Distinguishing between more and less suitable bentonites for storage of high-level radioactive waste

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ABSTRACT: One of today's big challenges is to store safely the increasing amount of high-level radioactive waste (HLRW) in the world. In some of the concepts devised for this challenge, bentonite, a natural swelling clay, plays a key role in encasing the canisters containing the waste. The use of bentonite as a geotechnical barrier in HLRW repositories is a new venture; specifications to ensure either optimum performance or that a minimum standard is reached at least do not exist yet. The present study summarizes relevant research and discusses possible HLRW-bentonite specifications. The importance of these specifications for any given repositories has to be assessed on a case by case basis, depending on the concept being employed and any special circumstances for the individual repositories.

Ten key issues were identified which were used to discuss bentonite specifications. In some of these key issues the optimum bentonite performance depended more on processing and production (compaction) than on the bentonite type (*e.g.* swelling pressure and thermal conductivity). In contrast, in some of the other key issues, the type of bentonite was found to influence possible specifications: the bentonite should not alter its mineral composition or its geotechnical parameters such as the swellability. Therefore, the bentonite should contain neither soluble nor reactive phases (*e.g.* organic matter, pyrite, gypsum). The structural Fe content of the smectites should be small because of the lesser stability and greater reactivity of the Fe-rich bentonites. Also, a large layer-charge density of the swelling clay minerals leads to less corrosion at the iron–bentonite interface (relevant if iron canisters are used). The hydraulic conductivity and swelling pressure can be tailored by compaction of the bentonite resulting in different dry densities. From an engineering point of view, a bentonite with least dependence of the hydraulic conductivity/swelling pressure on the dry density would be best. Using a bentonite which has been investigated extensively over many years means less uncertainty compared to unknown materials.

The safe disposal of HLRW is a big challenge for the nuclear energy industry. The disposal of HLRW in deep geological formations is favoured. Various concepts are under investigation with a view to isolating the HLRW for a period of up to 1 million years. In some of these concepts, bentonite, a natural swelling clay with appreciable cation exchange capacity, is suggested for use as a geotechnical barrier between the metal canister containing the waste and the host rock. As an example, Sweden and Finland are planning to locate the repository in crystalline rocks (SKB, 2010; Dohrmann *et al.*, 2013a) and enclose the canisters in highly compacted bentonite (Fig. 1). In other concepts (*e.g.* Switzerland) bentonite may be applied as highly compacted pellets or granulates (Fries *et al.*, 2008). Regardless of the differences between the various concepts, bentonite plays a role in
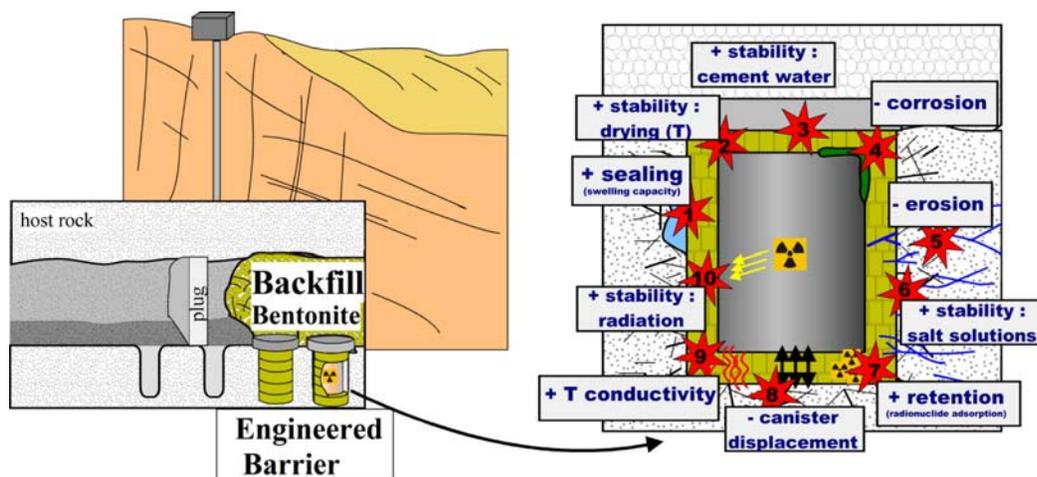
Fɪɢ. 1. Schematic representation of the planned application of bentonite as a barrier material for HLW both as backfill material and as compacted blocks directly around the canister. Specific backfill issues are not discussed here. + should be maximum (*e.g.* sealing); – should be minimum (*e.g.* corrosion).

most of them. The bentonite swelling capacity results in a low hydraulic conductivity and the ability to seal cracks even in contact with the partially fractured crystalline host rock. Bentonites are mined worldwide and their properties are highly variable. The quality of a specific bentonite is commonly determined by application tests and comparison with reference materials or standards. For example, in order to be suitable for use as cat litter, bentonite is investigated with respect to water uptake and is compared with existing products using a specific procedure. Very often a specific bentonite might be suitable for one application but not another. Thus far bentonite has not been used in the storage of HLRW because the disposal of the waste, using the methods described above, has not yet commenced in any country. Because of this lack of experience, specifications to distinguish more suitable from less suitable 'HLRW bentonites' are not yet available.

