ABCRad Deliverable 1: Desktop study and basic characterisation of alternative buffer materials.

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Abstract

ABCRad is a research project based at the University of Helsinki (UH) Radiochemistry Unit. It aims to provide quantitative and mechanistic information for end-users on the properties of the two alternative bentonite materials, making them viable candidates as buffer / backfill material replacements for use in KBS-3 style high-level radioactive waste repositories to the current reference Wyoming Na-bentonite. Expanding the knowledge base of alternative materials will provide robustness on the safety case for spent nuclear fuel disposal in the event that there are problems with the Wyoming bentonite supply chain. ABCRad studies the materials physico-chemical structure, stability following heating, and interactions between the materials and radionuclides under conditions specific to the ONKALO® repository. In the first year, ABCRad will achieve this by: i) studying the basic properties of the bentonites; ii) assessing the impact of high temperatures on geotechnical and mineralogical properties of the bentonites; iii) determining K_d values using sorption isotherms; and iv) by studying the mechanisms governing solution-to-solid partitioning *via* modern spectroscopic techniques such as Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, and Time Resolved Laser Fluorescence Spectroscopy (TRLFS). The results of the project will provide an enhanced understanding of material evolution and potential radionuclide interactions with the bentonites, directly informing the safety case for the storage of spent nuclear fuel. In collaboration with POSIVA Oy, UH have received seven alternative bentonite materials for a desktop study that will be used to inform the decision on which two materials are carried forward in ABCRad.

Contents

List of abbreviations

ABM – Alternative buffer material, in reference to the ABM experiment series carried out at Äspö hard rock laboratory, Sweden.

CEC – cation exchange capacity

EURAD - European Joint Programme on Radioactive Waste Management

HITEC – Influence of temperature on clay-based material behaviour, a work package in the EURAD program,

MEAEF – ministry of economic affairs and employment, Finland.

STUK - The radiation safety centre. An administrative authority of the Ministry of Social Affairs and Health, which oversees radiation and nuclear safety in Finland.

THM – thermal-hydraulic-mechanical

**TSM** – thermodynamic sorption model

UH – the University of Helsinki

Introduction

Bentonite is a geological clay mineral of the smectite group and is composed mostly of montmorillonite, which has unique swelling properties when in the presence of water which leads to low water permeability (approximately 10^{-13} ms^{-1} for compacted bentonites). Bentonites are mined globally, but vary widely in mineralogy and properties, influencing its industrial application. In Finland, the ONKALO® deep geological disposal facility is designed for the disposal of spent nuclear fuel. Here, bentonites play a critical role in three geotechnical barriers: i) as a buffer material surrounding the waste canisters to provide protection and limit water and radionuclide movement, and ii) as a backfill material to fill deposition tunnels and maintain stability iii) as closure material for filling central tunnels, access tunnel and shafts. In ONKALO® alone, there is an estimated 27 tonnes bentonite required for use as a buffer material per buffer (with 3000 deposition holes this would mean approximately 81 000 tonnes of buffer material), a further estimated 400 000–500 000 m^3 of backfill material required, and finally approximately 700 000–800 000 m^3 of closure material, which will be composed of a 70/30 mixture of crushed rock and bentonite. The basic physico-chemical properties of various bentonites have been studied for potential use in spent nuclear fuel disposal in Finland (e.g., Kiviranta et al., 2011 & 2018; POSIVA, 2012 & 2021); however, most experimental work has focussed on POSIVA's current reference material for the repository: Wyoming-type high-grade Na-bentonite (commercial names such as MX-80 and BARAKADE)(POSIVA, 2012 & 2021). Given the operational lifetime of ONKALO® , the volume of buffer required, and potential changes in "*the global market*" (e.g*.,* logistics / supply chain issues, global political instabilities), it is essential that multiple bentonite types are considered in order to "*future-proof*" the disposal concept (as recommended by the Finnish ministry of economic affairs and employment)(MEAEF, 2022). The buffer material can be changed as long as the alternative material meets requirements (POSIVA, 2012 & 2021). Indeed, STUK (the Finnish regulator) has requested that "*POSIVA describe how a buffer material can be changed without compromising the performance of the buffer*" (STUK, 2015). To help meet these requirements POSIVA Oy have supplied UH with seven alternative bentonite materials (**Table 2**). The current desktop study and basic chemical characterisation will be used to inform the decision on which two materials are carried forward in experimental work as part of the SAFER2028 funded ABCRad project. Moreover, this document outlines the experimental setup for the remainder of ABCRad considering the current literature.

