

1 Systematic evaluation of rock mechanical behavior
2 of chalk reservoirs in presence of variety of water
3 compositions

4 *AUTHOR NAMES: Bizhan Zangiabadi¹; Sina R. Gomari²*

5 AUTHOR ADDRESS:

6 ¹ Ph.D. Candidate, Department of Petroleum Engineering, Faculty of Science and Technology,
7 University of Stavanger, Stavanger, Norway(Corresponding author). E-mail:
8 bizhan.zangiabadi@outlook.com

9 ² Senior Lecturer, School of Science and Engineering, University of Teesside, Middlesbrough
10 TS1 3BA UK. E-mail: S.Rezaei-Gomari@tees.ac.uk

11 KEYWORDS: chalk, chemo-mechanical, saline solutions, weakening, creep rate

12 ABSTRACT:

13 Principally, the interaction between chalk surface and saline water is vital for reported
14 subsidence, formation compaction (the decline in pore fluid pressure within a solid structure and
15 increase in stress on formation rock), as well as enhanced oil recovery (EOR) in chalk reservoirs.
16 To understand the mechanisms of rock-fluid interaction and the role of specific ions in seawater,

17 rock mechanical tests combined with chemical analysis of effluents were performed on chalk
18 outcrops using synthetic brine solutions. All the chalk cores are treated with strictly aqueous
19 solution meaning no hydrocarbon involved in any stage of experiments from preparation to post-
20 processing (chemical analysis). The two objectives in the present study are the examination of
21 diffusion and transport-controlled phenomena in the presence of different aqueous chemistry and
22 the proposal of possible processes/explanations based on distinct experimental scenarios. The
23 experiments supply information on chemical mechanisms in chalk water weakening and the
24 effect of saturation and flooding with synthetic brine solutions: NaCl, Na₂SO₄, MgCl₂, CaCl₂,
25 and seawater without magnesium (SSW-1[Mg²⁺]). Two different thermodynamic conditions
26 (flooding state) were applied to the compacted cores within the creep phase: flooding steadily
27 through the core and bypassing the core, both at high temperature and high pressure. The method
28 provided measurements to investigate the effect of flow rate on the chemical reactions between
29 the rock and fluid. Yield stress level, bulk modulus value, and creep strain rate are three
30 mechanical properties of samples which were measured and analyzed together with chemical
31 analysis of effluents taken periodically during the creep phase of each experiment. The results
32 subsequently provide information about weakening/strengthening behavior within a time-
33 dependent period. Switching of flooding fluid from distilled water to the NaCl solution tripled
34 the creep strain rate and produced calcium content equal to seawater concentration. Performing a
35 similar action on a distilled water to Na₂SO₄ solution generated enhanced creep of close to a
36 factor of three. In addition, adsorption of sulfate to the chalk surface was identified. Flooding
37 solely with NaCl solution or Na₂SO₄ solution caused 25% and 50% decrease in chalk mechanical
38 strength compared to distilled water flooded cores, respectively. MgCl₂ solution flooding
39 experiments generated cores with 10% higher mechanical strength compared to cores treated

40 with Na₂SO₄ solution. The observation was confirmed by testing cores with SSW-1[Mg²⁺] where
41 relatively low hydrostatic yield and enhanced creep strain were observed compared to Na₂SO₄
42 solution testing. Chalk cores flooded with MgCl₂ solution showed 25% and 50% lower
43 mechanical strength values compared to cores tested with NaCl and distilled water. Collected
44 samples from MgCl₂ and SSW-1[Mg²⁺] flooding showed simultaneous processes of magnesium
45 retention inside chalk and production of calcium. Changing the flooding state to bypass with
46 Na₂SO₄ solution did not generate any difference in the creep strain rate whereas a change of
47 flooding state from bypass to flooding triggered production of calcium equal to one-third of
48 calcium content in seawater. However, an opposite observation was recorded when the flooding
49 state changed when using MgCl₂ as a flooding fluid. Change of the flooding state from flooding
50 to bypass created enhanced compaction in case of MgCl₂. The observed trend was similar when
51 changing from bypass to flooding in case of testing with Na₂SO₄ and SSW-1[Mg²⁺]. The
52 extensive experiments provide a foundation for analyzing the behavior of chalk-brine in the
53 presence of oil and building verified models to simulate the effect of flooding complex brine and
54 seawater on the mechanical characteristics of chalk and predicting the chemo-mechanical
55 behavior of chalk.

56 INTRODUCTION

57 Hydrocarbon production, mining activities, and ground water removal could create a
58 downward movement of Earth's surface, compared to a reference, for example, sea-level or
59 seabed, which is addressed as subsidence. This phenomenon has received great attention in the
60 field of hydrocarbon extractions (Allen and Mayuga, 1970; Andersen et al., 1992; Dusseault,
61 1983; Fredrich et al., 1996; Ruddy et al., 1988; Schoonbeek, 1977). Reservoir compaction due to
62 hydrocarbon removal, as a consequence of surface subsidence, was detected for the first time in

63 the Goose Creek oilfield located along the Texas Gulf Coast in the U.S. (Pratt and Johnson,
64 1926). Compaction of the Ekofisk field in the Norwegian sector of the North Sea, as a costly
65 case, was recognized and reported in the late twentieth century (Smith, 1988; Sulak, 1990).
66 Researchers have attempted to explain and predict the compaction issue in the chalk layers of the
67 Ekofisk field in terms of primary depletion and rock compressibility (Andersen et al., 1992; Chin
68 et al., 1994). Although water injection in the Ekofisk field was started in 1987 in order to
69 improve oil recovery and maintain the average reservoir pressure, the subsidence is still
70 persisting (Gauer et al., 2002; Nagel, 2001; Spencer et al., 2008; Sulak, 1990). In spite of oil
71 displacement by water, the chalk immediately becomes weaker in the presence of water, a
72 phenomenon referred to as the water weakening effect of chalks. Therefore, several studies have
73 been initiated in the area of chalk-fluid interaction in order to investigate the sensitivity of chalks
74 to water from a chemo-mechanical point of view (Gutierrez et al., 2000; Heggheim et al., 2005;
75 Homand and Shao, 2000; Korsnes et al., 2008; Madland et al., 2009; Madland et al., 2008;
76 Maury et al., 1996; Risnes et al., 2003; Zangiabadi et al., 2009; Zangiabadi et al., 2011). In most
77 of these studies the effect of seawater-like brines on chalks' mechanical stability was
78 investigated. However, the presence of several different types of ions in seawater-like brines
79 makes chalk-fluid interactions complicated to analyze.

80 Experiments show molar concentration of cations in SSW is Na^+ , Mg^{2+} , Ca^{2+} , and K^+ ,
81 mentioned in descending order. Anion components present in SSW, in descending order, are: Cl^- ,
82 SO_4^{2-} , and HCO_3^- . The order is more or less similar in comparison to the water flooding fluid
83 components, i.e., Ekofisk brine, except the fact that sulfate is not present (Heggheim et al., 2005;
84 Zangiabadi et al., 2009). In addition, changing the salinity, total dissolved solids, in
85 waterflooding and EOR methods is not uncommon (Zangiabadi et al., 2009). Therefore, the

86 strategy in this study sets out to show how aqueous solutions of common salts (NaCl, Na₂SO₄,
87 MgCl₂, and CaCl₂) could affect the mechanical strength of chalk. Thereafter, the impact of more
88 complex aqueous brines, i.e., SSW-1[Mg²⁺], on the mechanical stability of chalk is studied.
89 Meanwhile, answering the question on the rate dependence of fluid inside the core on the
90 mechanical behavior of the rock is attempted. Toward a comprehensive study of chalk-fluid
91 interaction, this paper combines the result of rock mechanical tests, i.e. hydrostatic loading and
92 time-dependent behavior, with chemical analysis for major ions (Ca²⁺, Mg²⁺, and SO₄²⁻) from
93 sampled flooding effluent. Subsequently, a chemo-mechanical coupling in chalk is discussed in
94 terms of different proposed chalk-fluid weakening mechanisms such as physical and/or chemical,
95 which in turn can be used to develop a chemo-mechanical modeling of chalk in the future.
96

97 MECHANISMS OF CHALK-WATER INTERACTIONS

98 As a widely accepted observation, water-saturated chalks are mechanically weaker than dry
99 chalks. A description of this phenomena was attempted, based on the capillary forces of chalk.
100 Chalk has an open pore structure but at the same time narrow pore throats because of small
101 grains. Therefore, the capillary forces in the chalk are higher compared to the value of the
102 capillary forces in sand. Several studies were carried out with the aim of explaining chalk-water
103 interactions based on capillary forces (Andersen et al., 1992; Delage et al., 1996; Plischke, 1996;
104 Schroeder and Shao, 1996). Basically, the idea was taken from the fact that water at low
105 saturation forms capillary menisci in the small pores of chalk, which pulls the grains toward each
106 other. This attractive force is called capillary force or capillary pressure. Because of the
107 instantaneous deformation of chalk at the onset of water injection or water flooding (Newman,
108 1983), it was concluded that capillary forces, as a chalk-water interaction mechanism, are
109 responsible for the observed water weakening effect (Brignoli et al., 1994; Papamichos et al.,
110 1997). This mechanism has been questioned by Gutierrez et al. 2000 and Risnes et al. 2003).
111 They concluded that capillary effects could not solely account for the chalk-water interactions.