The identification of generally valid quality-determining parameters of HLRW bentonites is complicated by the fact that a number of different aspects have to be considered. For most established applications one main quality-determining parameter exists (*e.g.* viscosity for drilling fluids).

According to Sellin & Leupin (2014) the key parameters of HLRW bentonites are low hydraulic conductivity, high self-sealing ability, and durability (stability). In order to compare bentonites these key issues needed to be specified. As an example, the stability/durability of bentonites can be modified chemically or mechanically. One additional parameter,

the retention capacity for radionuclides, was added to this list of parameters. Overall, ten key issues sketched in Fig. 1 were identified and discussed in the following.

The present study focuses on bentonite in highly compacted blocks (located around the canister). The specifications for bentonites used as backfill (to seal tunnels and shafts) are not as important because of less relevant concentration gradients (of ions in porewater, Fe from corrosion, OH from cement, *etc.*) and temperature gradients compared to the geotechnical barrier material and the larger distance to the canister. However, a far larger amount of bentonite or other impermeable clay will be used as backfill material. The choice of the backfill material, therefore, is important with respect to the amount of components introduced into the entire repository system.

BENTONITE KEY ISSUES

The key issues summarized in Fig. 1 concern both immediate performance (*e.g.* issues 1 and 7) and durability (affecting long-term performance = stability). In the following, an overview rather than a comprehensive review of research results concerning the different key issues is presented. For some issues minimum and maximum values are available (*e.g.* swelling pressure affecting sealing); for others it is difficult to present values (*e.g.* stability). Required and desired parameters, however, differ from one concept to another. Values are, therefore, only discussed to explain the issues or relative differences.

Issue 1 – sealing (low hydraulic conductivity and gas permeability)

One of the most important properties of a HLRW bentonite is the sealing of possible fissures anywhere in the multicomponent system and a generally low hydraulic conductivity. The hydraulic conductivity for a relatively pure bentonite is related to the swelling pressure (Pusch *et al.*, 2010). A minimum swelling pressure is needed to keep the canister in place and to guarantee sealing of fissures and/or cracks. Large swelling pressures also reduce the probability of microbial growth (Fru & Athar, 2008).

Both parameters, the hydraulic conductivity and the swelling pressure, can be tailored by precompaction of the bentonite. The result of compaction, in turn, is commonly monitored by the dry density. The dry density, therefore, is taken as an indirect measure of the hydraulic conductivity and different bentonites can be compared based on their dry density–swelling pressure relation. Some published curves are shown in Fig. 2. Karnland *et al.* (2006) showed that the swelling pressures of the Ca- and Na-forms of one bentonite differ only at low dry density ($<\sim$1.6 cm^3/g). However, comparing different types of bentonites from different locations confirms the well-known variability of bentonite properties. Some of these differences can be explained by the different ways of varying the dry density (different water content or different compaction load), non-compactable porosity, and different smectite contents (Kaufhold *et al.*, 2015b).

Bentonites with large swelling pressures despite low compaction should be better HLRW bentonites than bentonites with low swelling pressure. From an engineering point of view, however, additional aspects must be considered. On one hand, in some concepts the swelling pressure should not exceed a critical value (Sellin & Leupin, 2014). On the other hand, an ideal bentonite should display minimum dependency of dry density on swelling pressure/ hydraulic conductivity. In other words, bentonites which provide more or less the same swelling pressure/ hydraulic conductivity both in low and dense areas are preferable because they guarantee low pressure gradients and homogeneous performance anywhere in the barrier. However, in order to identify such materials, additional research is needed, preferably at elevated ionic strength, to mimic realistic conditions. Therefore, at present, no generally valid required swelling pressure can be stated. The gas permeability should also be considered. The swelling pressure may be reduced by less compaction and thereby by increase

of the hydraulic conductivity (at least partial) to provide sufficient gas permeability (if necessary). As a consequence, bentonites with low dependency of swelling pressure on compaction are advantageous. In a comparative study, bentonites compacted with 75 MPa, which is applicable on a large scale, showed appreciable swelling pressure because the smectite content exceeded 60 wt.% (Kaufhold *et al.*, 2015b). Therefore, in general, recommendation of a specific bentonite with respect to the swelling pressure cannot be given at present.

Issue 2 – extensive drying

Water entering the bentonite will lead to swelling and hence to sealing. In combination with the elevated temperature of $\sim$100°C, mineral alteration reactions may occur. In addition, the absence of water (drying) in combination with high temperatures may affect the swelling capacity of the swelling clay minerals. Greene-Kelly (1953) and Hofmann & Klemen (1950) were the first to report on the loss of the swelling capacity upon heating. They recognized that small interlayer cations may enter the octahedral sheet at a specific critical temperature, neutralizing the permanent octahedral charge, thereby reducing the swelling capacity. However, the temperature expected in a repository will not be high enough for this process to happen. In many clay laboratories, however, clay samples are not dried above 60°C prior to analysis to avoid loss of swelling capacity. Kaufhold & Dohrmann (2010) investigated a set of different bentonite powders before and after drying at 90–120°C for up to 4.5 y and confirmed partial loss of swelling and cation exchange capacity (CEC). They concluded that the process of thermal reduction of swelling capacity is limited. It was also shown that within the first years of extensive drying more divalent cations were fixed than monovalent cations. The model explaining this behaviour still has to be validated. Furthermore, the degree of CEC loss at a given temperature varied among the bentonites. Those bentonites keeping more of their swelling capacity upon drying are preferable for a repository. The reason for this difference, however, is not yet understood.