Bentonite general structure

The main component in any bentonite is a swelling mineral, usually montmorillonite, which represents approximately 50 – 80% of the bentonite. The remainder is accessory minerals, which may vary substantially in both mineralogy and concentration, typical accessory minerals include: other clay minerals, quartz, feldspars, gypsum, calcite, pyrite, iron oxides/hydroxides, and amorphous or organic compounds. Montmorillonite is a clay mineral of the smectite group that has a layered tetrahedral-octahedral-tetrahedral (TOT) alumina-silicate sheet structure with a well-defined thickness (~1 nm) and a lateral extension from 100 – 1000 nm. These 2:1 layers consist of two tetrahedral silicate sheets and one octahedral aluminate sheet. Montmorillonite particles hold permanent negative charge, due to isomorphous substitutions in the crystal structure (mostly Mg^{2+} for Al^{3+} in the octahedral sheets and Al^{3+} for Si^{4+} in the tetrahedral sheets). The permanent negative structural charge of the montmorillonite is compensated for by positively charged counterions (mostly Na^+, Ca^{2+}, but they could also be cationic radionuclides e.g., Cs^+, UO_2^{2+}). An illustration of an individual montmorillonite particle is shown in **Figure 1** below.
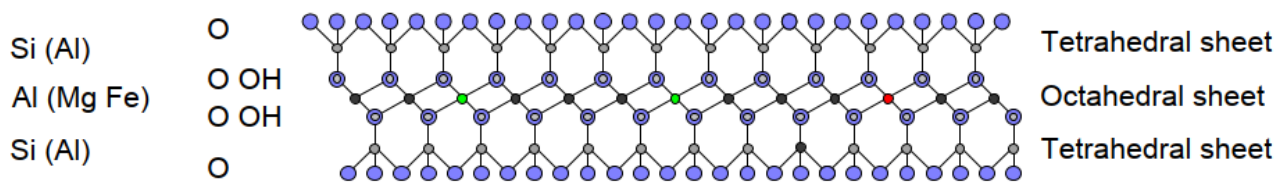
Figure 1: Crystal structure of the individual montmorillonite particle. Taken from (Birgersson *et al.*, 2017).

