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# Long-term effect of water chemistry on the swelling pressure of a bentonite-based material

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28 **Abstract**

29 Compacted bentonite-based materials have been proposed as possible sealing and backfill  
30 materials in geological repositories for the high-level radioactive waste disposal in several  
31 countries. During the long time lifespan of a repository, as the chemical composition of  
32 porewater can change, the swelling and sealing capacity of the material may also change. From  
33 a point of view of storage safety assessment, it is important to evaluate this possible change of  
34 swelling capacity. In this study, a mixture of bentonite and crushed Callovo-Oxfordian  
35 claystone was investigated. The long-term effect of pore water chemistry on the swelling  
36 pressure was studied at constant-volume conditions for 700 days. Distilled water and synthetic  
37 water having the chemical composition similar to that of in-situ pore water were used for  
38 hydration. The results obtained in an initial period of 100 hours revealed no significant  
39 influence of the water composition on the swelling pressure evolution, and the maximum  
40 swelling pressures observed were close to 4.30 MPa for a dry density of 1.70 Mg/m<sup>3</sup>. Over a  
41 longer time period, on the contrary, the swelling pressure eventually decreased for all samples,  
42 especially for the sample saturated with synthetic water. In addition, comparison of a one-step  
43 soaking test with a multi-step soaking test showed no wetting procedure effect on the long  
44 term swelling behaviour. All the results are analysed by considering the physico-chemical  
45 interaction between the minerals of claystone, minerals of bentonite and different fluids  
46 involved.

47 **Keywords:** Radioactive waste disposal; bentonite based materials; pore water chemistry;  
48 time dependence; swelling pressure

49

## 50 **1 INTRODUCTION**

51 Compacted bentonite-based materials have been proposed as possible  
52 sealing/backfill materials in deep geological repositories for high-level radioactive wastes  
53 (HLW) in several countries. Due to their favourable swelling characteristics, these materials  
54 are expected to fill up all voids left in the system after construction and emplacement of the  
55 waste packages. An important long-term safety function of bentonite-based barriers is to  
56 ensure a relatively impermeable zone around the high-level radioactive waste thereby limiting  
57 groundwater flow and waste package degradation rates and, ultimately, waste leaching rates.  
58 This role termed as “sealing” (Komine, 2004; Komine and Ogata, 2003) is essential to  
59 ensure the overall safety of the geological disposal: the disposed waste is isolated from  
60 the biosphere over long time. For this purpose, the swelling property becomes a key factor in  
61 the design and fabrication of the sealing/backfill materials, and needs to be studied in depth.

62 The swelling properties (i.e. swelling pressure or swelling potential) of bentonite-based  
63 materials have been widely investigated (Pusch, 1982; Komine and Ogata, 1994, 2003, 2004a;  
64 Delage et al., 1998; Agus and Schanz, 2005; Komine et al., 2009). They depend strongly on  
65 the initial state such as dry density and water content (Komine and Ogata, 1994; Villar and  
66 Lloret, 2008). After being installed in the field, especially in some geological host formations  
67 relatively rich in salts (e.g. salt formation, claystone, granite formations, etc.), site water of  
68 certain salinity can interact with bentonite (Herbert et al., 2008); as a result, the hydro-  
69 mechanical behaviour of the bentonite-based materials and in turn the performance of the  
70 barrier may be notably affected. Moreover, the water composition can change over time.

71 Frequently, bentonite/sand mixtures are considered for the reason of good control of swelling  
72 pressure, enhanced thermal conductivity as compared to pure bentonite and a better  
73 mechanical resistance. For instance, a 70/30 bentonite-sand mixture was proposed as buffer

74 material in Japan while a 50/50 bentonite/sand mixture was suggested in the Canadian  
75 repository concept (Dixon et al., 1985). In France, Callovo-Oxfordian (COx) claystone has  
76 been considered as a possible geological host-rock for high-level radioactive waste disposal,  
77 and the mixture of bentonite and crushed Callovo-Oxfordian (COx) claystone is proposed as  
78 a possible sealing/backfill material for environmental and economic reasons (Andra, 2005;  
79 Tang et al., 2011a; Tang et al., 2011b; Wang et al., 2012). If physico-chemical interactions  
80 essentially take place only between groundwater and bentonite in the case of sand/bentonite  
81 mixture, it is not the case for the bentonite/claystone because of the additional interactions  
82 between these two materials and the water. Due to the low permeability of the bentonite-based  
83 materials, these interactions might develop over long time and the resulting effects will not be  
84 immediate. Hence, particular attention should be paid to their long-term behaviour.