112 Meanwhile, some studies tend to introduce chemical effects in combination with physical
113 effects as mechanisms of interaction. Among the studies that proposed physical and/or chemical
114 mechanisms, Risnes and Flaageng (1999) suggested a possible model for the chalk-water
115 interaction that contains repulsive electrostatic and attractive (capillary) forces between chalk
116 grains. Moreover, Risnes et al. (2003) proposed water activity of the fluid in contact with chalk
117 grains as an important parameter in the field of chalk-fluid interactions. Later on, a series of
118 studies have been performed in order to scrutinize the role of chemical effects on the water
119 weakening of chalk, such as dissolution and re-precipitation, changes in surface chemistry, and

120 pressure solution. Apparently, many experiments suggest the experimental fact that chalk-water
121 interaction cannot be described thoughtfully without taking into account the role of chemical
122 effects between pore fluid and chalk (Newman, 1983; Gutierrez et al., 2000; Risnes et al., 2003;
123 Hellmann et al., 2002b; Heggheim et al., 2005; Korsnes, 2007). Therefore, the intention here is
124 to give an insight into the chemical chalk-water mechanisms relevant to the presented results,
125 rather than giving a summary of all the proposed chemical mechanisms.

126 The experimental pressure solution compaction of chalk in aqueous solutions was studied
127 comprehensively by Hellmann et al. (2002a,b). They drew a conclusion based on redistribution
128 of dissolved mass from the chalk matrix and precipitation in pore spaces. Zhang and Spiers
129 (2005) proposed that intergranular pressure solution is controlling the compaction in pure calcite
130 samples. Calcite dissolution at the grain contacts, which can cause two possible chemical effects,
131 namely local weakening and modification of calcite surface, was suggested by Gutierrez et al.
132 (2000). More recently, Korsnes (2007) suggested a chemical mechanism for water weakening of
133 chalk based on a process called “ion substitution.” The suggested model was described in terms
134 of the interexchange between calcium (from the chalk surface) and magnesium (in the fluid layer
135 adjacent to the chalk surface) at intergranular contacts in presence of sulfate. The proposed
136 mechanism could lead the chalk to compact more due to incorporation of the smaller sized Mg^{2+}
137 ions compared to Ca^{2+} ions (as part of the surface). However, the idea was challenged by a series
138 of study on rock-fluid interactions in chalk (Hiorth et al., 2008a; Hiorth et al., 2008b; Madland et
139 al., 2008; Madland et al., 2009; Zangiabadi et al., 2009; Zangiabadi et al., 2011). In these series
140 of studies, the importance of dissolution processes in chalk was stressed. Moreover, they showed
141 that $MgCl_2$ brine, which has no sulfate, causes a weakening effect in the chalk on a similar order
142 of magnitude to that of seawater as pore fluid. They also presented that calcium produces and

143 magnesium precipitates in chalk core when the chalk core flooded with brines contain no sulfate.
144 Therefore, a conclusion was drawn, yet not directly related to the weakening of the chalk matrix,
145 that dissolution and precipitation could play an important role in chalk-water interaction
146 mechanism.

147 MATERIAL, EQUIPMENT, AND PROCEDURES

148 Chalk samples and brines

149 All the tests were performed on outcrop chalk from the quarry of Stevns Klint (termed SK
150 hereafter) near Copenhagen. This chalk was used for two reasons. First, the chalk is very pure in
151 calcite content (> 98 %) (Hjuler, 2007), which simplifies analyzing the direct effects of different
152 aqueous chemistries on the mechanical behavior of chalk without concern for any other
153 perturbations. Secondly, the results obtained from this study can be critically compared with
154 previous studies as the chalk has been frequently used by other researchers (Korsnes, 2007;
155 Madland et al., 2009; Madland et al., 2010). In spite of relatively high porosity of SK chalk, 45 –
156 50 %, its permeability is usually a few mD, 2 – 5 mD, due to the fact that the pore throats are
157 rather narrow. The non-carbonate content of SK chalk (Smectite, Quartz, and Mica) is less than 1
158 %. SK chalk has a specific surface area around 2 m²/g (Hjuler, 2007). It is worth mentioning that
159 the porosities for all the prepared cores are quite similar.

160 All SK cores were saturated and tested with only aqueous solutions, synthetic brines, meaning
161 that no hydrocarbon was used during the experimental work. Therefore, SK chalk cores are not
162 oil saturated and do not have oil, and phenomena like relative permeability, oil-water
163 interactions, and others are not covered in present study. The brines were used in the study as
164 saturation and/or flooding fluid. All the brines were filtered through 0.5 µm filters after

165 preparation and degassed before usage. The brine compositions are listed in the Table 1. The
166 ionic strength of all the selected brines is equal to ionic strength of synthetic seawater of 0.657.

167

168

169 Samples preparation, equipment, and experimental procedures

170 A total of twenty-one cores were drilled with an oversized core bit, cooled by circulating
171 water. The outcrop chalks were oven-dried at about 100 °C to constant weight (at least 24 hours)
172 before being machine-turned to the required diameter (37 or 38.1 mm). The length of cores was
173 kept at approximately 70mm (± 0.5 mm) to ensure a practical rule of core length twice the core
174 diameter, accepted in experimental rock mechanics to decrease stress concentration, frictional
175 end effects, and buckling. Afterwards, the cores were saturated with distilled water (DW) using
176 an evacuator (at least three hours). Any pre-adsorbed ions in the saturated cores, for example,
177 sulfate ions, were washed out by flooding with five pore volumes (PV) of distilled water
178 (Punternold, 2007). Finally, the cores were oven-dried and thereafter saturated with one of the
179 different artificial testing brines.

180 The triaxial cell used for rock mechanical tests in this study is a hydraulically operated cell as
181 presented schematically in Figure 1. Three high-pressure pumps control the axial pressure,
182 confining pressure, and fluid circulation. Design of the piston chamber of the cell is “auto-
183 compensated” so that the confining pressure is also applied axially. The pump in the axial circuit
184 will thus only provide an additional axial pressure, maximum seven bars, to overcome the
185 friction inside the cylindrical piston chamber and keep the piston in contact with the sample.
186 Therefore, the axial stress will always be slightly higher than the confining stress as an
187 alternative to pure hydrostatic tests in the cell. However, the loading, with good accuracy, could
188 be assumed hydrostatic. Axial deformations were measured by an outside Linear Voltage
189 Displacement Transducer (LVDT). Lateral deformation is measured by the use of a chain
190 surrounding the sample and an extensometer for measuring any difference of the circumference

191 of the cylindrical sample. The cell is equipped with a heat regulating system that allows a
192 temperature control from ambient conditions up toward 150 ± 0.2 °C. Warming the cell up to
193 target temperature usually takes an hour to reach a stabilized temperature and is performed after
194 pressurization of confining pressure and pore pressure to 1.2 and 0.7 MPa, respectively. By using
195 vent valve and Back Pressure Regulators, the confining and pore pressure were maintained
196 constant. As shown in Figure 1, by opening the bypass valve the flooding fluid does not flow
197 through the core, hereafter in this paper referred to as “bypass condition.” Closing the bypass
198 valve will re-initiate the core flood. Therefore, two different test conditions were studied in the
199 conducted experiments: (1) Continuous flooding of different brines through the core; and (2)
200 “Bypass,” no flooding, by opening the bypass valve, e.g., leaving one pore volume of brine
201 inside the core. It is worth mentioning that differential pressure of 0.7MPa between the core
202 flooding inlet and outlet line was kept constant for all the tests during flooding and bypass
203 condition by using positive displacement pumps.

204 Effluent sampling was performed more or less daily during the flooding period. An auto-
205 sampler was used when several samples were sampled in rapid succession during changes in
206 flooding status or brine. Samples were collected during bypass periods. An ion chromatograph
207 (ICS-3000) measured the concentration of major cations (i.e., Li^+ (as a tracer), Na^+ , Mg^{2+} , and
208 Ca^{2+}) and anions (i.e., Cl^- , SO_4^{2-} , and SCN^-) in the collected effluents.

209 The cores, placed in the triaxial cell, were submitted to additional flow (about 1.5 PV) prior to
210 the compression test in order to assure “perfect” saturation and equilibrium inside the core. All
211 the cores were tested mechanically (hydrostatic loading) at an elevated temperature with a pore
212 pressure of about 0.7 MPa. The test temperature in all experiments is 130 °C, Ekofisk reservoir
213 temperature, unless otherwise stated. During the hydrostatic tests, yield stress values of the cores

214 were determined by plotting axial effective stress versus axial strain. The yield strength was
215 determined based on the method that is described in Figure 2a.

216

217 After defining the yield stress value, the samples were further loaded to approximately 2.7
218 MPa above the yield strength before they were left to creep. This approach was selected over
219 loading all cores to a constant stress level, which leads to a different post yield loading
220 timeframe, and affecting the initial state of creep stage. In addition, the primary focus after
221 loading phase is to establish a settled time-dependent behavior of chalk or in other words steady-
222 state creep stage and leaving behind any primary, transient period, or consolidation process
223 (Risnes 2001). Creep behavior is presented at two time scales: regular creep time and logarithmic
224 creep time. The slope of the creep strain-logarithmic time graph (m) is calculated and reported
225 for all the experiments, Figure 2b. In EOR operations water injector wells play a vital role.
226 However, the operation mode of injector wells are subject to periodical shut down and start up.
227 The operation mode change in real life affects the formation nearby the well, both physically and
228 chemically. The operation is simulated in these experiments by introducing two different test
229 conditions on the core: (1) Continuous flooding of different brines through the core; and (2) no
230 flooding by opening the bypass valve, e.g., leaving one pore volume of brine inside the core.
231 Both of these described conditions were applied on cores with similar brines in opposite orders.
232 First, during the loading phase and for approximately one week of creep before the test
233 conditions were changed after one week in the creep phase. The pore fluid can be assumed to be
234 in thermodynamic equilibrium with the rock sample when the core was bypassed, which means
235 no net driving force or bulk mass transfer occurs across the boundary of the system, core inside
236 the cell. The flow rate of the brine in all of the experiments is one PV/day unless otherwise

237 stated. Almost all the cores were flooded at the end of the creep phase by at least 1.5 PV of
238 distilled water.