Montmorillonite particles then stack up to form layers, the layers can expand following hydration. When completely dry, montmorillonite layers have a basal spacing of ~9.7 Å. Increasing hydration increases this basal spacing where values close to 12.5 Å and 15.0 Å signify a monolayer and a double-layer of water respectively. At higher water content, the basal spacing increases more continuously.
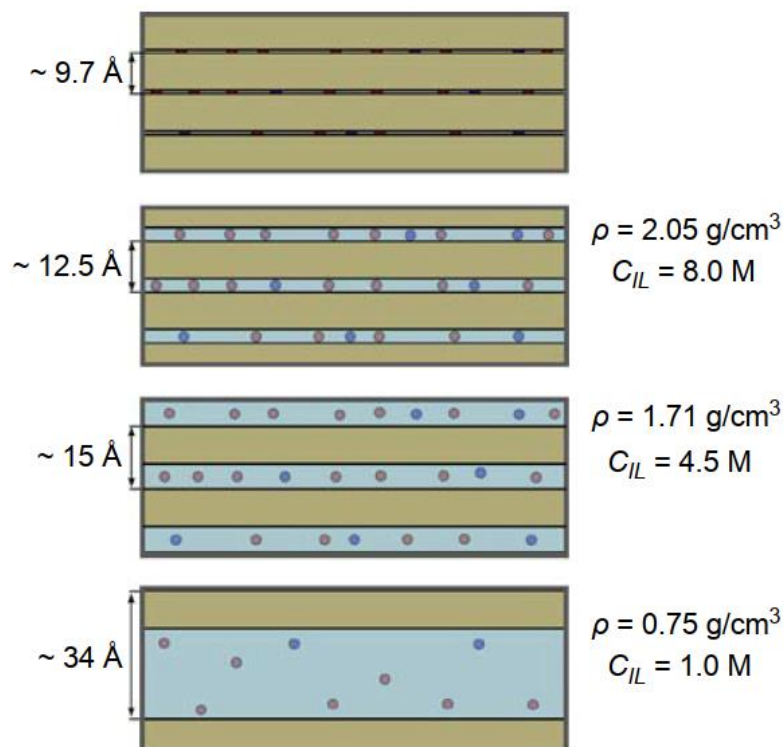
Figure 2: Schematic illustration of montmorillonite interlayers at different degree of hydration. Typical dry densities of the particle-water system (ρ), and average counterion interlayer concentrations (C_{IL}) are given. Taken from (Birgersson *et al.*, 2017).

## Alternative buffer material experiments

ABM at Äspö Hard Rock Laboratory

ABCRad is not the first project to study alternative buffer materials. For example, the Alternative Buffer Material (ABM) experiment series at Äspö Hard Rock Laboratory (Sweden) assesses the corrosion-induced changes in montmorillonite content, interlayer cations and overall Fe content of eleven different clays (SKB, 2021a). The main purpose of the ABM project was to characterise the long-term stability of various clays with respect to changes in hydro-mechanical properties, mineralogy and chemical composition. The ABM experimental design is similar to the Swedish KBS-3 concept with a copper canister containing spent nuclear fuel surrounded by clay in a crystalline bedrock ~450 m underground. The original experiment (2006) included three test-packages (Table 1) which each contain a central heater (to simulate heat produced from radioactive decay of the waste), surrounded by compacted clay buffer blocks. In 2012 a further three additional test packages were installed (Table 1), with some minor variation in the materials. Thus far, the

experiments have identified several important mineral reactions including redistribution of sulphate minerals, extensive cation exchange and the formation of corrosion products at the interfaces with the Cu canisters and Fe heaters (Olsson and Karnland, 2011; Kaufhold *et al.*, 2021; SKB, 2021b; Sudheer Kumar *et al.*, 2021).

Table 1: Test program for the ABM experiment.

Test #	Duration (years)	Temperature Range (°C)	Artificial Wetting	Installation Year
1	1	80 – 130	Yes	2006
2	3	80 – 130	Yes	2006
3	5	80 – 130	No	2006
4			Yes	2012
5	5	150 – 250	Yes	2012
6			Yes	2012
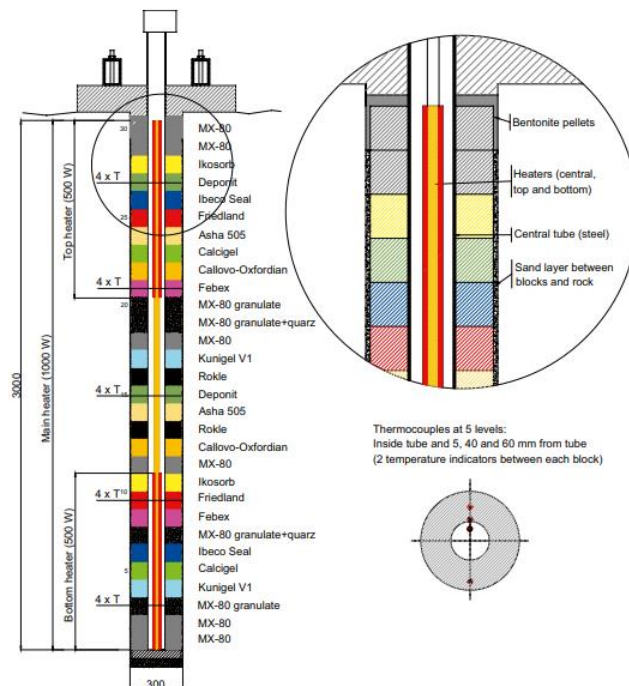
Figure 3: Schematic of the ABM experiment (Test 1). Taken from (Svensson *et al.*, 2011).