85 This study focuses on the swelling pressure of the compacted mixture of MX80 bentonite and  
86 crushed COx claystone. The long term effect of water chemistry on the swelling pressure and  
87 microstructure were investigated after 700 days in contact with water. Emphasis was put on  
88 the physico-chemical interaction between the minerals of claystone, minerals of bentonite and  
89 different fluids involved. The wetting procedure effect on the long term swelling behaviour  
90 was also investigated by comparing a one-step soaking test with multi-step soaking test.

## 91 **2 MATERIALS AND METHODS**

### 92 **2.1 Materials**

93 The bentonite used in this study is a commercial MX80 Na-bentonite, which contains large  
94 quantities of montmorillonite (75-90%). Silt is the dominant remaining fraction, which mainly  
95 consists of quartz and feldspars as well as micas, sulphides, and oxides (Pusch 1982). Table 1  
96 details the main mineralogical components of MX80 bentonite obtained by several authors.

97 The total cation exchange capacity (CEC) is between 0.78 and 0.85 meq/g (Table 2), the  
98 cation population at exchange positions is mainly composed of  $\text{Na}^+$  (60.0-67.0 meq/100g),  
99 other population being much lower:  $\text{Ca}^{2+}$  (5.0-8.0 meq/100g),  $\text{Mg}^{2+}$  (3.0-4.0 meq/100g) and  
100  $\text{K}^+$  (0.2-1.3 meq/100g). The grain size distribution (Fig.1) determined by hydrometer (AFNOR  
101 NF P94-057) shows that the fraction of clay-size particles ( $< 2 \mu\text{m}$ ) is 84%. The bentonite  
102 tested has an average specific gravity of 2.76, a liquid limit of 520%, and a plastic limit of  
103 42%.

104 Callovo-Oxfordian (COx) claystone was taken at 490-m depth from the  
105 Underground Research Laboratory (URL) at Bure in eastern France. It contains 40–45%  
106 clay minerals (mainly interstratified minerals of illite–smectite), 20–30% carbonates (mainly  
107 calcite) and 20–30% quartz and feldspar (Hoteit et al., 2000; Lebon and Ghoreychi, 2000;  
108 Zhang et al., 2004). The in-situ water content is 2.8–8.7 %; the bulk density is 2.32–2.61  
109  $\text{Mg}/\text{m}^3$  and the specific gravity is 2.70 (Hoteit et al., 2000; Tanget al., 2011a). The excavated  
110 claystone was air-dried and crushed into a powder. Fig.1 depicts the grain size distribution of  
111 the crushed powder obtained by dry sieving; it contains 18% of fine grains (0.08 mm). The  
112 grain size distribution determined by hydrometer confirms that the content of clay-size  
113 particles ( $< 2 \mu\text{m}$ ) is 40%.

114 Both distilled water and synthetic water were used for hydration. The chemical composition  
115 of the synthetic water (see Table 3) is similar to that of the groundwater at Bure site. The pH  
116 values are between 7.00 and 7.28; the concentration of  $\text{Na}^+$  is twice that of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and  
117 four times that of  $\text{K}^+$  (Gaucher et al., 2006; Marty et al., 2010).

## 118 2.2 Sample preparation

119 In this study, all tests were performed on samples of compacted bentonite/claystone mixture  
120 with a bentonite content of 70 % in dry mass. Bentonite and claystone powders, with the

121 initial water contents of 11.8 % and 2.64 % respectively, were first carefully mixed prior to  
122 compaction. Samples were statically compacted to a dry density of  $1.70 \text{ Mg/m}^3$  in a metallic  
123 cell (70 mm in internal diameter) at a controlled rate of 0.05 mm/min. After compaction, the  
124 sample height is about 10 mm. The total suction measured in these specimens using  
125 a hygrometer was  $s = 90 \text{ MPa}$ . The specimens are then carefully introduced into constant-  
126 volume cells (having the same diameter as the compaction cell) for the swelling pressure  
127 experiment.