Issue 3 – stability against alkaline solutions

Sealing of the canister/bentonite packages and tunnels and shafts is achieved by the use of some kind of cement in the repository. Common cement pore waters, however, are known to be alkaline and may
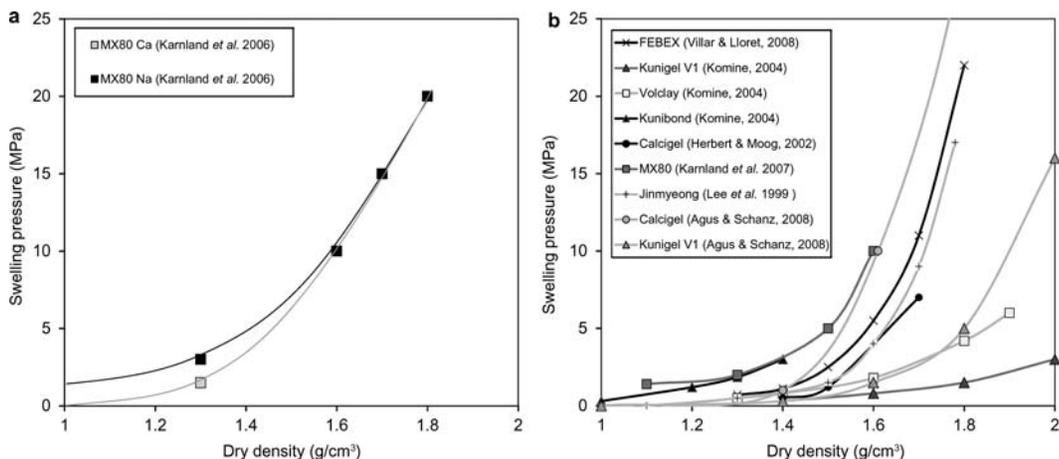
FIG. 2. Dry density/swelling pressure relations of MX80 measured in different laboratories.

alter the smectites or even other minerals. Smectite reactivity is low at pH = 12 becoming significant at pH ≈ 13 in laboratory conditions (Cuevas *et al.*, 2007; Fernandez *et al.*, 2010; Ramirez *et al.*, 2002). This would be different in real systems over reaction times which are much longer than the 1 or 2 y used in laboratory tests. Nevertheless, although most studies agree about the critical pH values, they differ in terms of the type of alteration products which include zeolites, feldspathoids or feldspars (Fernandez *et al,* 2010; Savage *et al.*, 2010) and illite or mixed-layer illite-smectite in K-bearing systems (Bauer *et al.*, 2006).

A suitable bentonite should be as stable as possible against alkaline cement pore water. Nevertheless, for a pH ≥ 13 which pertains for at least a limited period of time in the repository (NAGRA, 1995), congruent dissolution of the swelling clay minerals and precipitation of secondary minerals will occur regardless of the type of bentonite. The type and amount of secondary minerals and the concentration of dissolved elements depends heavily on the experimental conditions including continuous or occasional shaking (batch experiments) and on the type and chemical composition of the different bentonites (Kaufhold & Dohrmann, 2011). Therefore, a comparison of the reactivity of different bentonites in contact with highly alkaline solutions is difficult and cannot be based on the type of alteration product. However at pH = 12.5, expected in the repository (Berner, 1992), the structural elements of the swelling clay minerals are rather soluble and hence the progression of a dissolution/ precipitation reaction front will probably be

determined by the pH buffering capacity of the bentonite towards more acidic pH values. In this respect Ca-bentonites, which are generally more acidic (Kaufhold *et al.*, 2008), are advantageous over Na-bentonites (Na-activated bentonites were not considered). This property, however, may only be relevant in the very early deposition phase before the interlayer composition equilibrates with the host-rock fluid. Overall, issue 3 is less important if low-pH cements are used (*e.g.* Savage & Benbow, 2007). Some additional mineralogical modifications are expected when using low-pH cement (Hatem *et al.*, 2015). Distinguishing cement-stable from less stable bentonites is difficult because of the range of reactions

FIG. 3. Corrosion of an iron-pellet in contact with bentonite (aerobic corrosion is followed by anaerobic corrosion; image width ≈3 cm; after Kaufhold *et al.*, 2015).

depending on the chemical composition of the bentonite.

Issue 4 – stability against iron corrosion

Some concepts use iron canisters surrounded by blocks of highly compacted bentonite (*e.g.* Switzerland and France). However, bentonites affect the corrosion of iron and steel (Kaufhold *et al.*, 2015). The corrosion of iron in a HLRW repository will proceed under anaerobic conditions after the oxygen entrapped in the system has been consumed (red halo in Fig. 3). Corrosion can proceed anaerobically in spite of the fact that the exposition test here was not protected against oxygen (Fig. 3, after Kaufhold *et al.*, 2015a).

