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Abstract: The Danish Tertiary Holmehus clay belongs to the series of illite-smectite mixed-layer clays in northern Europe and has a potential to serve as an effective engineered barrier for isolating hazardous waste. Mineralogical specification was made of the components illite/smectite mixed-layer and dioctahedral vermiculite/smectite mixed-layer structures. The lower content of expandable phase than of smectite-rich clays like MX-80 gives somewhat higher hydraulic conductivity and somewhat lower swelling pressure but both are deemed suitable for isolating canisters with high-level radioactive waste in deep repositories for densities at water saturation of at least 1900 kg/m³. The lower swelling pressure, the potential of being chemically more stable, and the high buffer capacity by providing dissolved Si makes Holmehus clay a candidate for use in both deep and near-surface repositories.

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Holmehus clay – A Tertiary smectitic clay of potential use for isolation of hazardous waste

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Highlights

- Holmehus clay belongs to a series of illite-smectite mixed-layer clays
- Originally, Holmehus is more permeable and less expandable than MX-80
- However, smectitization during saturation can improve their barrier performance
- Additionally, Holmehus' high Si-buffer capacity protects it from cementation by Si
- The low alteration potential makes Holmehus suitable for isolating hazardous waste

Holmehus clay – A Tertiary smectitic clay of potential use for isolation of hazardous waste

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12

13 **ABSTRACT**

14 The Danish Tertiary Holmehus clay belongs to the series of illite-smectite mixed-layer clays in
15 northern Europe and has a potential to serve as an effective engineered barrier for isolating
16 hazardous waste. Mineralogical specification was made of the components illite/smectite mixed-
17 layer and dioctahedral vermiculite/smectite mixed-layer structures. The lower content of
18 expandable phase than of smectite-rich clays like MX-80 gives somewhat higher hydraulic
19 conductivity and somewhat lower swelling pressure but both are deemed suitable for isolating
20 canisters with high-level radioactive waste in deep repositories for densities at water saturation of
21 at least 1900 kg/m³. The lower swelling pressure, the potential of being chemically more stable,
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23 in both deep and near-surface repositories.

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25 conductivity; Swelling pressure; Si-buffer capacity

26

27 **1. Scope**

28 Smectitic clays are of great importance for isolating hazardous landfills including low-
29 level radioactive waste and for underground disposal of intermediate- and high-level radioactive
30 waste. A number of clays of this type have been examined by several investigators, which has led
31 to refinement of laboratory techniques and to considerable experience in constructing and testing
32 clay seals. The first commercial smectite-rich clay that was systematically investigated with
33 respect to its capability to isolate hazardous waste was American Colloid's brand MX-80. It has
34 served as reference clay since 1976 for various organizations that are responsible for such
35 isolation and is referred to here for comparison with Holmehus clay, which is in focus of the

present report. It represents mixed-layer illite/smectite clays, which appear to be more stable under hydrothermal conditions than smectite-rich clays and which have been found to undergo less degradation in contact with concrete of ordinary type (Pusch et al., 2003; Xiaodong et al., 2011). According to Foged & Bauman (Heilmann-Clausen et al., 1985), the Holmehus clay belongs to a Paleocene (Tertiary) formation that also comprises the Danish Æbelö and Rödbyhavn clays. Holmehus clay is composed mainly of weathered material from the Baltic area. After sedimentation it underwent diagenetic processes.

The present investigation comprised identification of the mineralogy and chemical constitution of the Holmehus clay and determination of its geotechnical properties. The paper ends with a brief discussion of possible applications of the Holmehus clay for isolating hazardous waste.