### 128 2.3 Experimental methods and programme

129 The constant-volume cell used in this study is presented in Fig.2. It consists of three parts: (1)  
130 the bottom part containing a porous stone and a drainage system; (2) the middle cell (70 mm  
131 inner diameter, 10 mm height) used to prevent radial swelling, with two air outlets; (3) the top  
132 part incorporating a total pressure sensor (working pressure of 5 MPa) to monitor the swelling  
133 pressure. The sample was wetted by connecting the water inlet to a water reservoir or a  
134 suction control system using vapour equilibrium technique at an ambient temperature of  $20 \pm 1$   
135 °C. More details can be found in Tang et al. (2011b), Wan et al. (2012).

136 Four swelling pressure tests were performed using the constant-volume cell (Table 4). In tests  
137 LT01 and LT02 (LT stands for long term), the samples were saturated with synthetic water  
138 and distilled water, respectively. The duration of these tests carried out to study the long-term  
139 effect of water chemistry on the swelling pressure was 700 days. In test LT03, three decreasing  
140 suctions (57 MPa, 38 MPa and 12.6 MPa) were first applied in steps using vapour equilibrium  
141 technique, prior to distilled water flooding in the last stage. This test also lasted 700 days. This  
142 test was performed to investigate the effect of the wetting procedure on the long term swelling  
143 behaviour by comparison with test LT02. Test ST (ST for short term) was performed by  
144 directly injecting synthetic water as in test LT01, but with a shorter duration of 100 hours.

145 After certain hydration time (see Table 4), the specimen was taken out of the cell for the  
146 analysis of pore-size distribution by Mercury Intrusion Porosimetry (MIP).

### 147 **3 EXPERIMENTAL RESULTS**

148 Fig.3 presents the results from tests LT01, LT02, and ST during the first 100 hours after the  
149 injection of water. The three curves are very similar, showing negligible effect of water  
150 chemistry for this duration and also the good repeatability of the tests. With water infiltration,  
151 swelling pressure first increased very quickly; after about 20 hours the swelling pressure  
152 reached a first plateau at about 3.4 MPa. After 32 hours, the swelling pressure started to  
153 increase again and reached a second plateau after 100 hours. The final values were in the  
154 range of 4.30 – 4.37 MPa for the three tests.

155 The results of test LT03 are presented in Fig.4. The application of the first suction of 57 MPa  
156 resulted in a swelling pressure of 0.57 MPa. Then, the second suction of 38 MPa was applied  
157 and the swelling pressure reached 1.43 MPa. With the third suction of 12.6 MPa the swelling  
158 pressure increased to 2.61 MPa. The zero suction applied by direct contact with distilled water  
159 led the sample to a maximum value of 4.39 MPa swelling pressure. This value is quite close to  
160 that from test LT02 (4.37 MPa) in which the sample was directly put in contact with distilled  
161 water. This indicates that the wetting procedure did not affect the short-term swelling  
162 behaviour for this material.

163 In Fig.5, all results from the three tests LT01, LT02 and LT03 during 700 days are presented.  
164 It appears that over this long period, the swelling pressure decreased somewhat for all samples,  
165 especially for the sample saturated with synthetic water (LT01). The final swelling pressure  
166 was 3.95 MPa (corresponding to a decrease of 9%), and 4.19 MPa (decrease of 3%) for



167 samples saturated with synthetic water (LT01) and distilled water(LT02 and LT03),  
168 respectively.