239

240 RESULTS AND DISCUSSION

241 The results of representative stress-strain and the time dependent behavior of cores in different
242 aqueous chemistries together with a chemical analysis of effluents taken while performing tests
243 are compared and discussed in this section. The experimental results detailed here are obtained
244 using no hydrocarbon, only aqueous solutions. Therefore, topics like aging in oil, residual oil
245 saturation, relative permeability, and wettability alteration are irrelevant to the discussion in the
246 present study. However, readers interested in such topics and detailed discussions of oil
247 interaction, both mechanical and chemical in chalk cores, are invited to consult with earlier
248 authors' work (Rezaei Gomari et al., 2006; Zangiabadi et al., 2008; Zangiabadi et al., 2009).

249 A summary of results from the loading and creep phases of all experiments, only on cores
250 saturated and flooded with one individual fluid entirely, are presented in Tables 2 and 3. The
251 results are tabulated into two groups: Group 1: Core is flooded during the first week of creep
252 (first phase) before the core is bypassed in the second week (second phase); Group 2: Core is
253 bypassed during loading and the first week of creep before flooding is initiated in the second
254 week of the creep phase.

255

256 Table 2 and Figure 3a show the stress-strain behavior of all the flooded cores. The core SK2
257 treated with Na_2SO_4 brine tended to produce the lowest yield stress value, 4.6 MPa. This value is
258 very similar to the yield stress value obtained for the core saturated with $\text{SSW-1}[\text{Mg}^{2+}]$, 4.7 MPa.
259 However, the total axial strain value within the loading phase of the Na_2SO_4 brine saturated core
260 is by a factor of two higher than the value recorded for the $\text{SSW-1}[\text{Mg}^{2+}]$ brine saturated core.
261 The yield stress value for cores saturated with MgCl_2 is 5.0. The core saturated with distilled
262 water has a high yield stress value, equal to 7.7 MPa. CaCl_2 brine saturated cores, SK26 and

263 SK28, have an average yield stress value equal to 4.95 MPa. The stress-strain behavior of
264 bypassed cores, group 2, is illustrated in Figure 3b. The core saturated with $MgCl_2$ obtained the
265 highest yield stress, 5.7 MPa.

266

267 The yield stress value for cores saturated with Na_2SO_4 and SSW were close to each other, 4.8
268 and 4.85 MPa, respectively. The yield stress value of the core saturated with the SSW-1[Mg^{2+}]
269 brine was determined to be 4.85 MPa. All over, in the second group of Table 3, the yield stress
270 and bulk modulus values do not point toward a solid conclusion beyond themselves, yet it is
271 possible to say that all the brines that have sulfate resulted in a lower yield stress value. The core
272 saturated with SSW is the most deformed core in this group, Figure 3b. As seen from Table 3,
273 the strain rate within the bypass period for the SSW core was decreased to more than half of it in
274 the flooding period. The strain rate of cores saturated with the Na_2SO_4 brine and SSW-1[Mg^{2+}]
275 were increased to more than five times after flooding initiation.

276

277 On the other hand, obtained creep strain, Table 3. and Figure 4a, reveals that the cores
278 saturated with the Na_2SO_4 brine and SSW-1[Mg^{2+}] were deformed the most and the core
279 saturated with the $MgCl_2$ brine obtained a lower creep strain in both phases, flooding and
280 bypassing. Additionally, these cores obtained a similar abrupt increase in the creep strain rate
281 when the flooding status was changed to bypass. It seems all brines that contain sulfate ions (i.e.
282 Na_2SO_4 , SSW-1 [Mg^{2+}]) create enhanced creep strain on the cores compared to the brines
283 without sulfate ions. However, under different aqueous chemistries the yield stress and bulk
284 modulus values of cores are scattered and show no clear trend. In the following figures, Figure
285 4a and Figure 4b, the time dependent behavior of the cores either flooded or bypassed is

286 illustrated. Core SK3, saturated with distilled water, obtained the least axial creep strain, owing
287 the value of 0.15 %, Table 3. Axial creep strain for the core saturated with $MgCl_2$ started to
288 increase after the onset of the bypassing period, as shown in from Figure 4a. The core saturated
289 with the Na_2SO_4 brine and the core saturated with $SSW-1[Mg^{2+}]$ showed quite similar creep
290 behavior, Figure 4b. The core saturated with $NaCl$ brine deformed less than the Na_2SO_4 and
291 $SSW-1[Mg^{2+}]$ brine saturated cores, but obtained more axial creep strain compared to the $MgCl_2$
292 brine saturated core. All the cores that were flooded after one week of creep are presented in
293 Figure 4b. In this case, the core saturated with SSW deformed the most, followed by the core
294 saturated with the Na_2SO_4 brine. The axial creep strain curves overlap for the core saturated with
295 $MgCl_2$ and $SSW-1[Mg^{2+}]$ until the onset of flooding. $SSW-1[Mg^{2+}]$ flooding tended to deform
296 the core more within the flooding period, compared to the $MgCl_2$ brine.

297

298 Chalk-water Interaction in the Absence of Ions (reference case)

299 In order to get a better understanding and documentation of the influence of different aqueous
300 chemistries on the mechanical strength of the chalk, mechanical tests on a core saturated with
301 distilled water were conducted as reference experiment. Core SK3 was saturated with distilled
302 water and hydrostatically tested, obtaining a yield stress value of 7.7 MPa, Table. 2. Therefore,
303 the hydrostatic loading increment was stopped at 10.5 MPa. Total axial strain within the loading
304 phase was around 0.80 %. The core obtained just 0.15 % total axial creep strain after three days
305 of creep with flooding (4589 minutes), Figure 5. The slope of creep strain versus the time within
306 the creep stage is calculated to be 0.06 %/time decade, Table 3., SK3.

307

308 Saline Solution Flooding

309 In this section, the impact of saline solutions, NaCl and Na₂SO₄ brines, on the mechanical
310 stability of the chalk cores, saturated and flooded with distilled water from the beginning of the
311 loading phase until a certain time during creep period, is demonstrated. Therefore the cores'
312 properties are listed separately, Table 4. It is worth mentioning that 0.2 MPa difference in yield
313 stress value, subsequently creep stress value) will not result in increase of strain rate by factor of
314 two. However, it should be noted that the methodology and experimental procedure is the same
315 as described in samples preparation, equipment, and experimental procedures section.

316 Solutions of NaCl were addressed as indifferent brine toward chalk according to studies
317 performed by Pierre, 1990; Rezaei Gomari et al., 2006; and Strand et al., 2006. In order to verify
318 the effect of NaCl flooding on the compaction behavior of chalk, a compression test was
319 designed on a core pre-saturated by distilled water, core SK20. The core was loaded up to 9.3
320 MPa, 2.8 MPa higher than its yield stress value (6.5 MPa).

321 The duration of the creep stage of core SK20, flooded with distilled water, was almost four
322 days. Subsequently, the flooding fluid was switched to the NaCl brine which clearly had an
323 impact on the creep strain rate, Figure 6. Introducing the NaCl brine increased the compaction
324 rate of the core by a factor of three, from 0.08 %/day to 0.25 %/day. However, after flooding 15
325 PV of NaCl brine, the compaction rate was slightly lower than the compaction rate at the end of
326 the period of distilled water flooding, 0.05 %/day.

327 In order to measure any possible adsorption of Na⁺ ion on to the chalk surface 1.02 g LiCl
328 tracer in 1 liter of NaCl brine solution, Table 1, was introduced to the core SK20 during the creep
329 stage, as the flood was performed. The ion chromatograph (ICS-3000) measured the
330 concentration of three major cations, Li⁺, Na⁺, and Ca²⁺, by analyzing some of the water samples

331 collected at the core outlet. The relative concentration of Na^+ and Li^+ is plotted versus pore
332 volume of the injected brine, Figure 7a. The small area between the relative concentration of Na^+
333 and Li^+ ions, adsorption curves, illustrates that only negligible amounts of Na^+ ions have been
334 adsorbed in the core. Additionally, the concentration of calcium was plotted in Figure 7b.
335 Concentration of Ca^{2+} ions in SSW was used as calcium reference concentration due to the fact
336 that no calcium is presented in the NaCl brine. It is shown that the concentration of calcium was
337 increased to calcium reference concentration when one pore volume of NaCl brine was flooded
338 through the core. Eventually, calcium concentration is decreased and stabilized around 30 % of
339 calcium reference concentration.