2. Methodology

2.1. Analytics

Determination of the mineral composition of Holmehus clay has been made by X-ray diffraction (XRD) analysis of randomly oriented powder of bulk samples including Rietveld refinement for semi-quantitative determination of essential mineral components by BGMN-software package, XRD-analysis of oriented samples of < 2 µm material in air-dry and ethylene-glycol-treated forms for identification of expandable clay minerals. The study also included X-ray fluorescence (XRF)-analysis of 26 elements including LOI, and cations exchange capacity (CEC) for determination of exchangeable Na, K, Mg and Ca, transmission electron microscopy (TEM)-examination of < 2 µm for shape characterization. Derivation of the mineral formula for the clay minerals comprised Fourier transform and infrared spectroscopy (FT-IR)-examination

for certifying XRD- and TEM-results respecting the octahedral and tetrahedral constitutions of the smectite.

Bulk samples were ground to $< 32 \mu\text{m}$ for XRD-investigation using a Philips PW1710–BASIS X-ray diffractometer equipped with a Cu tube ($K\alpha_{1,2}$ radiation) as well as a secondary monochromator. It operated at a current of 30 mA and a voltage of 30 kV (fixed divergence slit: 1° ; collimator: 0.2; measured interval: $3.0\text{--}63.0^\circ 2\theta$; measurement step: $1^\circ 2\theta/\text{min}$; continuous scan). The WinFit program (Krumm, 1994) was used for analyzing the line-profiles of clay minerals with broad and strongly overlapping XRD peaks and coherent scatter domains for approximating the particle thickness distribution. The BGMN program, which is based on Rietveld methodology, was used for the quantification and further characterization of each identified phase (Bergmann et al., 1998; Ufer et al., 2004; Ufer et al., 2008; Kleeberg & Ufer, 2010).

TEM investigations were carried out on the $< 2 \mu\text{m}$ fraction using a TECNAI G² 20 electron transmission microscope at the Hanoi University of Science, Vietnam National University, Hanoi. This equipment operated at 200 kV with a LaB₆-cathode and S-TWIN objective and was equipped with an EDAX energy-dispersive X-ray (EDX) system and a FEI Eagle™ 2k CCD TEM camera, which allowed characterization of morphology, crystal habit, and stack order (by electron diffraction) of the particles as well as to obtain element distribution images. Selected particles were analyzed chemically (semiquantitative data) by EDX, which allowed calculation of mineral formulae using the software toolkit of Kasbohm et al. (2002).

In this context, illite, recognized during the TEM investigation, is here referred to as illite in the sense of Środoń et al. (1992), i.e. conforming to the following structural formula of illite in *sensu stricto*:

where FIX represents fixed K+Na cations in the interlayer space. Furthermore, K- and/or charge-deficient dioctahedral micas, with tetrahedral Si ranging from 2.8 to 3.3 per $O_{10}(OH)_2$, are termed dioctahedral vermiculite. The acronyms “IS-ml” and “diVS-ml” refer to illite/smectite mixed-layer and dioctahedral vermiculite/smectite mixed-layer, respectively.

Samples were milled to $< 63 \mu m$ and dried at $40^\circ C$ before XRF measurement. Analysis was carried out on KBr-pressed pellets using a wavelength dispersive Phillips PW 2404 X-ray spectrometer with 10 mA current and 20 kV voltage. The results of the XRF-method were used to characterize the chemical composition of the clays as well as to verify the results of Rietveld-refinement by BGMN.

FT-IR spectra were taken of KBr-tablets (10 g sample was mixed with 990 mg KBr Uvasol) with recording of the mid-infrared range (400 cm^{-1} to 4000 cm^{-1}) using a MATTSON 3020 FT-IR spectrometer with 64 scans and 4 cm^{-1} resolution. The FT-IR-spectra were deconvoluted by Origin Pro 8.5 Peak Fitting. Gaussian distribution functions were applied with the aim of smoothing the spectra and providing the exact values of peak position, FWHM, intensity and area. The baseline corrections of 970 cm^{-1} and 720 cm^{-1} region were subtracted by the same software. The accuracy of decomposition is evaluated to be $R^2 > 0.98$.

