracted from the Kardzhali bentonite deposit located in Southern Bulgaria (Fig. 1) were used in this research:

- Raw bentonite (RB) – a composite sample obtained on-site from several locations within a mound of bentonite material excavated from the yellow-green layer;
- Powder bentonite (PB) – a bentonite product named Ca-BEN Plus B which is produced by non-activated Ca-bentonite undergone only drying and grinding processes;
- Fraction less than 2 μm (FB) derived from powdered bentonite - to identify the chemical and mineralogical composition of the bentonite clay, the fraction less than 2 μm was separated from the powdered bentonite. The separation was performed by gravitational sedimentation of an aqueous suspension of PB, with the settling time calculated according to Stokes' law.

The major element oxides, crystalline mineral phases, and their morphology were characterized using the following analytical techniques:

- X-ray Fluorescence (XRF): major element oxide contents of the non-activated powdered bentonite (PB) were determined by means of Malvern Panalytical Epsilon 3XLE energy-dispersive X-ray fluorescence spectrometer (EDXRF) on fused $Li_2B_4O_7$ pellets made in Pt-Au (95% Pt and 5% Au) crucibles at 1050°C.
- Additionally, major oxide composition of raw (RB) and non-activated powdered bentonite (PB) was determined byinductively coupled plasma-optical emission spectrometry (ICP-OES).
- Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): Trace element contents of the PB sample were measured on fused pellets with a PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser system. Transient LA-ICP-MS data were reduced with SILLS software (ver. 1.1.0) using Si as the internal standard (Guillong et al., 2008).
- X-ray diffraction (XRD): Phase identification was performed with a D2 PHASER diffractometer (Cu Kα, λ = 1.54 Å) and a HUBER Guinier Image Plate Camera G670 (Cu Kα, λ = 1.54 Å). Diffraction patterns were analyzed by the Match! software package (versions 3.15 and 3.16; Crystal Impact, Germany).
- Scanning Electron Microscopy (SEM): Carbon-coated fractured surfaces of representative samples were examined with a JEOL 6390 scanning electron microscope. Imaging was performed with a focused electron beam at an accelerating voltage of 15 kV.

Material characterization was performed through a comprehensive series of geotechnical and physical tests, including:

- particle size analysis – hydrometer and sieve testing, in accordance with BDS EN ISO 17892-4;
- Atterberg limits as stated in BDS EN ISO 17892-12;
- determination of particle density in the words of BDS EN ISO 17892-3;
- classification according to BDS EN ISO 14688-2;
- the specific surface area (SSA) of the bentonite samples were measured based on multi -point BET (Brunauer-Emmett-Teller) method applied to a nitrogen adsorption isotherm in a Quantachrome NOVA 1200e apparatus. The isotherms were measured at -195°C (approximately 77K);
- water absorption of bentonite by the porous plate method according to ASTM E 946.

Results and discussion

Mineralogical composition

The achieved XRD patterns indicate that the samples have similar mineralogical compositions, all dominated by smectite. The relatively broad diffraction peaks suggest a low degree of crystallinity and/or fine crystallite size, which is characteristic of smectite-rich materials and reflects the disordered layer structure typical of expandable clay minerals (Środoń, 1999).

Characteristic basal reflections, together with the (060) reflection in the range of 61.6–62.1° 2θ, indicate that the smectite mineral is montmorillonite (Moore, Reynolds, 1997; Środoń, 2006). Furthermore, the position of the d(060) reflection (1.495–1.498 Å) confirms that the montmorillonite is of the dioctahedral type (Grim, Güven, 1978). The identification of dioctahedral montmorillonite indicates that the material is likely to maintain its structural stability and functional properties under repository conditions. These mineral phases are documented to preserve their swelling capacity and self-sealing ability across a diverse range of THM regimes, a property that supports the

long-term reliability of EBS (Grim, Güven, 1978; Pusch, 1999; Sellin, Leupin, 2013). The montmorillonite content ranges from approximately 72% in sample RB to 85% in sample PB (Fig. 2), indicating a high proportion of the active clay mineral phase. These values are in line with those reported for typical bentonite deposits (Bozhinov et al., 1984; Murray, 2006; Christidis, Huff, 2009).