EURAD-HITEC project

Excess heat from the radioactive wastes, especially if above 100 °C, may trigger mineralogical alterations in the geotechnical barrier components that could have adverse effects on their geochemical properties. In order to improve the understanding of the transport processes among other things the EURAD-HITEC work package aims to "*develop and document improved THM understanding of clay based materials (host rock and buffer) exposed to elevated temperatures (>100 °C) for extended durations*". Still an on-going project, some experimental results from the HITEC project have demonstrated that excess heat (> 100 °C) can collapse the interlayer space, resulting in decreased Cation Exchange Capacity (CEC), as seen following heat treatment at 90 °C (9%) and at 120 °C (14%) (e.g., Kaufhold et al., 2010. As the HITEC project is still on going, most manuscripts are not yet published). Accordingly, STUK has identified the assessment of the mineralogical transformations of montmorillonite as a critical concern for the long-term safety case of SNF disposal (STUK, 2015).

Similar to current work in the ABM experimental series and the EURAD-HITEC work package, ABCRad will assess the long-term effects of heat load on the physico-chemical properties of the two chosen alternative bentonites. Samples will be dry heated at 150 °C and sub-samples will be analysed every 6 months.

Thermodynamic sorption behaviour in the context of radioactive waste disposal

Whilst the ABM and HITEC projects are, undoubtedly, extremely useful and relevant; their objectives are generally limited to characterising the thermal-hydraulic-mechanical (THM) coupled processes associated with changes observed in the bentonites. The chemical interactions of alternative buffer materials with radionuclides, however, is relatively poorly studied.

Thermodynamic sorption models (TSM) (based on laboratory experiments) can predict the mobility of contaminants in the subsurface and they are applicable to, for example, radioactive waste disposal scenarios (Payne *et al.*, 2013). Here, safety case calculations typically have two chemical processes that are necessary to evaluate the risks associated with radionuclide migration. These are: i) the sorption co-efficient (K_d), which quantifies the distribution of a radionuclide between the aqueous and solid phase at equilibrium; and ii) the solubility limit of the contaminant in the relevant geochemical environment. Where K_d values are experimentally determined, they describe both adsorption and desorption; solubility limits are generally assessed using thermodynamic data and models, they describe dissolution – precipitation reactions (Grenthe et al 1992). Indeed Kd is one of the most critical parameters for the assessment of a waste repository. K_d values are typically determined via batch sorption experiments where an exact mass of a geological material (e.g., host rock or bentonite clay) is mixed with an exact volume of solution (representative of the environment in study) which contains known concentrations of the contaminant in question. K_d is described in **Equation 1**, where C_i and C_{eq} are the initial and equilibrium concentrations of the contaminant and V and m are the volume and mass of the aqueous phase and the sorbent respectively. K_d typically has units mL/g, L/kg or m³/kg. The contaminant concentration is typically expressed in units such as mol, mg, or for radioactive isotopes Bq.

$$K_d = \frac{amount\ of\ radionuclide\ sorbed\ per\ unit\ mass\ of\ substrate}{amount\ of\ radionuclide\ dissolved\ per\ unit\ volume\ of\ solution} = \left(\frac{C_i - C_{eq}}{C_{eq}}\right).\frac{V}{m}$$

Equation 1: Kd in written form and as an equation.