CEC was measured using Cu-triethylenetetramine (Cu-trien) in accordance with Dohrmann & Kaufhold (2009) meaning that the CEC-result is related to the mass of Holmehus clay dried at $105^\circ C$. Additionally, ICP-AES was used for determination of the exchanged cations in the supernatant solution after the exchange with copper triethylenetetramine (after 2 hours shaking).

Additionally, overhead rotation experiments were carried out in order to simulate alteration of Holmehus clay (Nguyen-Thanh, 2012). The clay samples were ground to $<40 \mu m$ and saturated for 30 days at room temperature at a liquid:solid ratio of 50:1 in deionized water.

The resulting soft gels were mechanically agitated at room temperature by overhead rotator in 5 ml tubes at 5 or 20 revolutions per minute (rpm). This experiment implies that raising the speed of overhead rotator, increases the removal of dissolved elements from the parent particles.

2.2. Geotechnical experiments

The geotechnical properties were determined by conducting oedometer tests for evaluation of the hydraulic conductivity and swelling pressure for two types of porewater (distilled water and 3.5% CaCl₂ solution) and typical densities.

3. Mineralogical investigations of untreated clay

3.1. X-ray diffraction (XRD)

XRD-powder diffractogram of a bulk sample (Figure 1) and semiquantitative evaluation by BGMN-Rietveld refinement have shown dominance of IS-ml (55%), muscovite of 2M₁-polytype and quartz (Table 1). Small amounts of chlorite and feldspars were also found as well as traces of anatase, pyrite, gypsum and jarosite.

The IS-ml phases were fully expandable to 17 Å spacing by ethylene glycol saturation treatment (Figure 2). The fitting process of XRD spectra for the < 2 µm fraction made it possible to identify two groups of illite-smectite-interstratifications as main clay components of Holmehus clay (Figure 3). Following Moore & Reynolds (1997) comparison of the distances between the 001/002- and 002/003-interferences, showed that the smectite layer-fraction of the IS-ml was 60 % and that the diVS-ml was 20-25%.

130

131 **3.2. Transmission electron microscopy (TEM)**

132 The two mixed layer phases in fraction $< 2 \mu\text{m}$ were characterized by two morphological forms:
133 (i) xenomorphic flakes, probably products of diagenetic alteration; and (ii) laths with idiomorphic
134 ends (probably detrital material originating from weathered crust). Lath-like particles are
135 enriched in fraction $< 0.5 \mu\text{m}$.

136 The TEM-EDX analyses showed that the IS-ml structures make up 45 frequency-% and
137 the diVS-ml phases make up 15 frequency-% in Holmehus clay. The rest was found to consist of
138 quartz (18 frequency-%) and Fe- as well as Ti-phases. The content of smectite layers (S%) in IS-
139 ml was 60% and for the diVS-ml was 30% (Table 2), i.e. somewhat more than indicated by the
140 XRD analysis. The two mixed layer-series were characterized by high Fe-rich octahedral sheets
141 and distinguished mainly by remarkably different tetrahedral compositions (Table 2).

142 The same trend in composition of octahedral and tetrahedral sheets has been recognized
143 for Friedland clay from the places Siedlungsscholle and Burgscholle in Mecklenburg-Western
144 Pomerania. Friedland clay is also a diagenetically altered sediment like Holmehus clay composed
145 of weathered material of the same parent rocks.

146 MX-80 bentonite differs from the Holmehus and Friedland clays by its high octahedral Al
147 content and by having montmorillonite as main expandable clay phase (Table 2).

148

149 **3.3. Chemical composition**

150 The element composition of Holmehus clay and MX-80 is given in Table 3. The cation exchange
151 capacity of Holmehus clay was found to be 29.7-31.6 meq/100 g (using Cu-triethylenetetramine-
152 method (Dohrmann & Kaufhold, 2009)). MX-80 typically has 90 meq/100 g.

153

154 **3.4. Particle morphology**

155 Smectite of Na montmorillonite typically shows interwoven stacks of 3-10 lamellae with
156 10 Å thickness and they were also found in the Holmehus clay that also contains xenomorphic
157 flakes as indicated in Figure 4.