340 Another rock mechanical test was conducted on core SK5A, initially saturated and flooded
341 with distilled water. The aim was to perform an adsorption test of sulfate onto the grain surfaces
342 before and after the hydrostatic loading. Therefore, the core-flood of distilled water was first
343 switched to 2.33 gram of KSCN in 0.219 M Na_2SO_4 brine. The relative concentration of these
344 ions, compared to the original brine, versus pore volume of flooded brine is illustrated in Figure
345 8a. It can be noticed that the dispersion front of SCN^- corresponded to about 0.5 PV.
346 Additionally, the tracer curve passed the point, $(\text{PV}, C/C_0) = (1, 0.5)$, which means that the
347 injected fluid is in contact with the total pore volume of the core. The breakthrough curve of
348 sulfate ion was moved toward higher flooded pore volumes due to adsorption of sulfate ions.
349 Finally, the total area between the two adsorption curves is calculated, using a trapezoid method,
350 to be 0.26.

351 After performing the adsorption test, the core was cleaned by flooding several pore volumes of
352 distilled water. Distilled water flooding was continued until no sulfate was detected by a
353 qualitative batch test. Thereafter, the core was hydrostatically loaded to 8.2 MPa, creep stress

354 level. The creep period is shown in Figure 8b. The flooding fluid was switched to the Na_2SO_4
355 brine after 4745 min (around three days, Figure 8b) while the effluents were taken periodically,
356 Figure 8a. Obviously, the brine had a dramatic effect on the axial creep rate. The axial creep rate
357 is increased from 0.5 %/time decade during the period of distilled water flooding to a three times
358 higher value, 2.41 %/ time decade, by introducing the Na_2SO_4 brine, Table 4. The
359 chromatographic separation between SCN^- and SO_4^{2-} was tested for this compacted core, core
360 5A, within the creep phase, Figure 8a. The area between the effluent curves of the two
361 components was slightly changed, 0.25. Notably, the breakthrough for both tracer and sulfate
362 happened a little sooner in the compacted core.

363 Role of Sodium in NaCl Brine-Chalk

364 A hydrostatic compression test followed by two weeks of creep phase was performed on core
365 SK8, which was saturated with the NaCl brine. The core was loaded up to 9.4 MPa of isotropic
366 differential stress during the hydrostatic compression period, Table 2. The yield stress point and
367 bulk modulus were determined to be 6.2 MPa and 0.5 GPa, respectively. The axial strain of this
368 core at the end of the loading phase was measured to be 1.33 %.

369 During the following creep phase (Figures 9a and b), a sudden deviation occurred after
370 approximately 5500 minutes (about four days) where the pore pressure was partly lost for a short
371 period. However, the impact was not major and the trend showed a normal gradual rise before
372 the flooding was shut off at 9973 minutes, Figure 9a. This can also be seen from Figure 9b where
373 a flat trend was observed before the status of flooding was changed. The slope of axial creep
374 strain was approximately 0.45 %/time decade and is not influenced when the flooding status was
375 changed to bypass, Table 4 and Figure 9.

376 Chalk cores saturated with distilled water have been shown to be the strongest core from the
377 mechanical point of view among all the fully water saturated cores (Risnes, 2001; Risnes et al.,
378 2003; Madaland et al., 2008). The result of distilled water saturated core, SK3, is an indication
379 for the above statement since the hydrostatic yield stress value for this core was found to be 7.7
380 MPa, the highest value among all the obtained values for yield stress listed in Table. 2.
381 Additionally, the total axial strain value, obtained within the loading phase, is less than 1 %
382 which is the least value, comparing to the axial strain value for all the other brine saturated cores.
383 In parallel with the loading results, looking at the creep behavior of this core, SK3, showed that
384 the core was deformed only 0.15 % under 10.5 MPa creep stress level after three days of creep,
385 Figure 6 and Table 3.

386 The mechanism of chalk compaction, which was documented in terms of displacement, could
387 be manifested as spatial translation and rotation of calcite grains without significant collision,
388 and subsequently the breaking up of the grains called cataclasis process (progressive fracturing
389 and comminution of rock) (Powell et al., 1994). Many researchers have investigated chalk/water
390 interaction and discussed the various mechanisms in terms of physical and/or chemical effects
391 (Andersen et al., 1992; De Gennaro et al., 2003; Gutierrez et al., 2000; Heggheim et al., 2005;
392 Korsnes, 2007; Papamichos et al., 1997; Risnes et al., 2003; Schroeder and Shao, 1996). One or
393 a combination of the above mentioned chalk/water interactions, depending on the type of pore
394 fluid, might assist or enhance chalk compaction mechanism. It is worthwhile to mention that
395 saturation of dry chalk with different pore fluid caused a weakening effect on the mechanical
396 strength of chalk in the following order: dry < oil < methanol < water. The dry chalk showed the
397 highest yield stress value, followed by chalks treated with oil and methanol, respectively. The
398 chalk saturated with water possess the weakest mechanical strength.

399 According to the above explanation, the enhanced weakening effect of distilled water as
400 observed in core SK3 could be explained both physically and/or chemically. The physical
401 mechanism, capillary phenomena, was adopted from soil mechanics in partially saturated porous
402 media (mechanisms of chalk water interactions). Water injection into chalk within compression
403 tests on chalk resulted in an instantaneous compaction, which was discussed in terms of capillary
404 forces (Brignoli et al., 1994; Schroeder and Shao, 1996). It was proposed that water flooding
405 could destroy water bridges in dry or partially saturated chinks. In other words, full water
406 saturation could diminish the cohesion of material and subsequently the mechanical strength of
407 chalk. However, findings after more investigation downgraded the role of capillary forces in
408 water weakening (Risnes, 2001; Risnes et al., 2003). Chemical mechanisms have been paid more
409 attention in a series of investigations (Gutierrez et al., 2000; Korsnes, 2007; Risnes et al., 2003).
410 Distilled water could affect the surface property of chalk or facilitate the dissolution of chalk
411 (Gutierrez et al., 2000; Pierre et al., 1990). Measurement of zeta potential shows the change of
412 surface charges for chalk powders treated with distilled water and synthetic brines (Kolnes et al.,
413 2008).

414 Although the solubility of calcite in distilled water is not high (Segnit et al., 1962), distilled
415 water could cause the easier abrasion and dissolution of asperities at intergranular contacts, thus
416 assisting the sliding and rotation of the grains. The local process resulted in a weakening process
417 in the case of a distilled water saturated core in comparison with the dry core. Finally, it should
418 be emphasized that, yet again, distilled water caused less weakening to the chalk core when
419 compared to all the other aqueous solutions, e.g., different brines.

420 The NaCl solution was shown as an indifferent fluid toward calcite/chalk surface (Pierre et al.,
421 1990; Rezaei Gomari et al., 2006). However, our experiments clearly showed an actual effect of

422 fluid substitution from distilled water to the NaCl brine within the creep phase, Figure 6. It is
423 presented in Figure 7a that the adsorption of Na⁺ ions towards calcite is negligible, while
424 introducing NaCl resulted in calcium production, Figure 7b. Thus, the observed weakening in
425 chalk strength is not due to adsorption of sodium ions to the surface but is likely a result of the
426 dissolution of chalk in the NaCl brine. Newman (1983) showed that subjecting the chalks to non-
427 equilibrated waters induces dissolution and, subsequently, mechanical instability. Moreover,
428 Millero et al. (1984) measured the solubility of calcite in solutions of NaCl at 25 °C. In their
429 experiments, the concentration of Ca²⁺ did not exceed 0.006 mol/l. An atomic force microscopy
430 of calcite dissolution in saline solutions showed that the dissolution rate of calcite increased in
431 concentrated NaCl (Ruiz-Agudo et al., 2009). It was shown that salinity, i.e., NaCl content, plays
432 a very significant role in the solubility of calcite and the kinetics of calcite dissolution and
433 precipitation (Mucci, 1983). The solubility of calcite in saline solutions was increased at
434 temperatures up to 300 °C (Ellis, 1963). In a study by Zhang and Spiers (2005), the compaction
435 strain rates of calcite samples in 0.1 - 0.5 M NaCl brine and salinity-free samples were compared
436 to each other. The saline samples were compacted three times more than the salinity-free
437 samples. In light of the above experimental facts, it appears that salinity is the key parameter in
438 the observed behavior of NaCl flooding on the compaction strain rate of chalk, Figures 6 and 7.

439 Core SK8 was initially saturated with a 0.657 M NaCl brine. The hydrostatic yield stress value
440 is the second lowest value, compared to all the other experiments, Table 2. Furthermore, in the
441 experiment on core SK8, NaCl brine, the flooding status was changed to bypass in order to
442 quantify the impact of the shut-in period. The aim of the shut-in period within the creep phase of
443 the rock mechanical experiments is to evaluate diffusion, kinetics, and transport processes in the
444 chalk/fluid system. The creep strain and rate of deformation has not been influenced by inserting

445 any changes in the fluid flow path, Figures 9a and b. The diffusion of Na^+ ions in the core, within
446 the bypass period, has not shown any impact on the creep behavior of the core. Also it has been
447 shown that shut-in and reinjection of NaCl did not affect the compaction behavior of the core.
448 However, introducing the NaCl brine to a clean core increased the compaction rate, Figure 6.
449 Based on the observation from Figure 7b, it could be considered that the NaCl brine increased
450 the dissolution of the chalk; hence, it enhanced the compaction of the core within the time
451 dependent period.