169 The pore size distribution curve for all the samples taken at the end of the tests are presented  
170 in Fig. 6. It is observed in Fig. 6a that the final values of intruded mercury void ratio ( $e_m =$   
171 intruded mercury volume over soil solid volume) are between 0.4 and 0.5, much lower than  
172 the global void ratio ( $e = 0.61$ ). This shows that a large amount of porosity is inaccessible to  
173 mercury. Comparison between the curves obtained after different durations clearly shows that  
174 the amount of accessible porosity after 700 days is larger in both cases of distilled water  
175 (LT02 and LT03) and synthetic water (LT01) than after 100 hours with synthetic water. In  
176 addition, for samples hydrated for 700 days, more quantity of accessible porosity is observed  
177 in the case of synthetic water (LT01).

178 The incremental pore volume  $de_m/d\log(d)$  (Fig. 6b) refers to the volume of mercury that  
179 intrudes into the pores between pressure increments. For all samples a typical bimodal  
180 porosity can be observed; thus, two pore groups can be defined: a group of micro-pores  
181 having a mean size of  $0.02 \mu\text{m}$  and a group of macro-pores having a mean size of  $20 \mu\text{m}$ .  
182 After 700-day saturation (LT01, LT02 and LT03), the macro-pores and micro-pores quantity  
183 increased when comparing to the short-term test (ST). Change in macro-pores is more  
184 significant especially for the samples saturated with synthetic water (LT01). For tests LT02  
185 and LT03 which were hydrated with distilled water, very similar curves were observed  
186 suggesting no effect of the wetting procedure on the pore-size distributions. As far as changes  
187 in pores size are concerned, it can be observed that over time the group of micro-pores had a  
188 size slightly decreased. On the contrary, the group of macro-pores had a size slightly increased.  
189 Changes for test LT01 were more marked.

## 190 4 INTERPRETATION AND DISCUSSION

191 Various studies showed that the swelling capacity of bentonite is lower in saline water;the  
192 higher the dissolved salt concentration, the lower the swelling pressure. This  
193 phenomenon becomes less pronounced in case of high dry density (Studds et al., 1998;  
194 Karland et al., 2005; Suzuki et al., 2005; Karland et al., 2006; Castellanos et al., 2008;  
195 Katsumi et al., 2008; Siddique et al., 2011). In general, with a high void ratio (low dry  
196 density) and/or high salt concentrations, the influence of pore water chemistry on  
197 bentonite behaviour is significant and can be qualitatively explained by the diffuse double  
198 layer (DDL) theory (Karland, 1997; Mata, 2003; Castellanos et al., 2008). For dense bentonite,  
199 since there is little water present between adjacent clay platelets, there can be little or no  
200 development of a DDL associated with the clay particles (Dixon, 2000; Pusch and Yong,  
201 2006); thus it becomes difficult even impossible to describe the bentonite behaviour by the  
202 DDL theory.

203 In this regard, Karland et al. (2005) studied the effect of salinity on the swelling pressure of  
204 MX-80 bentonite, and noted that the effect of salinity of the saturating fluid was relatively  
205 lower with a higher density. For MX80 bentonite, Dixon (2000) also concluded that at an  
206 effective bentonite dry density (bentonite dry density in the bentonite/sand mixture) higher  
207 than  $1.22 \text{ Mg/m}^3$ , changes in water chemistry do not significantly affect the swelling  
208 behaviour due to the small number of water molecule layers between clay sheets.  
209 Confirmation was made by Castellanos et al. (2008) on the FEBEX bentonite: an increase in  
210 salt concentration reduced the swelling pressure, but this change was much less marked for  
211 high density. It can be deduced that for the studied bentonite/claystone mixture, the high  
212 density ( $1.70 \text{ Mg/m}^3$ ) and the low salinity of the synthetic water (see Table 3) representative

213 of the present in situ conditions resulted together in the negligible effect of water chemistry on  
214 the swelling pressure in short term.