Because of the importance of the metal barrier, bentonite–iron interactions have been studied thoroughly (Lantenois *et al.*, 2005; Xia *et al.*, 2005; Perronnet *et al.*, 2007; Carlson *et al.*, 2007; Osacký *et al.*, 2010). Most of these studies have focused on the type of the corrosion product. Magnetite and neo-formed layered silicates such as saponite, berthierine, and/or chlorite have been reported (Gauillaume *et al.*, 2003; Wilson *et al.*, 2006a; Osacky *et al.*, 2010). Most of the studies concluded that a 1:1 Fe layered silicate (berthierine) forms at lower temperatures and a chlorite-type Fe layered silicate prevails at elevated temperature, *i.e.* >100°C (Wilson *et al.*, 2006b). The role of the bentonite with respect to the corrosion mechanism, however, is not fully understood yet. Kaufhold *et al.* (2015b) compared 38 different bentonites in five different exposition tests which were performed anaerobically at 60°C for 5 months. An iron pellet was cleaned, dried and weighed before and after the exposition tests. The interlayer composition was varied by cation exchange followed by dialysis. The corrosion rates ranged from 2 to 20 µm/a. The much smaller rater of corrosion (0.1 µm/a,) reported by Xia *et al.* (2005) can be explained by different solid/liquid ratios and the extent of the experiments.

Na-rich bentonites were slightly less corrosive than Ca/Mg-bentonites, but most of the bentonites with low charge were more corrosive (Fig. 4). Some Wyoming bentonites containing low-charged Na-smectites were rather corrosive which suggests that the layer-charge density is more important with respect to the corrosion rate than the type of interlayer cation. Generally, high-charge smectites are less corrosive and hence bentonites containing such smectites should be preferred. In these studies the Fe content of the smectites was not connected to the tendency to corrode. However, to identify a less corrosive and hence more suitable bentonite unambiguously, comparative tests should be performed (*e.g.* Kaufhold *et al.*, 2015b).

Issue 5 – stability against erosion and detachment of colloidal particles

Flow of water in contact with the bentonite may detach colloidal smectite particles leading to erosion and hence weakening of the barrier. Detached colloids could also act as a vehicle for radionuclides if they are strongly adsorbed to the colloid surface (Missana *et al.*, 2002; Mayordomo *et al.*, 2016, this volume). The parameters affecting the erosion can be subdivided into those affecting the mechanical erosion and those affecting the colloidal properties of the smectites, which lead to the detachment of colloidal particles out of aggregates. Mechanical erosion can detach entire aggregates because the velocity of the flowing water is large enough to exceed the attractive forces holding bentonite aggregates in place. Therefore, erosion depends on the velocity of the water in the fissure (Pusch, 1999; Birgersson *et al.*, 2009). Recently, Svoboda (2013) found that erosion also depended on the aperture of the fissure. Colloidal detachment, however, may even take place in contact with static water. The detachment of colloidal particles depends on the ionic strength and the pH of the surrounding solution (Missana *et al.*, 2003). Those parameters affect the extent of the diffuse double layer and hence the interaction of the particles. A low affinity of smectite TOT-layers towards each other can lead to delamination and hence detachment of colloidal particles. Kaufhold & Dohrmann (2008) compared different bentonites with respect to the tendency to release colloidal particles in dilute systems of low ionic strength (Fig. 5).

Na-rich bentonites released far more colloidal particles than Ca/Mg-rich bentonites because of different hydration characteristics. With excess water Na-smectites tended towards infinite swelling which allows delamination and hence detachment of colloidal particles (*e.g.* Suquet *et al.*, 1975). Increased salinity and/or exchange of Na^+ by Ca^{2+}/Mg^{2+} from solution generally reduces the probability of detachment of colloidal particles. No effect of the layer-charge density of the smectites was observed. This issue is only relevant if flowing water is present in contact with the bentonite. Therefore, no general recommendation can be given. Recent up-scale tests showed quick equilibration of the interlayer cation population with
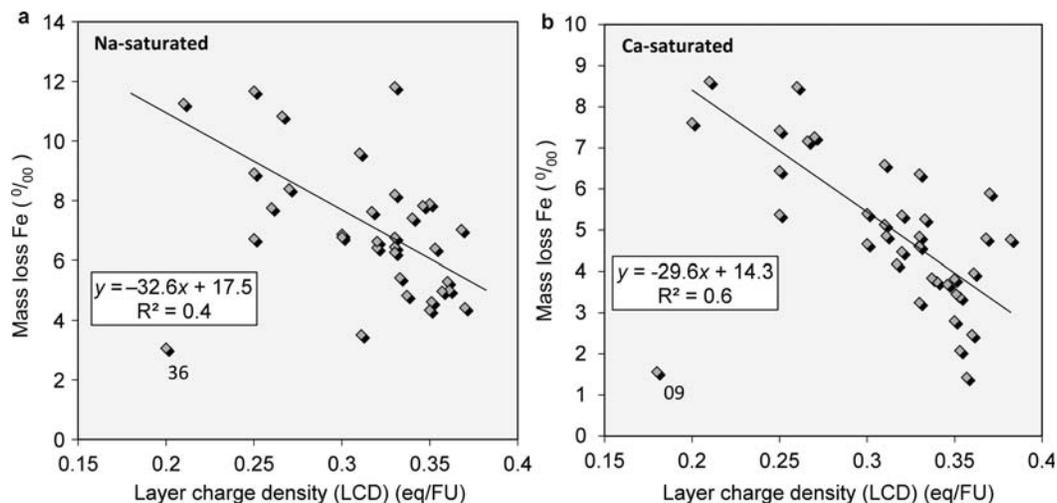
FIG. 4. Effect of smectite layer-charge density on the corrosion at the bentonite–iron interface (after Kaufhold *et al.*, 2015a).