452 Role of Sulfate in Na_2SO_4 Solution Flooding

453 One core, SK5A, was saturated and flooded with distilled water within the first three days of
454 creep stage; thereafter, Na_2SO_4 brine was introduced to the system containing chalk and distilled
455 water, Figure 8b. In this section, the results of the rock mechanical tests, both from hydrostatic
456 compression and creep phase, on cores saturated with Na_2SO_4 , are presented. Core SK2,
457 saturated with Na_2SO_4 , was hydrostatically loaded to 7.7 MPa of differential stress since the
458 yield stress value was defined as 4.6 MPa, Table 2. Total axial strain obtained within the loading
459 phase was around 2.2 % and the bulk modulus for this core was determined to be 0.32 GPa.

460 The core was flooded for 9683 minutes (about a week) before changing the flooding status to
461 bypass, Figure 10a. The flooding status was changed when the creep strain had reached a steady
462 trend, Figure 10b. The illustration in Figure 10b shows that the deformation rate was
463 approximately 1.21 %/time decade in this period and it did not change after shutting off the flow
464 of pore fluid in the core, Table 3. At the end of the test, flooding of distilled water did not cause
465 any additional effect on the slope of creep curve. The value of yield stress, core SK2, is smaller
466 than the value for cores saturated with distilled water and NaCl brine, comparing values in Table
467 2. The comparison is in line with rock mechanical experiments performed on the other chalk

468 outcrops (Madland et al., 2009). The zeta potential measurement of the suspension of chalk
469 powder/ Na₂SO₄ brine showed that sulfate ions can change the surface potential of the chalk
470 towards negative values by forming an adsorption layer around chalk grains (Kolnes et al., 2008;
471 Rezaei Gomari et al., 2006). Therefore, it is concluded that sulfate ions could adsorb to the chalk
472 surface through a thin layer adjacent to the chalk grains; consequently, the potential of the
473 surface could be changed toward negatives values. The electrostatic force created by this layer,
474 as a repulsive force between grains, could be responsible for the observed weakening behavior
475 under the influence of sulfate-rich brines (Risnes and Flaageng, 1999; Hiorth et al., 2008a;
476 Hiorth et al., 2008b; Madland et al., 2009). The switch from flooding to bypass did not generate
477 any deviation in the steady state time dependent behavior of core SK2, as depicted in Figure 10a,
478 b. Therefore, the diffusion of SO₄²⁻ ions, if any, does not affect the compaction rate of the core
479 fully saturated with the Na₂SO₄ brine.

480 It is shown that the concentration of Na⁺ and SO₄²⁻ ions in the sampled effluents was more or
481 less around the original concentration of these ions in the Na₂SO₄ brine, Figure 11a. Chemical
482 analysis of the sampled effluent at the core outlet, core SK2, shows that in comparison with the
483 concentration of calcium in seawater, only a little calcium is produced during the flooding
484 period, Figure 11b. The calcium concentration remains stable within the bypass period which is
485 expected since the flooding brine contains no calcium. When distilled water was flooded through
486 the core, the production of calcium increased and reached the amount of one-third of the
487 seawater concentration in the last three collected samples.

488

489 Core SK5 and SK6, saturated with 0.219 M Na₂SO₄, were also mechanically tested, but in this
490 case the brine was bypassing the cores for one week of creep. These cores were loaded to 7.6

491 MPa and 7.7 MPa of isotropic differential stress since the point of yield stress for cores SK5 and
492 SK6 was found out to be 4.8 MPa and 5.9 MPa, respectively. Since the result of hydrostatic
493 loading on core SK5 was reproduced in the experiment on the core SK6, only the bulk modulus
494 value and total axial strain of core SK5 is shown in Table 2.

495 The flooding status was changed from bypass to flooding after about a week for both cores
496 (9584 minutes for core SK5 and 9567 minutes for core SK6), as seen in Figure 12a. From Figure
497 12b, a change in the slope of creep strain becomes obvious when the cores are bypassed
498 compared to the flooding period. The axial creep strain rate, valid for both cores SK5 and SK6
499 during the bypass period, is 0.5 %/time decade, which is increased to 2.9 %/time decade within
500 the flooding period, Table 3. The flow rate of the brine through core SK6 was increased to 2
501 PV/day after two weeks of creep (20703 minutes) which did not tend to create any deviation on
502 the slope of the creep curve, Figure 12a. Distilled water flooding also had no impact on the creep
503 trend. The rock mechanical test on core SK5 was performed in the same manner as in the test on
504 core SK6. After a similar creep trend was obtained, the flooding brine was changed from Na_2SO_4
505 to SSW-1[Mg^{2+}] at around 12834 minutes (about 9 days), Figure 12a. The brine was substituted
506 during the steady state of the creep phase. The intention for this change was to study the effect of
507 SO_4^{2-} ions on the chalk in the presence of calcium. Core SK5 was predicted to follow the same
508 trend as core SK6 if the brine had not been changed and any diversion from the predicted trend is
509 therefore assumed to be caused by the new brine. Apparently, no change was observed due to
510 this substitution. The core was flooded by distilled water at the end of the creep phase which had
511 no impact on the creep behavior.

512 In the experiments conducted on cores SK5 and SK6, the objective is to examine the influence
513 of flooding initiation of the Na_2SO_4 brine to the cores, which are entirely bypassed from the

514 beginning of the loading phase and the first week of the creep phase, Figures 12a and b. First, the
515 result of hydrostatic loading, listed in Table 2, indicates that the average yield stress value of
516 cores SK5 and SK6 is very close to the value for core SK2, treated with Na₂SO₄. In addition, the
517 mean bulk modulus value for cores SK5 and SK6 is reasonably similar to the calculated value for
518 core SK2, treated with Na₂SO₄. A substantial difference appeared during the creep phase of core
519 SK5 and SK6 in comparison to the creep behavior of core SK2, Figures 11a and 13a. When the
520 bypass period changed to flooding after one week of creep, a substantial deviation happened in
521 the slope of the axial strain. This clearly shows the effect of flooding fresh SO₄²⁻ ions and,
522 consequently, disturbing the equilibrium condition inside the core. The brine, an Na₂SO₄
523 solution, has a concentration of sulfate ions ten times higher than the concentration of sulfate in
524 SSW. However, the solution has an ionic strength similar to NaCl brine; hence, the observed
525 enhancement on the axial creep strain could not be explained by the difference in the ionic
526 strength.

527 In Figures 14a and b the chemical analyses of the effluents that were taken during the bypass
528 and flooding periods of the test on core SK6 are plotted. The status change from bypass to
529 flooding had no effect on the concentration of sodium and sulfate, Figure 13a. The concentration
530 of calcium was increased after the change in the flooding status, Figure 13b.

531

532 A possible explanation would be the abrasion and dissolution of chalk grains (Hiorth et al.,
533 2008a, b). Some studies showed that SO₄²⁻ ions have the ability to make an ion pair with the
534 desolvated ions from the surface of calcite and lead to enhanced dissolution (Ruiz-Agudo et al.,
535 2009). The thickness of the adsorbed layer of sulfate ions onto the chalk surface is on the order
536 of the molecular diameter that is surrounded by the hydrodynamic boundary layer and bulk

537 solution. The thermodynamic equilibrium in the aquatic system, saturated chalk and solute, could
538 be disturbed by flooding initiation, characterized by the flow of sulfate ions in the bulk solution
539 and affecting the already formed adsorption layer around the chalk grains. As a principle, any
540 change in the equilibrium condition of a system would cause the system to counteract the effect
541 of the change. If the concentration of sulfate ions inside the bulk solution is assumed to be
542 increased markedly, over a short period of time after flooding, some counter-ions, cations such
543 as Ca^{2+} , need to be added in order to turn back the system to the equilibrium condition. The
544 deficit of counter-ions in the bulk solution should be supplied by a dissolution of Ca^{2+} from the
545 chalk grains. Based on this scenario, the amount of calcium ions in the effluents was increased.
546 As shown in Figure 13a, the concentration of sulfate as well as the sodium ions concentration
547 remained stable after initiation of the flooding phase for one week of creep. Figure 13b shows
548 that calcium is also produced around 30 % of calcium reference concentration when the flooding
549 is started. The observed weakening effect could be explained, yet not directly, by dissolution
550 from calcite grains.

551 Role of Magnesium in the Brine-Chalk System

552 Core SK7 was saturated with 0.219 M MgCl_2 brine. The applied hydrostatic stress was
553 increased to 9.2 MPa, creep stress level, and kept constant. The yield stress value was
554 determined as 5.7 MPa, Table 2. The values of bulk modulus and total axial strain of the core
555 SK7 are reported in Table 2 as 0.46 GPa and 1.82 %, respectively.

556 The core was bypassed during the first six days of creep, Figure 14a. The obtained axial strain
557 was 1.27 % and the core deformed with the rate of 0.84 %/time decade, Figure 14b and Table 3.
558 The first change from bypass to flooding was made after 8550 minutes. The core flood was
559 continued for one week and a decrease in the deformation rate was detected, 0.37 %/time decade,

560 Table 3. It is also clear from Figure 14a that the creep trend immediately shows a flattening
561 creep. Thereafter, by bypassing the core, the creep rate was increased again, 0.77 %/time decade,
562 Figures 14a, b. The final change, where the status was changed back to flooding, was done after
563 23378 minutes (about 16 days). The flooding rate was increased to 2 PV/day during this period
564 and the deformation rate did not change substantially compared to the pervious flooding phase. It
565 is obvious from Figure 14a that within flooding periods the rate of deformation was slowed
566 down.