158

159 **4. Geotechnical properties of Holmehus clay**

160 **4.1. Test program**

161 The examination comprised determination of the grain size distribution by sieving after
162 crushing and milling air-dry raw material, and determination of hydraulic conductivity and
163 swelling pressure of crushed and milled clay compacted in 50 mm oedometer cells for
164 subsequent percolation with distilled water and 3.5% CaCl₂ solution in parallel tests.
165 Furthermore, overhead rotation experiments in deionized water were made as a simple practical
166 way of identifying mineralogical alteration processes.

167

168 **4.2. Grain size distribution**

169 Sieving of crushed and milled material that had been dried at 60 °C gave a composition
170 with maximum 2 mm grain size and 40 % smaller than 0.063 mm. The material was used for all
171 the geotechnical investigations.

172

173 **4.3. Hydraulic conductivity**

174 The conductivity was evaluated from percolation tests with a hydraulic gradient of 100-
175 300 m/m (meter water head per meter flow length) using Darcy's law. This gradient causes less

microstructural disturbance and gives more accurate conductivity data than testing under the 30 to 100 times higher gradients used by most other investigators (Al-Taie et al., 2014) (Figures 5, 6).

Comparison with smectite-rich MX-80 montmorillonite clay (Table 4) shows that Holmehus clay saturated with electrolyte-poor water is up to 5 times more permeable than MX-80 for a density of 1675 to 1900 kg/m³. For this density interval Holmehus clay saturated and percolated by 3.5% CaCl₂ solution is up to 10 times more permeable than MX-80. The smaller effect of salt porewater on the hydraulic conductivity of Holmehus than on MX-80 by for the same density interval is believed to be due to the larger amount of collapsible clay gels in the latter.

4.4. Swelling pressure

The swelling pressure was measured in the course of the water saturation process (Table 5). Comparison with smectite-rich MX-80 montmorillonite clay shows that Holmehus clay saturated with electrolyte-poor water has a swelling pressure that is around 50-100% of that of MX-80 for a density of 1675 to 1900 kg/m³. For this density interval Holmehus clay saturated with 3.5% CaCl₂ solution has a swelling pressure that is also about 50-100 % of that of MX-80. The lower pressure of Holmehus clay saturated with distilled water and salt solution than of MX-80 is because of its lower content of expandable minerals.

4.5. Overhead rotation experiments

Overhead rotation experiments should offer indications about the development of alteration processes in contact with water. The two reaction products have shown a disaggregation of particles. This observation was valid for the platy and also for the lath-like

smectite-bearing structures (Figure 7). Furthermore, the IS-ml and diVS-ml phases in the reaction products were characterized by an altered chemical composition in octahedral and tetrahedral layers as well as in interlayer space (Table 6). Al-enrichment and reduction of Fe and Mg were typical processes in the octahedral sheet. At the end of the treatment the tetrahedral sheet showed a reduced charge deficit, hence indicating smectitization. Especially Na and Mg have substituted K in interlayer space to a remarkable extent. The same changes in the octahedral and tetrahedral sheets of the reaction products were recognized also in comparable experiments with Friedland clay by Nguyen-Thanh (2012).

5. Longevity

5.1. General

The most important matter concerning use of smectitic clays for isolating hazardous waste like radioactive rest products is that the clay seals must operate according to given criteria for a given time that can be from a few hundred years to a hundred thousand years. It has been in focus for a long time and led to the conclusion by various investigators that smectite-rich clays like the commercial MX-80 will stay largely intact for very long periods of time under the hydrothermal conditions that will prevail in repositories (Pusch & Yong, 2006). The threat is basically that exposure of the clay to temperatures of up to 150 °C for several decades in salt environment can cause dissolution of the swelling minerals and thereby loss of tightness, expandability and self-sealing ability of the clay (Pusch et al., 2013). Precipitation of dissolved elements can take place in the long subsequent cooling period by which cementation will occur, causing further reduction of the expandability that has to be preserved for maintaining tight contact with the surroundings. These can be rock or concrete constructions, which makes it necessary to consider chemical interaction of clay and cement and degradation of both (Pusch et

al., 2003). In following, the various degrading mechanisms in hydrothermally treated smectite clay are confined here for assessing the function of montmorillonite-rich clay (MX-80) and illite-smectite mixed-layer clay (Holmehus) in waste repositories.