215 Basically, the swelling pressure of bentonite is mainly related to the crystalline swelling and  
216 double layer swelling. Crystalline swelling is caused by the hydration of exchangeable cations  
217 ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) between mineral layers that have a structure with one alumina  
218 octahedral sheet sandwiched between two silica tetrahedral sheets. It is a process which  
219 involves the adsorption of a maximum number of hydrates depending on the nature of cations.  
220 After three to four water monolayers, i.e. at interlayer separation distances  $\geq 1$  nm, the surface  
221 hydration becomes less significant and the electrical double-layer repulsion becomes the main  
222 swelling mechanism (Bradbury and Baeyens, 2003; Suzuki et al., 2005). For clay at high  
223 density, the low amount of water taken up is to all intents and purposes pseudo-crystalline  
224 interlayer water, and insufficient to form the DDL (Pusch and Yong, 2006). Therefore, the  
225 swelling pressure is mainly governed by the crystalline swelling (interaction between the  
226 layer surfaces and water) and the double layer repulsion makes only a limited contribution. In  
227 this case, the exchangeable cations are the key elements that control the clay-water interaction  
228 (Abdullah et al., 1997).

229 As far as the pore water is concerned, it may significantly affect the chemical compositions of  
230 clays through the exchangeable cations (Yukselen et al., 2008). The cation exchange reaction  
231 is mainly controlled by the exchange capacity of the clay minerals (Mata, 2003); the ease with  
232 which a cation of one type can replace a cation of another type depends mainly on the valence,  
233 relative abundance of the different cation types, and the cation size. Other factors being equal,  
234 the higher the valence of the cation, the higher the replacing power; for cations of the same  
235 valence, the replacing power increases with the size of the cation (Laine and Karttunen, 2010).  
236 Atypical replaceability order is:  $Na^+ < K^+ < Mg^{2+} < Ca^{2+}$  (Mitchell, 1976; Pusch, 2001; Mata et al.,

237 2003). According to this order, for the Na-bentonite as in this study, it tends to change from  
238 sodium ( $\text{Na}^+$ ) to other types (i.e.  $\text{K}^+$ ,  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ ) depending on the cations present in the  
239 permeating water.

240 One of the most common cation exchange reactions in the Na-bentonite is the one involving  
241 sodium and calcium (Mata, 2003). Mata (2003) investigated the evolution of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in a  
242 specimen of sodium MX80 bentonite hydrated with saline water (NaCl and CaCl<sub>2</sub>, 50/50 by  
243 mass) and distilled water. Analysis of the collected pore fluid showed an increase of sodium  
244 concentration and a decrease of calcium concentration as compared to the injected water. This  
245 suggests that the sodium bentonite was transformed to a calcium bentonite. Montes-H. et al.  
246 (2004, 2005) investigated the chemical transformation of Na/Ca-MX80 bentonite ( $\text{Na}_{0.18}\text{Ca}_{0.10}$ )  
247 in a representative pore water (pH = 7.3) from Bure site (-180 m), the Na/Ca- to  
248 Ca-montmorillonite conversion was identified as the main chemical transformation. At  
249 a constant temperature, this transformation is affected by the groundwater composition (pH  
250 and cation concentrations) and solid/liquid ratio as well as the reaction time (Mitchell, 1976;  
251 Herbert et al., 2004; Fernández and Villar, 2010; Laine and Karttunen, 2010). For the short  
252 term swelling pressure test in this study, it was actually the low cation concentration (low  
253 salinity of synthetic water mentioned above) and high solid/liquid ratio (i.e. high density) that  
254 led to the negligible effect of water chemistry on the swelling pressure. Nevertheless, after a  
255 long time period of reactions, the effect became evident because the presence of  $\text{Ca}^{2+}$  in Bure  
256 site water (see Table 3) enabled part of Na-montmorillonite to change to Ca-montmorillonite  
257 which has a much lower expansibility. This process resulted in a decrease of swelling pressure  
258 overtime as shown in Fig.5.

259 The transformation from sodium to calcium montmorillonite is critically dependent on the  
260 amount of available calcium ( $\text{Ca}^{2+}$ ) in the pore water (Muurinen and Lehtikoinen, 1999;

261 Fernández et al., 2004, Fernández and Villar, 2010). For the sample saturated with distilled  
262 water, the pore water chemistry evolved over time to reach equilibrium with the claystone  
263 minerals (the claystone contains 20–30% carbonates, mainly calcite). Consequently, it was as  
264 if diluted Bure site water infiltrated to the MX80 bentonite, leading to the degradation of  
265 swelling pressure. However, with a much lower cation concentration (only 30% claystone in  
266 the mixture), the decrease of swelling pressure was less significant than in the case with  
267 synthetic water.