It must be noted that, whilst K_d measurements are key to describing contaminant mobility, they are conditional parameters that are specific to the experimental conditions employed during their determination. Meaning that K_d is very sensitive to changing parameters (changing geological material, solution composition and pH, radionuclide concentration, temperature). K_d values therefore cannot be extrapolated to a wide range of conditions and must be calculated using well-controlled experimental regimes, that are specifically designed to mimic the desired environment (e.g., Tsai, Ouyang and Hsu, 2001; Missana, García-Gutiérrez and Alonso, 2004; Missana *et al.*, 2014; Izosimova *et al.*, 2022).

Understanding TSM at a molecular level

Although K_d delivers useful quantitative information on sorption reactions under specific conditions, it cannot describe the mechanisms that govern the partitioning of contaminants between the solid and the solution, and the data cannot be extrapolated to a wider range of conditions (Payne et al., 2022). It is therefore imperative to develop a TSM model that looks at the molecular scale. This molecular-scale understanding will build on our current scientific understandings of bentonite – radionuclide interactions; adding value to the safety case for radioactive waste disposal.

At the molecular scale, K_d values and TSMs conceptualise the functional groups available on a mineral surface that interact with dissolved species (e.g., radionuclides) via sorption or ion exchange. The mineral surface sites may be considered as one of two classes: variable and permanent charges (Sposito, 2008). Variable charge surfaces (e.g., Fe-oxides) are strongly affected by pH where acid-base reactions govern mineral – radionuclide interactions. Permanent charge sites (e.g., clays) have fixed structural charges that are compensated for by the binding of counterions (cations, in the case of clays). Often a mineral can exhibit both classes of charge sites, as is seen in clays. The number of surface sites and the number of ion exchange sites can be estimated by measuring the specific surface area and the cation exchange capacity (CEC), respectively.

Then, the research must provide a molecular scale model of the interaction between the mineral surface and the radionuclides. Here, the key distinction lies between inner-sphere and outer-sphere surface complexes, where inner-sphere complexes form a direct bond between the surface and the absorbed radionuclide, and outer-sphere complexes form a bond with the water molecules in the hydration sphere of the absorbed radionuclide (**Figure 4**). Generally, inner-sphere complexes are involve a strong, chemical bond and, outer-sphere complexes involve weaker physical bonds via electrostatic forces of attraction. Modern spectroscopies such as Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy (Williamson et al., 2021; Vettese, et al., 2020b; Ho et al., 2022), and Time Resolved Laser Fluorescence Spectroscopy (TRLFS)(Kammerlander *et al.*, 2021; Philipp *et al.*, 2022) can distinguish the various sorption mechanisms and will be employed in ABCRad.
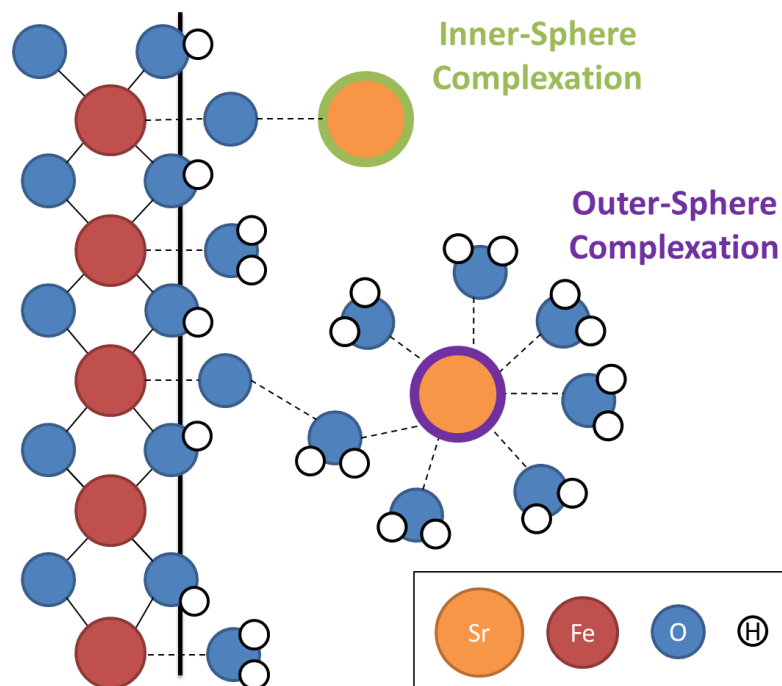
Figure 4: Ball and stick representation of inner-sphere (top, green) and outer-sphere complexation (bottom, purple) of Sr to bentonite surfaces. Image adapted from (Vettese et al., 2020).