5.2. Hydrothermal impact on “buffer clay”

5.2.1. Practical cases

Clay material that is planned to embed canisters with highly radioactive waste in the form of spent fuel, i.e. buffer clay, must have a low hydraulic conductivity and be dense enough for carrying the up to 25 ton heavy canisters (Figure 8). The criteria are that the conductivity should be lower than that of the rock surrounding the deposition holes ($K < 10^{-11}$ m/s), and that the swelling pressure, interpreted as preconsolidation pressure, must be higher than the contact pressure exerted by the canister load (0.3 MPa). One finds from Tables 4 and 5 that the required density of salt-water saturated MX-80 and Holmehus clay is about 1,900 kg/m³. The question is, however, if the clays still fulfill the criteria after a period of at least 10,000 years. The most harsh conditions are represented by the “deep-hole” concept according to which the temperature can be up to 150°C and the salinity higher than that of the oceans (Pusch et al., 2013). The canisters being in contact with the clay can be made of copper or steel.

5.2.2. Present views on the degradation of smectite “buffer” in a repository

The open reaction system represented by the overhead rotator would indicate ‘illitization’ but the smectite-bearing components in Holmehus clay have instead led to smectitization by the agitation (Table 6), in complete agreement with earlier studies of Friedland clay (Table 6). The mechanisms involved in the conversion of smectite yielding illitization and smectitization have been investigated by Herbert et al. (2011) and Nguyen-Thanh (2012). They focused on the

interaction of smectite-rich clay and iron identifying mineralogical reactions in laboratory experiments of compacted smectitic clays interacting with iron powder for simulating the contact of “buffer” clay bentonite with steel containers. These experiments included overhead rotation experiments on a large number of smectite-bearing clays and led to the conclusion that different smectite clays have specific dissolution potentials. These investigators called smectite with low dissolution potential “Sleeper” and smectite with high dissolution potential “Sprinter”. This specific dissolution potential can also explain the different conversion paths also for the Holmehus and MX-80 clays. As long as the amount of dissolved Si does not exceed the Si-loss driven by permeation of the physically and chemically open system, the alteration process leads to ‘illitization’, while smectitization is the dominating alteration mechanism if more Si is dissolved than lost. Considering this one concludes that clays composed of illite-smectite mixed layer structures buffer dissolved Si and illite layers become converted to smectite layers. The process reduces the tetrahedral charge deficit which represents smectitization. This mechanism was identified in open systems like overhead rotation and percolated batch experiments and is applicable also for close systems. Close systems represent here only a special case of open systems even with a zero flow rate.

5.2.2.1. Major outcome for Holmehus clay from the hydrothermal impact

Applying the “Specific Dissolution Potential”- and “Si-buffer”-concepts of Herbert et al. (2011) and Nguyen-Thanh (2012), Holmehus clay has shown only the low dissolution potential of “Sleepers” by low-intensity treatment, i.e. a rotation speed of 5 rpm (Table 6), while the increased energy input by 20 rpm rotation changed the Holmehus clay into a “Sprinter”. The high amount of dissolved Si exceeded the loss of this element by the treatment, hence causing smectitization. The comparison with Friedland clay indicated that further increase of the energy input (60 rpm) would continue the smectitization process in Holmehus clay (Table 6).

The observed disaggregation of particles by overhead rotator (Figure 7) and the recognized high Si-buffer capacity of Holmehus clay (Table 6) suggest that the barrier performance of Holmehus clay may be improved in the hot environment of deposition holes in repository holes, which represent chemically closed conditions early after emplacement.