In addition to the dominant smectite phase, accessory minerals such as cristobalite, oligoclase, and calcite were identified in all analyzed samples, which is similar to the mineralogical composition commonly reported for natural bentonites (Środoń, 2006; Cuadros, 2012; Brigatti et al., 2013).

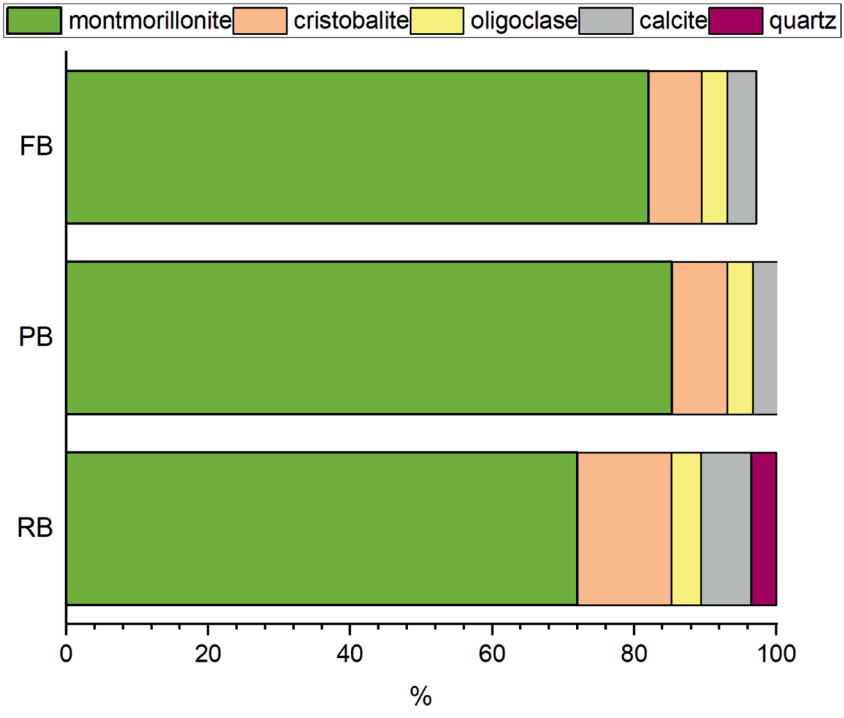


Fig. 2. Mineralogical composition of the tested samples.

Chemical composition and trace elements

Given the overall similarity in mineralogical compositions, only minor variations are observed in the major element proportions, most of which are within the typical ranges reported for bentonites (Murray, 2006; Weaver, 1989). The tested RB and PB samples exhibit bulk chemical compositions which correspond to the identified mineralogy (Fig. 3).

The dominant oxides are SiO_2 and Al_2O_3, followed by Fe_2O_3, MgO, and CaO, whereas Na_2O, K_2O, TiO_2, MnO, and P_2O_5 are present only in amounts below 1%. The significantly higher Ca^{2+} content compared to Na^+ and K^+ indicates that the raw clay can be classified as Ca-bentonite, which is in agreement with the XRD data (Güven, 1988; Moore, Reynolds, 1997; Yildiz et al., 1999). Further analyses will be conducted to determine the reason for the elevated Ca^{2+} content observed in the investigated bentonite. Furthermore, the SiO_2/Al_2O_3 ratio is approximately 3.59, falling within the typical range of 2÷5 reported for bentonites (Brigatti et al., 2013).