the surrounding water (Dohrmann *et al.*, 2013b) and that the type of interlayer cation initially present is less important (van Geet & Dorhmann, 2016, this issue).

Issue 6 – stability in the presence of Na- and KCl-solutions

Intensive work has been carried out on the stability of bentonites in contact with different solutions. Particular focus has been placed on specific reactions leading to decreasing swelling capacity. The first reaction to consider is cation exchange. The interlayer composition (type and amount of exchangeable cations) will soon re-equilibrate if bentonite is in contact with saline waters. Such cation exchange processes are surprisingly fast, even in highly compacted bentonite blocks (Dohrmann *et al.*, 2013b). Cation exchange may affect physico-chemical and geotechnical properties such as swelling or hydraulic conductivity. These changes are reversible and hence do not represent a serious threat to the barrier system. At temperatures of >100°C, however, hydro-thermal reactions may alter the bentonites irreversibly (Pusch *et al.*, 1995) probably by dissolution of smectites and precipitation of non-swelling minerals. Reduction of the smectite content generally leads to
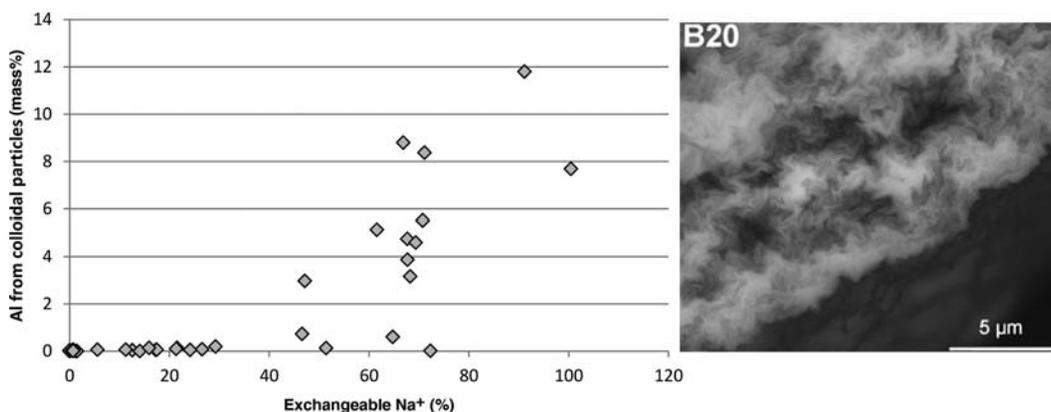

FIG. 5. Comparison of the amount of exchangeable Na$^+$ with aqueous Al^{3+} used as a measure of the concentration of colloidal particles in suspension. The colloidal particles belong to smectitic layers (after Kaufhold & Dohrmann, 2008).

lower swelling and hence lower sealing capacity. Suzuki *et al.* (2008) reported irreversible changes (reduction of CEC and precipitation of brucite) at 90°C. The reactivity of the bentonites in this respect is variable and probably depends on the chemical stability of different smectites. To investigate the influence of different, smectites, Kaufhold & Dohrmann (2009) reacted a set of different, well characterized bentonites with a 6 M NaCl solution at 60°C for 5 months. As expected, exchange of Ca^{2+} and/or Mg^{2+} for Na^+ was observed. The extent to which the cation exchange occurred depended on carbonate abundance. Bentonites containing at least partly soluble carbonates (*e.g.* calcite) contained less exchangeable Na^+ after the long-term test than their carbonate-free counterparts, suggesting that the presence of carbonates buffers cation exchange reactions to some extent.

The similar CEC values before and after the NaCl long-term test indicates the absence of irreversible mineral alteration reactions (Fig. 6). After a similar test conducted with KCl, however, an average decrease in the CEC values of ~10% was recorded (Kaufhold & Dohrmann, 2010b; Fig. 6).