567

568 Additional tests, involving cores flooded with 0.219 M or 0.110 M MgCl_2 brine within the
569 loading phase and the first week of creep, were conducted in order to elaborate the observed
570 behavior of core SK7 during the bypass period, Figures. 14a, b. In a creep test performed on core
571 SK1, illustrated in Figure 15a, it was observed that the deformation rate was increased after the
572 flow of brine into the core was shut off. Apparently, the obtained creep strain was increased from
573 0.85 % to 1.3 % after one week of bypass. Additionally, the creep strain rate was increased from
574 0.3 %/time decade within the flooding phase to 1.7 %/time decade during the bypass period,
575 Figure 14b.

576 The observed phenomenon was confirmed in other tests using a lower concentration of MgCl_2
577 brine, 0.110 M, as saturation brine, Figures 15a, b. The figures also show that the cores saturated
578 with a lower concentration of MgCl_2 brines, core SK22 and SK25, obtained more creep during
579 the bypass period. It is worth noting that the creep strain of these cores is in comparison with the
580 core saturated with a higher concentration of MgCl_2 brine, 0.219 M, core SK1.

581

582 Rock mechanical experiments on cores saturated with MgCl_2 brine showed that bypassing with
583 MgCl_2 during the shut-in period causes an enhancement in the deformation rate within the creep
584 phase, Figures 14 and 15. Additionally, saturation of the cores with a half concentration of
585 MgCl_2 brine, 0.110 M, and bypassing them also caused an enhancement in the obtained value for
586 the axial creep strain, Figures 15a and b; however, to a lesser extent.

587 To attain a better understanding of the chemical reactions between the MgCl_2 solution and
588 chalk, the concentration of major ions (Mg^{2+} and Ca^{2+}) in the effluents, taken periodically during
589 the creep phase at the outlet of core SK7, was measured by the ion chromatograph. The
590 concentrations of Mg^{2+} and Ca^{2+} ions in the effluents are plotted in Figure 16. In the figure the
591 original concentration of magnesium (0.219 M) and the calcium concentration in SSW (0.013 M)
592 are included as reference values. The x-axis in Figure 16 corresponds to the x-axis in Figure 14a.

593 During the first phase, bypass, the concentration of Mg^{2+} is fluctuating around its original
594 value and no calcium is detected. Flooding with the MgCl_2 brine causes a sudden drop in the
595 magnesium concentration; whereas, it increases the calcium concentration. After its initial
596 maximum, the Ca^{2+} concentration during the flooding phase, the concentration of calcium is
597 finally close to concentration in seawater, 0.013 M. No sampled effluents were analyzed from
598 the second bypass period. As soon as the core flood is initiated again, the concentrations of
599 magnesium and calcium follow the imaginary extrapolation of the trend within the flooding
600 period. At the end of the experiment, the calcium concentration decreased and stabilized a little
601 below the concentration in seawater; the concentration of magnesium is close to the original
602 Mg^{2+} ion concentration. A clear observation could be drawn as magnesium is retained inside the
603 core and calcium is being produced during the flooding phases.

604

605 It was stated that within the bypass period, diffusion and transport phenomena are of great
606 importance. It is indicated in Figure 16 that an intricate chemical chalk/fluid interaction occurred
607 due to the $MgCl_2$ brine as saturation brine. Within the flooding periods, magnesium is retained
608 inside the core; meanwhile, calcium is produced. Initiation of flooding, after the first bypass
609 phase, contributed to a dramatic decrease in the magnesium ions concentration and substantial
610 production of calcium ions. As the experiment progressed with time, concentration of
611 magnesium ions is recovered sharply toward the magnesium reference concentration, 0.219 M.
612 Concurrently, calcium production is stabilized around 0.013 M, calcium reference value, after a
613 gradual decline. Retention of magnesium and production of calcium during the experiment
614 clearly indicated the existence of the two opposing reactions: dissolution (calcium production)
615 and precipitation (magnesium-bearing minerals). A series of similar experiments showed that
616 $MgCl_2$ brine has a significant weakening effect on the mechanical strength of Liège chalk
617 (Madland et al., 2009). The observed weakening effect could be discussed in terms of
618 precipitation of magnesium bearing minerals and dissolution of calcium from the chalk. The
619 proposed explanation is not directly linked to the weakening of the chalk matrix. However, the
620 dissolution and precipitation, together with any possible change in the surface charge could be
621 the dominant factors in the weakening mechanism of chalk (Zangiabadi et al., 2009).

622 In this study, the enhanced deformation of the $MgCl_2$ brine saturated cores within the bypass
623 period could be explained tentatively by the following hypothesis. During the flooding phases,
624 $MgCl_2$ brine has a tendency to flow through the highly permeable zones (macro-porosity pores)
625 of the porous medium (chalk). Diffusion to the low permeable zones and transport-controlled or
626 surface-controlled dissolution and precipitation of solute are the dominant phenomena as soon as
627 flooding has been stopped. These types of reactions, dissolution and precipitation, in low

628 permeable zones (nano-porosity pores) which assist the compaction of the chalk, sliding, and
629 rotation of grains, might explain the observed enhanced weakening. The sketch in Figure 17
630 explains the flow paths within the flooding phase and probable pathways within the bypass
631 period.

632

633 CaCl₂ Solution Flooding of Chalk Cores

634 Two cores, saturated and flooded continuously with 0.219 M CaCl₂, were tested mechanically.
635 The hydrostatic loading and creep behaviors of these cores are presented in Figures 18a and b.
636 The average value of yield stress for cores SK26 and SK28 is 4.95 MPa. The hydrostatic phase
637 of these two cores was almost identical, which can be seen from the values reported in Table 2.
638 The cores were left to creep under 6.6 MPa isotropic differential stresses, Figure 18a. The
639 average deformation of the cores reached 0.93 % after a week (about 10000 minutes) and the
640 strain rate was 0.45 %/time decade. The Ca²⁺ concentration in the sampled effluents, taken
641 during the creep phase of the test on core SK26, was determined by ion chromatography, Figure
642 18b. The Ca²⁺ concentrations do not show a clear trend during the creep phase/sampling period;
643 they vary around the original Ca²⁺ concentration (0.219 M) in the brine.

644

645 The amount of dissolved calcium carbonate in the brine, 32.2 g/l, roughly corresponds to the
646 concentration of this salt in typical formation brines, e.g., Ekofisk brine. Moreover, activity of
647 the equilibrium chalk powder with CaCl₂ brine is around 0.99, according to the fluid properties
648 taken from a table in Hughes, 1999. In a study by Risnes et al. (2003), the rock mechanical test on
649 cores saturated with NaCl and CaCl₂ brine, showed that the mechanical stability can be described

650 independent of the type of ions presented in the pore fluid. Thus, it concluded that the water
651 activity plays an important role in the weakening process of chalk.

652 In the present experiments, the ionic strength of NaCl and CaCl₂ brine are similar, Table 1.
653 Apparently, adsorption and/or precipitation from CaCl₂ brine would not be the case in the
654 condition of our study. Similar values of the axial creep deformation are obtained for the cores
655 saturated with NaCl and CaCl₂, Figures 18a and b. Therefore, the observed similar compaction
656 could be explained by the salinity of the brines.

657 Verification Tests: Flooding of Seawater Without Magnesium (SSW-1[Mg²⁺])

658 Cores SK4, SK16, and SK11 were saturated with SSW without magnesium (SSW-1[Mg²⁺]).
659 Hydrostatic compression tests were conducted on all of these cores, Table 2. Core SK16 was
660 flooded from the beginning of the loading phase to the end of the first week of creep stage
661 whereas the brine bypassed core SK4 and core SK11 in the same period. The yield stress value
662 for cores SK4, SK16, and SK11 was found to be 5.7, 4.7, and 4 MPa, respectively. Accordingly,
663 the creep stress level was set to 9, 7.9, and 6.9 MPa. The average axial strain by the end of the
664 loading phase for cores SK4 and SK11 is very similar to the value for SK16, Table 2. Both cores
665 SK4 and SK11 deformed less within the first week of creep stage compared to core SK16, Figure
666 19a. At the end of the first week of creep, the total axial creep strain of core SK16 is close to 2
667 %, around two times higher than the axial creep strain of cores SK4 and SK11 at the same time.
668 As soon as the flooding is initiated, the axial creep deformation of cores SK4 and SK11 begins to
669 increase. In core SK16, the same behavior can be seen when flooding is again initiated (at around
670 26000 min creep time), after a period of bypass for ten days.

671 The axial creep strain for core SK11 is changed from 0.46 %/time decade within the bypass
672 period to 2.3 %/time decade after initiation of flooding, Figure 19b and Table 3. On the other

673 hand, the axial creep strain for core SK16 remains stable around 1.43 %/time decade until the
674 second stage of flooding, Figure 19b. The axial creep strain of cores SK16 and SK4 are on top of
675 each other from 26000 minutes. After three weeks of creep (21500 min), the flooding rate was
676 decreased for core SK11 to one half of its original value. The drop in the flow rate had no effect
677 on the axial creep strain rate.

678

679 In a study by Korsnes (2007), it is shown that seawater without magnesium, at a temperature of
680 90 °C, could cause more axial strain within the creep phase compared with the seawater. It was
681 suggested that an irreversible thermodynamic condition could be responsible for the observed
682 behavior. Additionally, in a study by Madland et al. (2008) on a different type of chalk, the cores
683 saturated with seawater without magnesium obtained more deformation during the creep stage
684 than the cores saturated with seawater. This observation was also seen in experiments performed
685 by Zangiabadi et al. (2009 and 2011). They showed that SSW-1[Mg²⁺] could facilitate the
686 formation of anhydrite and promote increased CaCO₃ dissolution due to the reduced
687 concentration of Ca²⁺ ions in the equilibrium solution. Further, it was concluded that for both
688 higher and lower porosity chalks, the impact of varying the flooding fluid causes a weakening in
689 the following order: distilled water < seawater without sulfate < seawater < seawater without
690 magnesium.