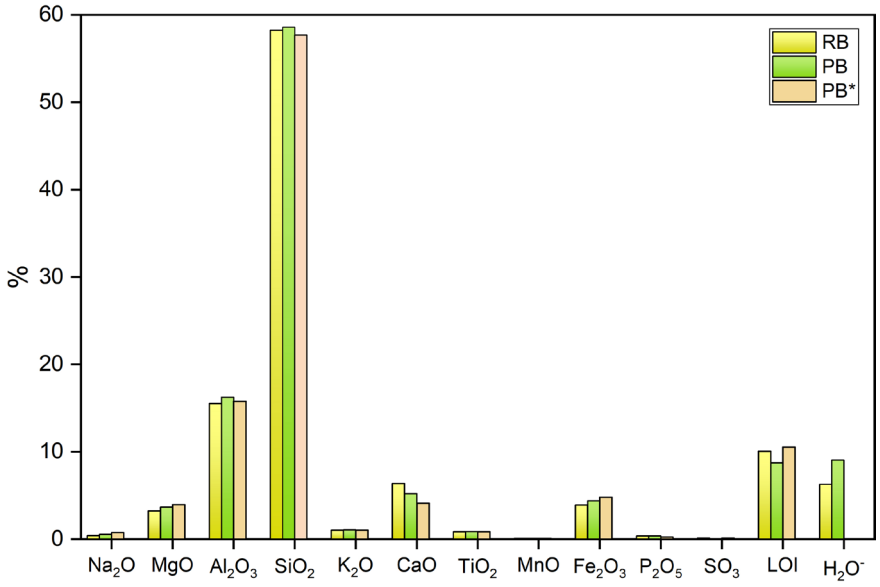


Fig. 3. Major oxide concentrations of sample RB and sample PB. PB* denotes bulk composition measured by XRF.

Trace element analysis was performed on sample PB, and the results are presented in Fig 4. The most abundant trace elements include Ba (1153 ppm), Zr (293 ppm), Rb (99 ppm), Ce (97 ppm), La (52 ppm), and Pb (51 ppm) whereas elements such as, Nd, Th, Y, etc. occur in concentrations below 50 ppm. These values are comparable to those reported for Ca-bentonites from other localities (Yildiz et al., 1999; Karakaya et al., 2011; Ivanova et al., 2020). The relatively low concentrations of transition metals suggest minimal contamination from detrital sources and are consistent with a volcaniclastic origin for the parent material (Christidis, 1998).

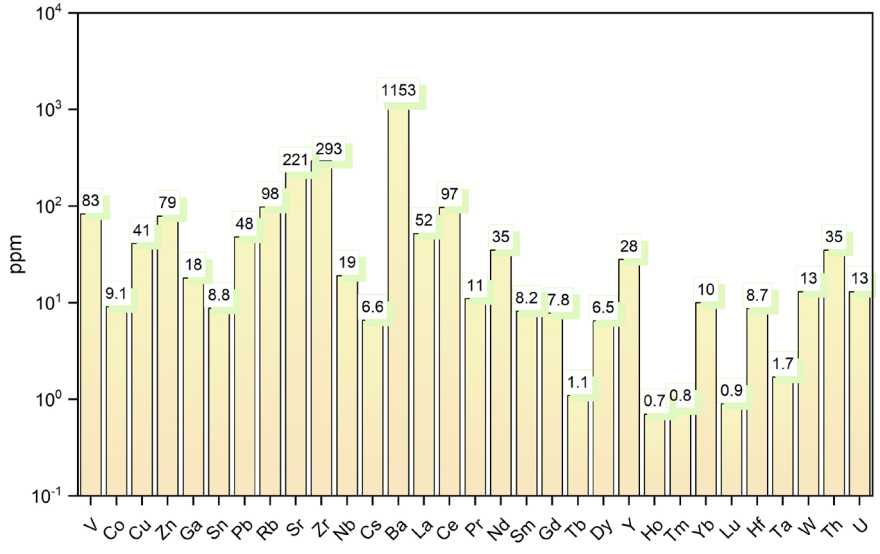


Fig. 4. Trace element analysis of sample PB.

Micromorphology analysis

Scanning electron microscopy (SEM) was used to examine the microstructure of the FB sample (Fig. 5). The sample displays a typical honeycomb texture, with platy smectite particles showing edge-to-edge and edge-to-face contacts (Grim, Güven, 1978; Moore, Reynolds, 1997). This open matrix is characteristic of smectite-rich materials and is directly related to their high water absorption capacity and swelling potential (Pusch, 1999; Sellin, Leupin, 2013). The observed microstructural arrangement are potentially favorable for self-sealing behavior and low hydraulic conductivity of the bentonite buffer, which are essential properties for its performance in EBS (Horseman et al., 1996; Madsen, 1998; Sellin, Leupin, 2013).