5.2.2.2. Alteration of smectite in the vicinity of hot canisters

The high temperature of the buffer clay promotes higher chemical reactivity simulated by the stronger mechanical agitation in the overhead rotation experiments. Smectitization of Holmehus clay is therefore expected to be the main alteration process even under higher temperature because of the low flow rate in the barrier system as indicated by experiments with native iron in contact with compacted MX-80 bentonite and Friedland clay at 90°C (Herbert et al. 2011).

5.2.2.3. Expected behavior of Holmehus clay by hydrothermal experiments under thermal gradients

Xiaodong et al. (2011) exposed confined MX-80 bentonite and Friedland clay samples to considerable thermal gradients that drove porewater through the tested samples. This caused salt accumulation in the most heated parts and differences in density in all parts. In contrast to Friedland clay, MX-80 clay had undergone considerable changes, particularly in the form of a very significant loss of swelling pressure and a rise in hydraulic conductivity by 100 times in the hottest part. The central and cold parts were also significantly changed with respect to conductivity but they retained their expandability. The swelling pressure of the mixed-layer clay had dropped significantly in the hottest part but only slightly in the central and cold parts. The hydraulic conductivity of the hot part was about 50 times higher than of virgin clay but remained

unchanged in the central and cold parts. The most heated clay parts had undergone slight dissolution and minor precipitation of siliceous material can had taken place causing cementation and partial loss of expandability. Copper, forming the heated ends of the hydrothermal cells, had dissolved and migrated by more than a millimeter into the clay by diffusion in a few weeks (Kasbohm et al. 2013).

The small degrading impact of the hydrothermal treatment on MX-80 bentonite respecting the mineral composition shows that it performed as a “Sleeper” while the obvious cementation by precipitated Si as documented by considerable stiffening in compression tests, demonstrated that the tetrahedral Si in montmorillonite offered only a low Si-buffer capacity. Such impact on Friedland clay was significantly lower because of its higher Si-buffering capacity.. Experiments by Herbert et al (2011) with Friedland clay have shown that the swelling pressure and permeability of this clay and MX-80 bentonite with admixed native Fe at low concentration for 25°C, 60°C and 90°C are less permeable when the swelling pressure increases but that this is no longer the case for high Fe^0 -concentration and temperatures at 90°C. Cemented aggregates caused decreasing permeability by clogging voids and decreasing swelling pressure. Breakage of cemented aggregates raised the permeability without decreasing the swelling pressure at further increased reactivities.

In the light of these experiments the hypothesis of more effective Si-buffering of mixed-layer S/I clays one concludes that the Holmehus clay, being similar to the Friedland clay, will perform acceptably as buffer clay also because of its character as “Sleeper” in case of low chemical reactivities.

6. Conclusions

The general conclusion from the study is that smectite/illite mixed-layer clays of the presently examined kind have sufficiently good physical properties to qualify as “buffer” isolation of hazardous waste including highly radioactive rest products like spent reactor fuel. They can be regarded as weathered bentonites representing an intermediate stage between freshly formed montmorillonite and very old bentonites that have undergone complete conversion to nonexpandable clay minerals like the Ordovician clays on Gotland (Pusch et al., 2011). The impact on the chemical integrity of Holmehus clay of the hydrothermal conditions in a repository is believed to be similar to but less extensive than those of competing smectite-rich clays like MX-80.

The most important results reached in the study concerns the mineral stability and the role of dissolve silica under hydrothermal conditions. Firstly, different smectite clays have specific dissolution potentials. Smectite with low dissolution potential behave as “Sleeper” and retain their expandability and tightness for very long times while smectite with high dissolution potential is a “Sprinter” and undergoes early and significant convergence to non-expandable forms. IS-ml bearing clays like Holmehus clay compensate their fast alteration by smectitization. This smectitization coupled with the high Si-buffer capacity of IS-ml bearing clays improve the barrier performance concerning swelling pressure and permeability also by avoiding of cementation of particles.