In order to have a more fundamental understanding of radionuclide transport in the environment ABCRad will provide a TSM that contains K_d values for key, risk-driving radionuclides (Cs and U) under experimentally relevant conditions. It will also involve state-of-the-art analyses EXAFS and TRLFS, which will provide a molecular-scale explanation for the observed experiments.

Reflecting the above, batch sorption isotherms (to calculate K_d, using Equation 1) will be made using a 1:20 ratio of solids to solution. Here, 0.5 g of bentonite (sieved ≤ 200 μm) will be equilibrated with 10 cm³ of

ONKALO® water (see methodology section) spiked with a given concentration of Cs or U at a fixed temperature (293 ± 3 K) for a fixed period. The radionuclides used will be ^{134}Cs and ^{233}U, the tracers will be caesium chloride and uranyl nitrate. After equilibration, the suspension will be centrifuged at 2,522 g for 30 mins and the gross gamma activity in 5 cm^3 of the supernatant will be used to determine ^{134}Cs and ^{233}U partitioning. The pH of all experiments will be conducted at the natural pH between the bentonite. All solutions will be prepared with degassed, 18 MΩ cm^{-1} de-ionized water, and all manipulations (except for centrifugation) will be done under anoxic (H$_2$, N$_2$, Ar) conditions. Samples will be prepared for EXAFS and TRLFS analysis as described in (Philipp *et al.*, 2019).

Conclusions

The aim of this desktop study was to perform basic characterisation of the supplied bentonites and to perform a desktop study assessing the literature relevant to the experiments. Following discussions with POSIVA, ABCRad will continue to work with materials from Laviosa and LMS for the remainder of the project. Material from Laviosa was backfilling bentonite in Posiva's operation licence application and material from LMS is planned backfilling bentonite for operation, making them ideal to study as alternative buffer material. The methods that will be used (reflecting the relevant literature) are described in each relevant chapter and the basic characterisation of the seven bentonites is given below.

Measurements made at UH

As well as the desktop review, some preliminary data was collected at UH. The specific surface areas (SSA$_{N2BET}$) of all bentonites vary between 30 – 89 m^2/g. The XRD patters of the seven bentonites are shown in **Figure 5**; the strongest peaks of montmorillonite, calcite, quartz, Feldspar and cristobalite are indicated.

Table 2: Bentonite properties.