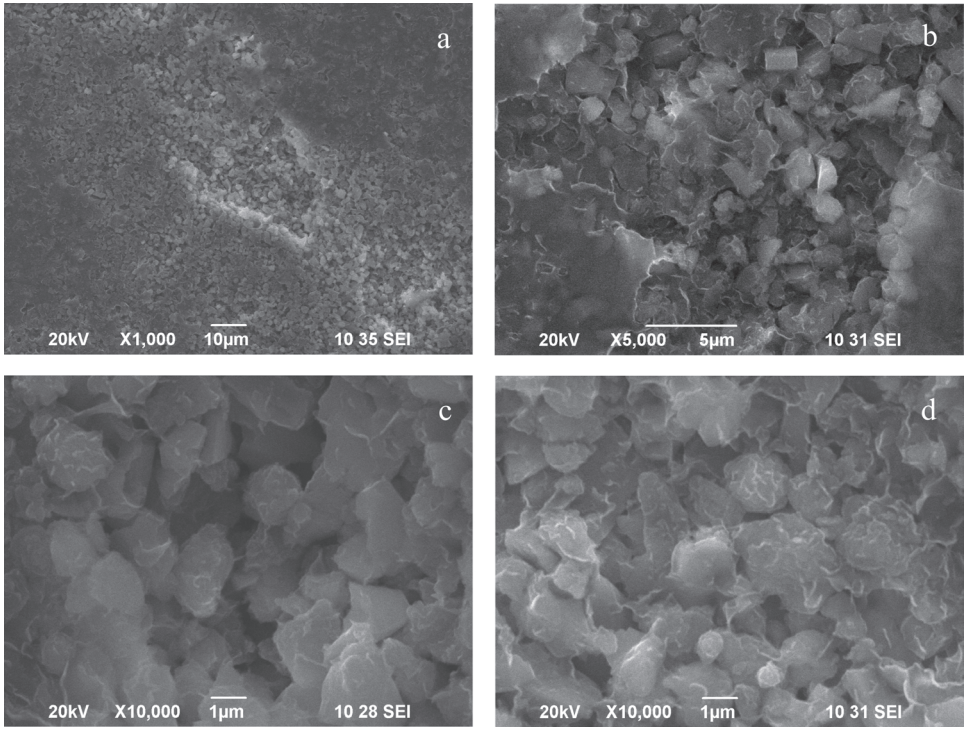


Fig. 5. Scanning electron microscope (SEM) images showing texture of the bentonite <2 µm fraction: (a) general aspect of the bentonites samples; (b) small flakes of smectites; (c-d) rose-shaped smectites.

Physical properties

The grain size distribution of the RB and PB samples was determined by a combination of dry sieving for coarser particles (>0.063 mm) and the hydrometer method for finer fractions (silt and clay). The results are presented in Fig. 6a and summarized in Table 1. Both samples contain sand, silt, and clay fractions.

The RB sample comprises 6% sand, 49% silt, and 45% clay, indicating a relatively higher proportion of coarser particles compared to the PB sample. In contrast, the PB sample is characterized by a reduced sand content (1%) and an increased clay fraction (59%).

These differences in grain size distribution directly correlate with the physical properties of the tested samples. The PB sample exhibited significantly higher liquid limit, SSA, and WA values compared to the RB sample (Table 1).

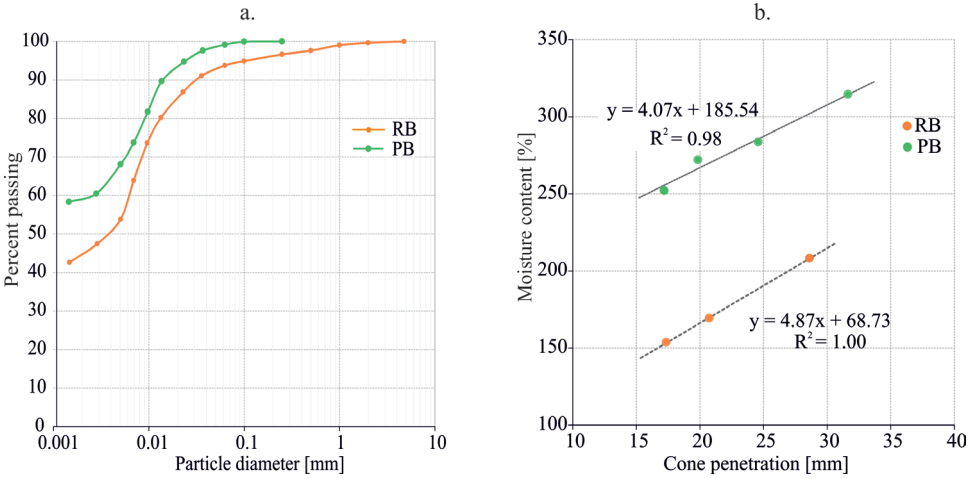


Fig. 6. Geotechnical properties of RB and PB: (a) Particle size distribution; (b) Liquid limit determination by cone penetration test.