Unlike Na^+, K^+ may be fixed by smectite, finally resulting in illite-like layers. Due to the importance of the illitzation of smectite for the oil industry, a vast amount of data on illitization is available (*e.g.* Hower *et al.*, 1976; Boles & Franks, 1979; Eberl *et al.*, 1986; Eberl *et al.*, 1993; Bauer & Velde, 1999; Mosser-Ruck *et al.*, 2001; Meunier & Velde, 2004; Honty *et al.*, 2004; Kaufhold & Dohrmann, 2010b, among many others). These studies suggest that the addition of K^+ to smectite may cause illitization. The mechanism of illitization, however, is still under discussion, and both solid-state transformation and dissolution (of smectite) and precipitation (of illite) have been considered. According to Kaufhold & Dohrmann (2010b), care is needed with respect to interpretation of experimental illitization tests because the appearance of a 10 Å diffraction maximum is not sufficient to identify illite *sensu stricto*. Those authors concluded that a multi-method approach is required for the characterization of the KCl reaction products because of the existence of non-swelling clay minerals with CEC. Illitization may occur if K is available in the system because smectite becomes unstable in the presence of K and illite forms, probably mainly by dissolution/precipitation. Based on long-term tests, Kaufhold & Dohrmann (2010b) identified differences in the reactivity of bentonites with respect to illitization. Similar to the drying experiments (issue 2) the batch experiments showed

that the CEC of some bentonites decreased more, and hence they were more reactive than others. The reason for these differences, however, is not understood yet.

Issue 7 – retention of radionuclides

An additional desired property of the bentonite is the capacity to adsorb radionuclides released by the HLRW in the canister. If the canister fails, different species of radionuclides would enter the bentonite, which might be adsorbed at the mineral surfaces and hence might be retained. However, a large number of different radionuclides must be considered. The interaction of smectites with different radionuclides has been studied extensively ([60]Co: Omar *et al.*, 2009; [241]Am: Basuki & Muzakky, 2010; [137]Cs: Basuki & Muzakky, 2010; Kerisit *et al.*, 2016; Seliman *et al.*, 2014; Eu: Seliman *et al.*, 2014; [90]Sr: Basuki & Muzakky, 2010; Seliman *et al.*, 2014; [99]Tc: Dejun *et al.*, 2004; U: Bachmaf *et al.*, 2008, Khalili *et al.*, 2013; Th: Khalili *et al.*, 2013). Depending on the different charge densities/charge distributions and/or chemical compositions of the smectites, the bentonites are supposed to differ with respect to their adsorption selectivities (Tournassat *et al.*, 2016). Therefore, it is difficult to decide if the bentonite with greater selectivity towards, *e.g.* a special uranium species, or that with a slightly greater selectivity towards, *e.g.* cesium, is more suitable as a HLRW bentonite. Moreover, the differences are small. To assess whether one bentonite is superior to another with respect to radionuclide retention, a ranking of the danger of the different radionuclides would need to be established. However, Oscarson *et al.* (1986) stressed the importance of [129]I amongst all other radionuclides. Iodide, however, would not be retained by a normal bentonite. To improve the affinity of a bentonite towards anions, the surface would have to be modified. Bors *et al.* (2000) suggested the use of organophilic bentonite for iodide retention. This idea was developed further (Dultz & Bors, 2005; Riebe *et al.*, 2005; Kaufhold *et al.*, 2007). On the other hand, organic matter would be introduced into the system. Several studies have been carried out on the interaction of different radionuclides with modified bentonites (*e.g.* Simsek & Ulusoy, 2012; Majdan *et al.*, 2010) suggesting that the affinity of the bentonite towards a specific radionuclide may be modified. The slightly different radionuclide adsorption of the different bentonites is less important and hence plays a minor role with respect to the selection of an ideal HLRW bentonite.
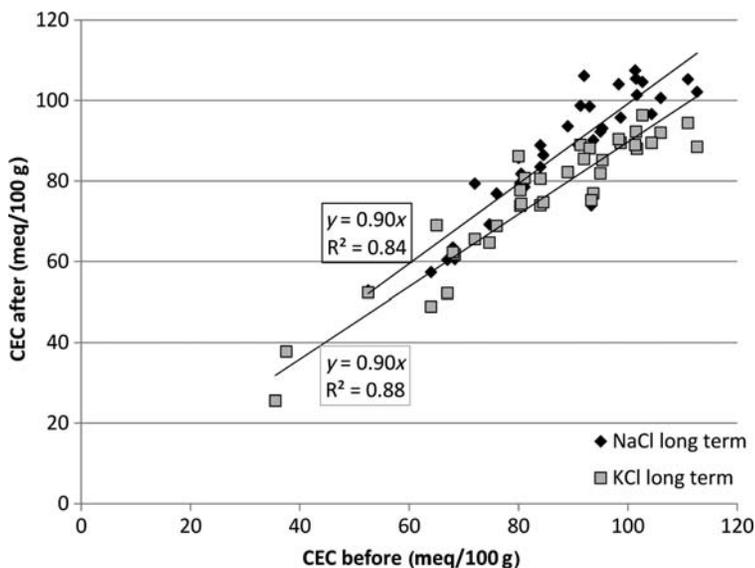
Fɪɢ. 6. Comparison of the CEC before and after long-term reaction with NaCl (diamonds) and KCl (squares) at 60°C for 5 months (reproduced from Kaufhold & Dohrmann, 2009, 2010b, with the permission of Elsevier).