691 The behavior of cores saturated with SSW-1[Mg²⁺] brine within the loading phase can be seen
692 in Figures 3a and b, which shows that the cores have quite a low yield point, most likely due to
693 the presence of sulfate ions. Heterogeneity of the chalk could explain the scatter in the yield
694 strength and obtained strain within the loading phase (Korsnes, 2007). Time dependent behavior
695 of these cores is illustrated in Figures 18a and b. Sulfate ions in the brine, SSW-1[Mg²⁺], could

696 be responsible for some aspects observed in the creep stage of the cores (role of sulfate in
697 Na_2SO_4 solution flooding). Thus, the results were explained by the use of similarities found in
698 the experiments on the cores saturated with Na_2SO_4 brine. Apparently, the higher value of the
699 axial creep strain within the flooding period compared to the bypass phase, both during the first
700 creep phase, is similar to the behavior of the cores saturated with the Na_2SO_4 brine. Thus, the
701 weakening effect is more pronounced when the brine is flowing through the pores.

702 One can see that initiation of flooding after one week of bypass caused the axial creep strain to
703 increase, Figure 19 and Table 3. The observed impact is similar to what happened after flooding
704 the Na_2SO_4 brine to the bypass core, Figures 12a and b. Due to the close correspondence of the
705 two creep phases, sulfate ions could be assumed to be responsible for the pronounced axial creep
706 deformation after the initiation of flooding SSW-1[Mg^{2+}]. It was stated that sulfate ions could
707 firmly adsorb to the chalk surface (role of sulfate in Na_2SO_4 solution flooding). The statement is
708 based on the surface potential measurement of chalk powder that was not disturbed when the
709 flooding state switched to bypass (diffusion). However, when changing from bypass to flooding,
710 the bulk flow of new sulfate ions could easily disturb the equilibrated system, chalk-pore fluid,
711 and initiate an irreversible, e.g., dissolution, reaction inside the core. The phenomena could be
712 explained by the ability of sulfate ions to make an ion pair with available desolvated calcite
713 surface ions. This formation of an ion pair is disrupted by the initiation of flooding, thus causing
714 enhanced weakening. On the other hand, the changing flooding status has a reverse effect on
715 weakening, when the brine is MgCl_2 . The diffusion and transport phenomena are playing a
716 critical role when the MgCl_2 brine is not flooded through the core where retained magnesium
717 from the flooding phase initiated the calcium production process.

718 CONCLUDING REMARKS

719 A systematic approach was encountered to investigate the rock mechanical behavior of chalk
720 reservoirs in presence of variety of water compositions. The aqueous solutions of common salts
721 (NaCl, Na₂SO₄, MgCl₂, and CaCl₂) as well as a more complex aqueous brines, i.e., seawater
722 without magnesium (SSW-1[Mg²⁺]), were selected to examine their effects on the mechanical
723 strength of chalk. Additionally, two different test conditions were studied in the conducted
724 experiments: (1) Continuous flooding of mentioned brines through the core under test; and (2)
725 No flooding by opening the bypass valve; leaving one pore volume of brine inside the core. The
726 results were discussed in terms of hydrostatic loading and time-dependent behavior, with
727 chemical analysis for major ions (Ca²⁺, Mg²⁺, and SO₄²⁻) from sampled flooding effluent. The
728 conclusions of the work are briefly listed as follows:

729

- 730 • Certain types of mechanisms could explain the chalk/fluid interaction in the presence of
731 individual ions
- 732 • Salinity is the key element when it comes to chalk water weakening
- 733 • Seawater without magnesium and Na₂SO₄ brine could substantially weaken the chalk
- 734 • Creep strain and its rate was found out to be similar for cores saturated with MgCl₂ or
735 seawater
- 736 • Diffusion and transport-controlled phenomena could cause a pronounced weakening
737 when it comes to seawater and MgCl₂ brine
- 738 • Creep strain induced by exposure to seawater or MgCl₂ occurred at greater rates during
739 periods of bypass than flooding
- 740 • Dissolution of chalk grains solely or together with precipitation (or re-precipitation)
741 should be taken into account in the field of water weakening of chalk

742 • Flooding rate plays an important role in the changing of the time dependent behavior of
743 chalk

744 ACKNOWLEDGMENT

745 The Norwegian Research Council (NFR) is acknowledged for the financial support provided.
746 The authors would like to thank rock mechanics group, national IOR center of Norway, and
747 Professor Merete V. Madland at the University of Stavanger. The authors would like to express
748 gratitude toward International Research Center in Stavanger (IRIS) and especially Professor
749 Aksel Hiorth.

750 ABBREVIATIONS

751 SSW, synthetic seawater; SSW-1[Mg²⁺], synthetic seawater without magnesium; DW, distilled
752 water.

753 REFERENCES

754 Allen, D. R., Mayuga, M. N. (1970) "Subsidence in the Wilmington oilfield, Long Beach,
755 California." *U.S.A. Land Subsidence Sym., Int. Ass. Sci. Hydrol. & UNESCO*, 66-87.

756 Andersen, M. A., Foged, N., Pedersen, H. F. (1992) "The rate-type compaction of a weak
757 North Sea chalk." *33rd U.S. Rock Mech. Sym.*, Santa Fe, New Mexico.

758 Brignoli, M., Santarelli, F. J., Righetti, C. (1994) "Capillary phenomena in impure chalk."
759 *EUROCK'94*, Delf, The Netherlands.

760 Cathles, L. M. (2006) "EQAlt-Equilibrium Chemical Alteration. Combined Physical and
761 Chemical Geofluids Modelling." University of Windsor, Ontario, Canada.

762 Chin, L. Y., Boade, R. R., Nagel, N. B., Landa, G.H. (1994) "Numerical simulation of Ekofisk
763 reservoir compaction and subsidence: Treating the mechanical behavior of the overburden and
764 reservoir." *2nd SPE/ISRM Rock Mech. In Petrol. Eng. (EUROCK 94), Int. Conf.* Delft, The
765 Netherland., 787-794.

766 De Gennaro, V., Delage, P., Cui, Y. J., Schroeder, Ch., Collin, F. (2003) "Time-dependent
767 behavior of oil reservoir chalk: a multiphase approach." *Soils and Foundations*, 43(4): 131-148.

768 Delage, P., Schroeder, C., Cui, Y. J. (1996) "Subsidence and capillary effects in chalks."
769 *Eurock'96*, Balkema, Rotterdam, The Netherlands.

770 Dusseault, M. B. (1983) "Identifying reservoirs susceptible to subsidence due to fluid
771 withdrawal." *Subsidence Due to Fluid Withdrawals Forum*, Checotah, Okla. U.S. Dept. Energy
772 & Venez Min Energy Mines, 6-14.

773 Ellis, A. (1963) "The solubility of calcite in sodium chloride solutions at high temperatures."
774 *Am. J. Sci.*, 261: 259-267.

775 Fredrich, J. T., Arguello, J. G., Thorne, B. J., Wawersik, W. R., Deitrick, G. L., De Rouffignac,
776 E. P., Myer, L. R., Bruno, M. S. (1996) "Three-dimensional geomechanical simulation of
777 reservoir compaction and implications for well failures in the Belridge Diatomite." *Annul. SPE*
778 *Tech. Conf.*, Denver U.S., 195-210.

779 Gauer, P. R., Sylte, J. E. Nagel, N. B. (2002) "Ekofisk field well log decompaction."
780 *SPE/ISRM Rock Mech. Conf.*, SPE/ISRM: 78177, Irving TX.

781 Gutierrez, M., Øino, L. E., Høeg K. (2000) “The effect of fluid content on the mechanical
782 behavior of fractures in chalk.” *Rock Mech. and Rock Eng.*, 33(2): 93-117.

783 Heggheim, T., Madland, M. V., Risnes, R., Austad, T. (2005) “A chemical induced enhanced
784 weakening of chalk by seawater.” *J. Petr. Sci. Eng.*, 46(3): 171-174.

785 Hellmann, R., Renders, P. J. N.; Gratier, J.-P., Guiguet, R. (2002a) “Experimental pressure
786 solution of chalk in aqueous solutions: Part 2. Deformation examined by SEM, porosimetry,
787 synthetic permeability, and X-ray computerized tomography.” *Water -Rock Interactions, Ore
788 Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar. The Geochemical
789 Society, Special Publication, 7.*

790 Hellmann, R., Renders, P. J. N., Gratier, J.-P., Guiguet, R. (2002b) “Experimental pressure
791 solution of chalk in aqueous solutions: Part 1. Deformation behavior and chemistry.” *Water –
792 Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A.
793 Crerar. The Geochemical Society, Special Publication, 7.*

794 Hiorth, A., Cathles, L. M., Kolnes, J., Vikane, O., Lohne, A., Korsnes, R. I., Madland, M. V.
795 (2008) “Chemical modeling of wettability change in carbonate rocks.” *Wettability Sym.*, Abu
796 Dhabi, UAE.