Bentonite	Country of origin	pH	Specific Surface Area$_{N2BET}$ (m²/g)	Main Mineral composition
LMS	Georgia	10.40	76.157	Montmorillonite, Feldspar, Mica, Zeolite
Luxgel	Egypt	10.23	40.670	Montmorillonite, Calcite, Cristobalite, Quartz,
Cetco CP5	USA (Wy)	10.01	38.628	Montmorillonite, Cristobalite, Quartz
Laviosa	Italy	10.76	33.165	Montmorillonite, Feldspar, Quartz, Cristobalite
Barakade	USA (Wy)	10.41	29.862	Montmorillonite, Calcite, Quartz, Feldspar,
IMERYS	Greece	10.24	89.068	Montmorillonite, Quartz, Calcite, Plagioclase, Feldspar
Ashagel	India	9.95	78.413	Montmorillonite, Quartz, Calcite, Plagioclase, Feldspar
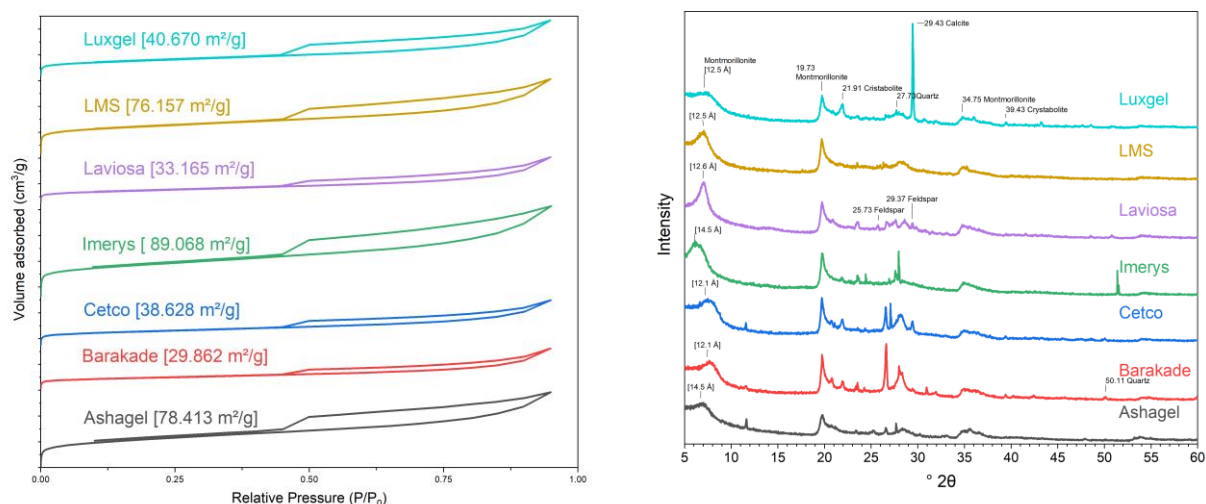
Figure 5: (**Left**) N_2 adsorption / desorption isotherms of the seven bentonite samples. Specific surface area (m^2/g) given in square brackets. (**Right**) XRD patterns of the seven bentonites. Montmorillonite d-spacing given in square brackets (Cu K_α radiation).

Methodology

ONKALO® Water recipe.

The reference water used for the sorption isotherms will be relevant to ONKALO® ; it will be the same as was supplied for the HITEC project. Per litre of de-ionised water it contains NaCl (6.47 g/L, 0.11 M), and $CaCl_2.5H_2O$ (3.53 g/L, 0.032 M). Its ionic strength is 0.365 M.

pH

1 g of bentonite was added to 20 mL 18 MQ de-ionised water and mixed. The pH was recorded after 1 hr using calibrated electrode (Mettler-Toledo, Columbus, OH, USA).

Powder X-Ray Diffraction

Bulk powder mineral samples were determined by XRD analysis using a Panalytical X'Pert3 Powder X-ray diffractometer with CoK_α-radiation (λ = 1.5406 Å, 40 kV, 40 mA). The samples were prepared as random powders without any preferred particle orientations by placing them on glass slides, the samples were then measured from 5° to 75° 2θ using a step size of 0.02° 2θ. The software HighScore Plus and the PDF-4^{+} database were used for mineral identification.

Surface area determination

The SSA_{N2BET} was measured by N_2 adsorption using a 7-point BET method. Measurements were performed by a Quantachrome Autosorb iQ Station 3 with ~0.5 g weight. Standard pre-treatment conditions are 110 °C and 9 h.

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