Issue 8 – mechanical stability (canister displacement)

The entire integrity of the multi-barrier system can only be guaranteed if all components remain intact. A theoretical earthquake might cause severe damage to the multi-component system and change the relative arrangement of the barrier components. However, details of such a scenario are difficult to predict, even after modelling. In the case of displacement occurring, large swelling pressure will facilitate the sealing of the voids generated. Apart from the earthquake issue, the canister could sink into the bentonite because of the plasticity of the bentonite. According to Sellin & Leupin (2014) a minimum swelling pressure of 0.1 MPa is sufficient to keep the canister in place and minimize friction. This issue, therefore, is not considered to be important, mainly because the desired swelling pressure should be much larger than 0.1 MPa in any case. Note that, because of the danger of damaging the canister, the swelling pressure should not exceed a critical value which depends on the host rock and the barrier concept. An ideal bentonite should hence provide a swelling pressure between the minimum and maximum values over a large range of dry densities. These requirements, however, vary from one concept to another and, hence, cannot be applied generally. As noted previously, the swelling pressure of a specific bentonite can be tailored by the compaction

and, to a much lesser extent, depends on the type of bentonite. An additional parameter which could be considered in this respect is the shear strength (Börgesson *et al.*, 2010; Dueck *et al.*, 2010) which depends significantly on the compaction but may also differ from one bentonite to another. The mechanical properties can be tailored by compaction and hence no bentonite specifications can be derived from issue 8.

Issue 9 – large thermal conductivity

Thermal conductivity should be as high as possible, because the heat emitted by the canister should dissipate from the system. The thermal conductivity of bentonite depends mainly on the porosity and degree of water saturation rather than the mineralogical composition. Air-filled porosity is a thermal insulator and water has a much larger thermal conductivity. Varying both parameters in a bentonite, Hökmark (2002) reported a linear relation between thermal conductivity and the degree of saturation with a thermal conductivity of 1 W/m/K at 60% saturation. For bentonites, typical values of ∼1 W/m/K were reported and different reasons for the observed variability were proposed such as water content and relation to bedding (Schärli *et al.*, 2004), water content and ambient pressure (Knutsson, 1983), degree of saturation (Villar, 2002) and particle–particle contacts (Plötze *et al.*, 2007).

The effect of the type of bentonite on the thermal conductivity is determined by the quartz content which has a significantly larger thermal conductivity than the other components (Clauser & Huenges, 1995). At a given degree of water saturation the thermal conductivity of a quartz-rich bentonite is larger than materials with less quartz. Therefore, to improve the thermal conductivity in some concepts, quartz is added to the bentonite (Jobmann & Buntebarth, 2009). For real applications, mixing quartz and bentonite is not feasible because several low-grade bentonite deposits exist, in which 50% smectite occurs along with 50% accessory minerals, mainly quartz. In conclusion, for the selection of a highly thermally conducting bentonite, a large quartz content is desirable. However, as the abundance of non-swelling, relatively inert quartz increases, other desired properties deteriorate (*e.g.* swelling pressure). The thermal conductivity of normal bentonites with quartz contents of <20 mass % depends mainly on the compaction and hence more on the production than on the type of material. A further alternative would be to select a smectite-rich material and add *e.g.* graphite, as suggested by Pacovsky *et al.* (2007) and Vašíček (2007). However, in this case an additional component is introduced to the system which may produce gas (species depends on availability of O_2) or participate in mineral alteration reactions or even corrosion. The differences in the thermal conductivity of different bentonites depend on the quartz content. The thermal conductivity of high-grade (low-quartz) bentonites depends more on water content and dry density than on the type of bentonite. No generally valid specifications can therefore be derived from issue 9.

Issue 10 – stability against radiation

Few studies in the past have investigated the possible degrading effect of radioactivity on the structure of the bentonite. The applied dose is very significant and has to be considered when comparing the published results. Irradiation with 1.1 MGy γ radiation increased the number of point defects but did not affect the geotechnical properties (Plötze & Kahr, 2002; Plötze *et al.*, 2003). These results are in agreement with those of Sorieul *et al.* (2002) who applied 100 MGy β radiation. Sorieul *et al.* (2008) showed that high temperature (300–400°C) in combination with large irradiation dosages may lead to partial amorphization. The expected dose for serious structural damage is too low (Pusch *et al.*, 1993; Sellin & Leupin, 2014). To affect the bentonite seriously, α radiation has to be in direct contact with the bentonite because of the limited penetration depth of the α nuclei. Fourdrin *et al.* (2010) applied a 73 MGy (dose significantly larger than that expected in the repository) to a bentonite (direct contact) and observed serious structural damage. Structural Fe may play a special role with respect to radiation effects and may, at least, be reduced (*e.g.* ferric to ferrous iron, Plötze *et al.*, 2003; Sorieul *et al.*, 2008). In summary, the data published to date suggest that the effect of radioactivity on the bentonite will be relevant only in a worst-case scenario (Fourdrin *et al.*, 2010) and that structural Fe may be more prone to radioactivity-induced changes than other structural cations.

DISCUSSION AND CONCLUSIONS

The aim of the present study was to identify favourable and unfavourable properties of bentonites in HLRW repositories. The bentonite requirements differ significantly from one concept to another which concerns geotechnical parameters such as minimum and maximum swelling pressure or thermal conductivity in particular. From an engineering point of view the compaction of the bentonite can be used to tailor the bentonite performance. In contrast, especially considering the stability of the bentonite, a few aspects were identified allowing for preliminary discussion of potential HLRW specifications.