268 For the sample first wetted by three steps of suction (LT03), after the sample was flooded with  
269 distilled water, the maximum swelling pressure was found close to that obtained by water-  
270 flooding the sample directly (LT02), indicating a negligible effect of wetting procedure on the  
271 swelling pressure (Figs. 3 and 4). This phenomenon can be explained by the mechanism  
272 identified by Cui et al. (2002): when hydrating by decreasing suction (57-38-12.6 MPa) under  
273 confined conditions, the macro-pores were progressively clogged by the invasion of exfoliated  
274 clay particles, whereas the micro-pores remained almost un-affected. The micro-pores started  
275 to change only when the water saturation is approached. This suggests that step-wetting by  
276 suction control and direct flooding with water may lead to similar microstructures after  
277 saturation, thus similar maximum swelling pressures. After 700-day hydration with distilled  
278 water, not only similar swelling pressures (Fig.5), but also similar pore-size distributions  
279 were observed for tests L02 and L03 (Fig.6), which enhanced this conclusion. In addition, the  
280 repeatability of swelling pressure test and the MIP test was verified.

281 It was noted that the chemical effect on the HM behaviour of clayey soils is due to changes at  
282 different structural levels and the interaction between them (Mata 2003). From the pore-size  
283 distribution observation in this study, it can be seen that the amount of accessible porosity  
284 increased after a long time period for both distilled (LT02 and LT03) and synthetic water

285 (LT01), with more increase for synthetic water (Fig. 6). If we relate these phenomena to the  
286 swelling pressure, it is clear that the sample with lower swelling pressure had a higher  
287 intruded mercury void ratio in both micro- and macro-pores. For samples with higher swelling  
288 capacity, more interlayer hydration occurred, leading to a constriction of accessible pores.  
289 When referring to the incremental pore volume, the same tendency can be identified, for the  
290 sample with higher swelling pressure, both the macro-pores and micro-pores decreased.  
291 However, most of changes in microstructure occurred in macro-pores family. The  
292 same observation can be made in terms of pore size changes. This is in agreement with  
293 the observation made by Mata (2003) who conducted MIP test on the compacted  
294 sodium bentonite MX80 and sand mixture (70/30) (dry density of 1.37 and 1.67  
295 Mg/m<sup>3</sup>) saturated with distilled water and saline water, and found that the saline water  
296 effects were significant on the macro-pores, the micro-pores remaining almost unaffected.

## 297 **5 CONCLUSION**

298 Long term swelling pressure tests and MIP tests on a bentonite/claystone mixture were  
299 performed. The effects of water chemistry as well as the hydration procedure on the swelling  
300 pressure were investigated in both short and long terms. The results are analysed by  
301 considering the physico-chemical interaction between the minerals of claystone, the minerals  
302 of bentonite and the different pore water chemistries involved.

303 There was no obvious effect of water chemistry on the swelling pressure in short term (100  
304 hours) due to the high dry density of the bentonite-based material and the low salinity of the  
305 synthetic water. However, after a long period of 700 days, the swelling pressure decreased for  
306 all samples, especially for the sample saturated with synthetic water.

307 Different hydration procedures led to comparable long term swelling behaviour and  
308 similar pore-size distributions.

309 The effect of the chemical composition of the pore water on the swelling pressure can be  
310 interpreted in terms of changes in microstructure. The sample with higher swelling pressure  
311 showed less macro and micro-pores associated with a higher interlayer hydration.

312 From a practical point of view, the specification and the design of the sealing/backfill material  
313 are often made based on the swelling properties measured in short term. However, a non-  
314 negligible decrease (9%) of swelling pressure was observed after 700 days even with a water  
315 of low salinity. This expected reduction of swelling pressure has thus to be taken into account  
316 when designing a repository to ensure that the bentonite-based barrier will also meet the  
317 requirements on which its long term performance rests. Considering the possible pore water  
318 chemical composition changes over the very long term lifespan of the repository is also  
319 recommended to avoid deterioration of the swelling capacity of these materials and thus of the  
320 self-sealing capacity of the system.

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