Table 1. Classification and geochemical parameters of tested samples.

Parameter \ Sample		RB	PB
Particle density, ρ_s	[g/cm^3]	2.74	2.74
Grain size distribution:			
Sand (2 ÷ 0.063 mm)	[%]	6	1
Silt (0.063 ÷ 0.002 mm)	[%]	49	40
Clay (< 0.002 mm)	[%]	45	59
Liquid limit, w_L	[%]	166	267
Plastic limit, w_P	[%]	45	45
Plasticity index, I_P	[%]	121	221
ESCS classification		ClV	ClV
Activity of clay		2.69	3.75
SSA	[m^2/g]	86	92
Water absorption	[%]	157	391

The obtained liquid limit values are extremely high, reaching 166% for RB and 267% for PB (Fig. 6b). According to the ESCS classification, both samples are classified as very high plasticity clays (ClV).

The clay activity (CA), which serves as an indicator of swelling potential (Skempton, 1953), is consistent with the montmorillonite content (Fig. 2), with values of 2.69 for RB and 3.75 for PB. The water absorption (WA) and specific surface area (SSA) further confirm the high plasticity and swelling capacity of the studied materials.

The substantially higher WA of the PB sample (391% compared to 157% for RB) suggests that it possesses a greater capacity for water retention, which is a critical parameter for swelling pressure development in EBS (Komine, Ogata, 1996; Sellin, Leupin, 2013).

The measured SSA values ranged from 86 m^2/g for the RB sample to 96 m^2/g for the PB sample, falling within the typical range of 20–100 m^2/g reported for bentonites determined by the BET method (Brunauer et al., 1938; Bergaya et al., 2006; Kuila and Prasad, 2013).

The results indicate that while both samples are suitable for EBS applications, the PB sample may offer better self-sealing capabilities due to its higher plasticity and WA, whereas the RB sample might provide better mechanical stability due to its coarser sand fraction (Madsen, 1998; Chapman, McCombie, 2003).

Conclusions

This study provides a preliminary characterization of Ca-bentonites from the Kardzhali deposit in south-eastern Bulgaria, with a focus on their mineralogical, geochemical, geotechnical, and microstructural properties relevant to engineered barrier systems (EBS) for radioactive waste isolation. The following conclusions can be drawn:

- *Mineralogical composition*. The tested samples are dominated by dioctahedral montmorillonite, with contents ranging from approximately 72% in the RB sample to 85% in the PB sample. Accessory minerals include cristobalite, oligoclase, and calcite.
- *Chemical composition*. The significantly higher Ca^{2+} content compared to Na^+ and K^+ confirms classification as Ca-bentonite, in agreement with the XRD data. The SiO_2/Al_2O_3 ratio (approximately 3.59) falls within the typical range of 2–5 reported for bentonites. Trace element analysis reveals low transition metal concentrations, suggesting minimal detrital contamination.
- *Microstructural features*. SEM observations reveal a characteristic honeycomb texture, with platy smectite particles forming edge-to-edge and edge-to-face contacts. This open structure is directly related to the high water absorption capacity and swelling potential of the material, contributing to its self-sealing behavior and low hydraulic conductivity.
- *Geotechnical properties.* Both samples are classified as very high plasticity clays (ClV) according to ESCS classification. The PB sample, characterized by higher clay content (59%) due to milling, exhibits significantly higher liquid limit (267%), SSA (92 m^2/g), and WA (391%) compared to the RB sample. The measured SSA values fall within the typical range of 20–100 m^2/g reported in the literature for bentonites analyzed by the BET method.
- *Aptitude* for *EBS applications*. The results indicate that both samples show promising properties for a potential application in EBS. The powdered bentonite may offer better self-sealing capabilities due to its higher plasticity and water absorption, whereas the raw bentonite might provide better mechanical stability due to its coarser sand fraction.

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