Similar to the commonly used landfill bentonites, the ideal HLRW bentonite should contain only a few soluble/partly soluble components such as halite and gypsum because their dissolution may change the dry density locally and participate in other reactions (*e.g.* redistribution of gypsum) which would not occur if they were absent (Karnland *et al.*, 2009). Similar reactions could occur for less soluble but not unreactive phases such as cristobalite, zeolites, amorphous silica, and eventually iron oxyhydroxides. Furthermore, sulfur, either from the surrounding water or from gypsum or pyrite dissolution, might participate in the corrosion of Cu (Karnland *et al.*, 2009), and pyrite oxidation may lead to H_2S formation and increase microbial feed as well as gas pressure. Hence, the gypsum and pyrite contents should be as small as possible. The presence of minor calcite is less serious because it is scarcely involved in redox-reactions. Calcite could even buffer cation exchange reactions (Kaufhold & Dohrmann, 2009) which in turn would reduce the risk of erosion. Organic matter should also be absent because it supports microbial growth and produces gas upon decomposition. Notably, the absence of the above-mentioned comparably

reactive minor constituents possibly present is one of the key specifications of bentonites used for the production of geosynthetic clay liners used in landfills.

Secondly, the hydraulic conductivity should be as low as possible. Despite existing differences in terms of the hydraulic conductivity of different bentonites it can be tailored by compaction, which in turn affects the swelling pressure. Hence the hydraulic conductivity/ swelling pressure of a given bentonite can be adjusted to the desired values. Nevertheless, rather different dry density/swelling pressure/hydraulic conductivity relations were observed. The most suitable materials would be those with least dependence of hydraulic conductivity and swelling pressure on the dry density. However, comparative studies allowing for the selection of the least sensitive bentonites in this respect have yet to be carried out.

At low dry densities, the swelling pressure of Na-rich bentonites is larger but this can be compensated by compaction (Pusch *et al.*, 1995). Otherwise, Ca(Mg) as the dominant exchangeable cation has some advantages over Na. It buffers alkaline pH values more effectively than Na-rich bentonites, which is relevant for the cement plug interface. In addition, Ca-rich bentonites do not tend to release colloidal particles as Na-bentonites do. Furthermore, the larger selectivity of Ca(Mg) towards the interlayer and the fact that most host-rock waters do contain some Ca will cause fast cation exchange if Na-bentonites are contacted with such solutions (Kaufhold *et al.*, 2013; Dohrmann *et al.*, 2013b). A general recommendation of the type of exchangeable cation initially present may be redundant because of the fast equilibration of the bentonite with the surrounding water. Depending on the barrier concept and particularly on the amount of rock water in contact with the bentonite barrier, the selection of the type of exchangeable cation is only relevant for the early phase of the buffer. In the Äspö rock laboratory the cation exchange (equilibration with rock fluids) was fast (Dohrmann *et al.*, 2013b) so that the cation initially present was less important than the composition of the host-rock water. The pH-buffering effect discussed above, however, is also more important in the early stages of the barrier because of the particularly high pH of the cement fluids at the beginning. Again, the specific requirements of specific repositories have to be taken into account and a general statement cannot be given.

With respect to Fe corrosion, medium–high-charged bentonites should be preferred (Kaufhold *et al.*, 2015a). Finally, structural Fe can be considered to be a weak point in the smectite structure. The Fe can be reduced either by microbial activity or even by radioactive radiation, thereby increasing its solubility. Ferric iron can also contribute to corrosion because it is an electron acceptor and the thermal stability of bentonites rich in structural Fe is lower.

In summary, the ideal HLRW bentonite should: be almost free of soluble or reactive (mainly C- and S-) phases such as gypsum, pyrite, organic matter; be low in structural Fe; and contain medium–high-charged smectites if iron canisters are used.

The importance of each specification varies from one concept or repository to another. Therefore, each of the key issues has to be assessed individually and no general ranking of the relative importance can be given. Using bentonites other than suggested does not mean that a repository may not be safe. However, using a bentonite within the above-stated specifications reduces the overall uncertainty and hence results in improved long-term barrier performance.

The preliminary specifications presented above are expected to be complemented by additional specifications depending on the results of ongoing research and have to be proven in large-scale experiments in the host rocks to be used. As explained above, the identification of bentonites with low dependency of swelling pressure/hydraulic conductivity on the dry density would improve the barrier performance. In this respect, additional research is needed to complement the specifications listed above. Of further scientific interest would be the identification of the reason for different reactivities. In different tests, similar trends towards the tendency to lose or keep the CEC of different bentonites were found. Hence, a bentonite which displayed considerable loss of its CEC after extensive drying also displayed loss of much of its CEC after the reaction with KCl or NaCl solutions. Yet no explanation for this trend was found. Explanations could be the solubility of the smectite which depends on the chemical composition, or degree of structural order, probably in combination with particle size. The identification of the reason for these differences would also complement the specifications given above.

Some of the properties–performance relations of bentonites are not yet fully understood. Therefore, using a bentonite which has been investigated extensively over many years is likely to bear less uncertainty compared to unknown materials.

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