The Holmehus clay is less expansive than pure montmorillonite clays which makes it preferable as “buffer” since it can be compacted to very high densities without exerting unacceptably high swelling pressure on radioactive waste canisters, a problem that puts a limit to the density of MX-80 clay (Pusch et al., 2011). Compaction of Holmehus granules dried to a few percent of water content at a density of 2,100 kg/m³ after saturation with very salt Ca-dominated

water is expected to give the clay a hydraulic conductivity of no more than E-12 m/s and a swelling pressure of about 5 MPa.

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Table 1. XRD, bulk sample: Major minerals in Holmehus and MX-80 other than those representing illite/smectite mixed-layer series (weight percentages; montmorillonite in MX-80 bentonite: 77-85%)

Clay	Musco- vite, 2M ₁	Chlorite	Quartz + Cristobalite	Plagio- clase	K-feld- spar	Anatase	Gypsum	Jarosite	Pyrite
Holmehus	10-20	<5	10-15*	<5	5	0.5	2	2	0.3
MX-80 ⁽¹⁾	1	-	5+3	13	-	-	-	-	-
MX-80 ⁽²⁾	2	-	4+2	5	-	-	<1	-	-
MX-80 ⁽³⁾	<1	-	15	5-8	-	-	-	-	0.3

Note: * - quartz only; ⁽¹⁾ Nguyen-Thanh, 2012; ⁽²⁾ Ufer et al., 2008; ⁽³⁾ Madsen, 1998.

Table 2. Mineral formula (average) per (OH)₂O₁₀ for major expandable dioctahedral clay mineral phases in fraction < 2 µm of Holmehus clay by TEM-EDX in comparison with MX-80 bentonite and Friedland clay

Phase	Ca	Mg	Na	K	Al	Fe ³⁺	Mg	Ti	Al	Si	XII	n ^{VI}	S%
Holmehus clay													
IS- + diVS-ml	0.02	0.01	0.04	0.50	1.04	0.77	0.14	0.00	0.34	3.66	0.63	1.96	49
IS-ml (45%)	0.01	0.01	0.01	0.54	1.07	0.72	0.15	0.00	0.26	3.74	0.59	1.94	60
diVS-ml (15%)	0.04	0.02	0.10	0.42	0.98	0.87	0.13	0.01	0.49	3.51	0.63	1.99	30
Friedland clay (Burgscholle) (Nguyen-Thanh, 2012)													
IS- + diVS-ml	0.01	0.11	0.03	0.23	1.55	0.30	0.12	0.02	0.38	3.62	0.50	1.99	43
IS-ml (12%)	0.00	0.08	0.01	0.36	1.30	0.41	0.25	0.01	0.20	3.80	0.52	1.97	71
diVS-ml (41%)	0.01	0.12	0.04	0.19	1.61	0.28	0.09	0.09	0.43	3.57	0.49	2.07	36
Friedland clay (Siedlungsscholle) (Henning & Kasbohm, 1998)													
IS-ml	0.03	0.07	0.04	0.35	1.11	0.64	0.18	0.01	0.25	3.75	0.59	1.94	62
diVS-ml	0.04	0.10	0.01	0.21	1.66	0.28	0.06	0.01	0.45	3.55	0.49	2.01	34
MX-80 bentonite (tradeware, 2005) (Nguyen-Thanh, 2012)													
Montmorillonite	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99	99

Table 3. Element data of bulk samples of Holmehus and MX-80 clays

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
Holmehus	58.6	15.3	6.5	2.2	0.7	1.4	2.8
MX-80	63.6	19.8	5.0	3.2	3.1	2.8	1.0

Table 4. Hydraulic conductivity K of Holmehus and MX-80 clays (hydraulic gradient 100-300 m/m)

Densities		K , Holmehus (m/s)		K , MX-80 (m/s)	
Wet density (kg/m ³)	Dry density (kg/m ³)	Distilled water	3.5% CaCl ₂ solution	Distilled water	3.5% CaCl ₂ solution
1900	1430	2.5E-12	7E-12	2E-12	1E-12
1800	1270	1.5E-11	3E-11	7E-12	2E-11
1675	1070	1.0E-10	1E-09	2E-11	1E-10

Table 5. Swelling pressure p_s of Holmehus and MX-80 clays

Densities		p_s of Holmehus (MPa)		p_s of MX-80 (MPa)	
Wet density (kg/m ³)	Dry density (kg/m ³)	Distilled water	3.5% CaCl ₂ solution	Distilled water	3.5% CaCl ₂ solution
1900	1430	2.4	1.5	5.0	3.5
1800	1270	1.3	0.6	1.5	1.0
1675	1070	0.3	0.0	0.3	0.0(5)

Table 6. Alteration experiments: Mineral formula as average of all dioctahedral 2:1 phyllosilicates per (OH)₂O₁₀ (determined by TEM-EDX)

	Ca	Mg	Na	K	Al	Fe ³⁺	Mg	Ti	Al	Si	XII	n ^{VI}	S%
Holmehus clay													
original material	0.02	0.01	0.04	0.50	1.04	0.77	0.14	0.00	0.34	3.66	0.63	1.96	49
treated (5 rpm)	0.03	0.09	0.18	0.23	1.32	0.36	0.31	0.00	0.36	3.64	0.63	1.99	46
treated (20 rpm)	0.04	0.07	0.12	0.18	1.34	0.37	0.29	0.00	0.22	3.78	0.52	2.00	67
Friedland clay (Burgscholle) (Nguyen-Thanh, 2012)													
original material	0.01	0.11	0.03	0.23	1.55	0.30	0.12	0.02	0.38	3.62	0.50	1.99	43
treated (20 rpm)	0.02	0.06	0.00	0.18	1.60	0.27	0.11	0.02	0.24	3.76	0.34	2.00	64
treated (60 rpm)	0.01	0.08	0.00	0.19	1.58	0.28	0.11	0.01	0.22	3.78	0.36	1.99	67

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Holmehus clay – A Tertiary smectitic clay of potential use for isolation of hazardous waste

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Figure Captions

Figure 1. XRD-spectrum of Holmehus bulk material

Figure 2. XRD-spectra of air-dried (AD) and ethylene glycol (EG) saturated Holmehus clay (< 2 μ m, oriented mounts; after background subtraction; Cu K $\alpha_{1,2}$ -radiation)

Figure 3. XRD-spectra of ethylene glycol-saturated Holmehus clay by using WinFit-software (< 2 μ m; Cu K $\alpha_{1,2}$ -radiation)

Figure 4. TEM micrographs of dispersed Holmehus clay. Left: lath-like illite-smectite mixed layer phases. Right: Xenomorphic particles in the coarser part of the clay fraction representing one of the mixed-layer mineral phases; squares are pyrite.

Figure 5. The evaluated hydraulic conductivity of Holmehus clay for medium-high densities at saturation and percolation with distilled water.

Figure 6. The evaluated hydraulic conductivity of Holmehus clay for medium-high densities at saturation and percolation with 3.5% CaCl₂ solution.

Figure 7. Alteration experiments (TEM-micrographs): Disaggregation of particles after overhead rotation experiments

Platy IS- and diVS-ml phases: A – aggregated particles of original material (magnification: 5,000×); B – disaggregated particles, reaction product 5 rpm (magnification: 4,000×); C – disaggregated and thinned particles, reaction product 20 rpm (magnification: 5,000×)

Lath-like IS- and diVS-ml phases: D – aggregated particles of original material (magnification: 29,000×); E – remarkable disaggregated particles, reaction product 5 rpm (magnification: 38,000×); F – disaggregated particles, reaction product 20 rpm (magnification: 38,000×)

Figure 8. Examples of repository concepts for highly radioactive waste with “buffer” clay placed as canister isolation in deposition holes of different depths.