797 Hiorth, A., Cathles, L. M., Kolnes, J., Vikane, O., Lohne, A., Korsnes, R. I., Madland, M. V.
798 (2008) “A chemical model for the seawater-CO₂-carbonate system- aqueous and surface
799 chemistry.” *Int. Conf. of Society of Core Analysts, Abu Dhabi, UAE.*

800 Hjuler, M. L. (2007) *Diagenesis of Upper Cretaceous onshore and offshore chalk from the
801 North Sea area.* PhD Thesis, Danish Technical University (DTU).

802 Homand, S., Shao, J. F. (2000) "Mechanical behavior of a porous chalk and effect of saturating
803 fluid." *Mech. Cohes.-Frict. Mater.*, 5: 583-606.

804 Hughes, B. (1999) *Fluid fact, Engineering Handbook*, Part Number 008902097. Baker Hughes
805 INTEQ.

806 Kolnes, J., Hiorth, A., Siqveland, O. K., Omdal, E., Zangiabadi, B., Madland, M. V. (2008)
807 "Contact angle measurement on calcite using model oils" *Wettability Sym.*, Abu Dhabi, UAE.

808 Korsnes, R. I. (2007) *Chemical induced water weakening of chalk by fluid-rock interactions, a*
809 *mechanistic study*. PhD Thesis, University of Stavanger (UiS), Stavanger.

810 Korsnes, R. I., Madland, M. V., Austad, T., Haver, S., Røsland, G. (2008) "The effects of
811 temperature on the water weakening of chalk by seawater." *J. Petr. Sci. Eng.*, 60(3-4): 183-193.

812 Madland, M. V., Hiorth, A., Korsnes, R.I., Evje, S., Cathles, L. (2009) "Rock fluid interaction
813 in chalk exposed injection of seawater, MgCl₂, and NaCl Brines with equal ionic strength." *15th*
814 *European Sym. on improved oil recovery*, Paris, France.

815 Madland, M. V., Midtgarden, K., Manafov, R., Korsnes, R. I., Kristiansen, T. G., Hiorth, A.
816 (2008) "The effect of temperature and brine composition on the mechanical strength of Kansas
817 chalk." *Int. Sym. of the Society of Core Analysts (SCA)*, Abu Dhabi, UAE.

818 Maury, V., Piau, J. M., Halle, G. (1996) "Subsidence induced by water injection in water
819 sensitive reservoir rocks: the example of Ekofisk." *5th North Sea chalk Sym.*, Reims, France.

820 Millero, F. J., Milne, P. J., Thurmond, V. L. (1984) "The solubility of calcite, strontianite and
821 witherite in NaCl solutions at 25°C." *Geochimica et Cosmochimica Acta.*, 48(5): 1141-1143.

822 Mucci, A. (1983) "The solubility of calcite and aragonite in seawater at various salinities
823 temperatures, and one atmosphere total pressure." *Am. J. Sci.*, 283: 780-799.

824 Nagel, N. B., (2001) "Compaction and subsidence issues within the petroleum industry: from
825 Wilmington to Ekofisk and beyond." *Phys. Chem. Earth (A)*, 26(1-2): 3-14.

826 Newman, G. H. (1983) "The effect of water chemistry on the laboratory compression and
827 permeability characteristics of some North Sea chalks." *J. Petr. Tech.*, 35(5): 976-980.

828 Papamichos, E., Brignoli, M., Santerelli, F. J., (1997) "An experimental and theoretical study
829 of partially saturated collapsible rocks." *Mech. Cohes.-Frict. Mater.*, 2: 251-278.

830 Pierre, A., Lamarche, J. M., Mercire, A., Foissy, A., Persello, J. (1990) "Calcium as potential
831 determining ion in aqueous calcite suspensions." *J. Dispersion Sci. & Tech.*, 11(6): 611-635.

832 Plischke, B. (1996) "Some aspects of numerical simulation of water-induced chalk
833 compaction." *5th North Sea Chalk Sym.*, Reims, France.

834 Powell, B. N., Lovell, G.L. (1994) "Mechanisms of chalk compaction." *SPE/ISRM Rock Mech.*
835 *in Petrol. Eng. Conf.*, Delf, The Netherlands.

836 Pratt, W. E., Johnson, D.W. (1926) "Local subsidence of the Goose Creek oilfield." *J. Geol.*,
837 34: 577-590.

838 Puntervold, T., Strand, S., Austad, T. (2007) "New method to prepare outcrop chalk cores for
839 wettability oil recovery studies at low initial water saturation." *Energy & Fuels.*, 21: 3425-3430.

840 Rezaei Gomari, K. A., Hamouda, A. A., Denoyel, R. (2006) "Influence of sulfate ions on the
841 interaction between fatty acids and calcite surface." *Colloids and Surfaces A: Physicochem. Eng.*
842 *Aspects.*, 287(1-3): 29-35.

843 Risnes, R. (2001) "Deformation and yield in high porosity outcrop chalk." *Phys. Chem. Earth*
844 *(A).*, 26(1-2): 53-57.

845 Risnes, R., Flaageng, O. (1999) "Mechanical properties of chalk with emphasis on chalk– fluid
846 interactions and micromechanical aspects." *Oil Gas Sci. Tech. IFP*, 54(6): 751-758 (Éditions
847 Technip).

848 Risnes, R., Haghghi, H., Korsnes, R.I., Natvik, O. (2003) "Chalk–fluid interactions with
849 glycol and brines." *Tectonophysics*, 370: 213-226.

850 Ruddy, I., Anderson, M.A., Pattillo, P.D., Bishlawi, M., Foged, N. (1998) "Rock
851 compressibility, compaction, and subsidence in a high-porosity chalk reservoir: a case study of
852 Valhall field." 63rd *Annul. SPE Tech. Conf.*, Houston, 179-186.

853 Ruiz-Agudo, E., Putnis, C.V., Jiménez-López, C., Rodriguez-Navarro C. (2009) "An atomic
854 force microscopy study of calcite dissolution in saline solutions: The role of magnesium ions."
855 *Geochimica et Cosmochimica Acta.*, 73(11): 3201-3217.

856 Schoonbeek, J. B. (1977) "Land subsidence as a result of gas extraction in Groningen." The
857 Netherlands, 2nd *Int. land subsidence Sym.*, Anaheim, Calif., 267-284.

858 Schroeder, C., Shao, J. F. (1996) "Plastic deformations and capillary effects in chalks." 5th
859 *North Sea chalk Sym.*, Reims, France.

860 Segnit, E. R., Holland, H. D., Biscardi, C. J. (1962) "The solubility of calcite in aqueous
861 solutions -I: The solubility of calcite in water between 75 and 200 °C at CO₂ pressures up to 60
862 atm." *Geochimica et Cosmochimica Acta.*, 26: 1301-1331.

863 Smith, D. J. (1988) "Project management of subsidence and Ekofisk jacking project." 20th
864 *Annu. SPE Offshore Tech. Conf.*, (OTC 88), Houston TX, 341-368.

865 Spencer, A. M., Briskeby, P. I., Christensen, L. D., Foyn, R., Kjølleberg, M., Kvadsheim, E.,
866 Knight, I., Larsen, M. R., Williams, J. (2008) "Petroleum geoscience in Norden – exploration,
867 production and organization." *Episodes*, 31, 115-124.

868 Strand, S., Høgnesen, E. J., Austad, T. (2006) "Wettability alteration of carbonates-effects of
869 potential determining ions (Ca²⁺ and SO₄²⁻) and temperature." *Colloids and Surfaces A:*
870 *Physicochem. Eng. Aspects.*, 275: 1-10.

871 Sulak, R. M. (1990) "Ekofisk field: The first 20 years." 65th *Annual SPE Tech. Conf.*, New
872 Orleans, LA., 521-529.

873 Zangiabadi, B., Korsnes, R.I., Hildebrand-Habel, T., Hiorth, A., Sutarjana, I.K., Lian, A.,
874 Madland, M.V. (2009) "Chemical water weakening of various outcrop chalks at elevated
875 temperature." In: H.I. Ling, Smyth, A., and Betti, R. (Editor), 4th *Biot conference on*
876 *poromechanics*. DEStech Publication Inc. Columbia University, New York, 543-548.

877 Zangiabadi, B., Kulathilagon P., Midtun, B. (2011) "Evaluation of rock-fluid interactions in an
878 outcrop chalk: Experimental study with MgCl₂ solution." 45th *US Rock Mech. Sym.*, 4th *U.S.-*
879 *Canada Rock Mech. Sym.*, Asheville, NC.

880 Zhang, X., Spiers, C. J. (2005) "Compaction of granular calcite by pressure solution at room
881 temperature and effects of pore fluid chemistry." *Int. J. Rock. Mech. Mining Sci.*, 42: 950-960.

882

883 **Table 1.** Brine composition; M = molar

Brine Salts (g/l)	0.657 M NaCl	0.657 M NaCl with tracer	0.219 M Na ₂ SO ₄	0.219 M Na ₂ SO ₄ with tracer	0.219 M MgCl ₂	0.110 M MgCl ₂	0.219 M CaCl ₂	SSW-1[Mg ²⁺]	SSW
LiCl (Li ⁺ : tracer)		1.02							
NaCl	38.40	38.40						27.62	23.38
Na ₂ SO ₄			31.1	31.1				3.41	3.41
KSCN (SCN ⁻ : tracer)				2.33					
NaHCO ₃								0.17	0.17
KCl								0.75	0.75
MgCl ₂ + 6 H ₂ O					44.5	22.25			9.05
CaCl ₂ + 2 H ₂ O							32.2	1.91	1.91

884

885 **Table 2.** Experimental observations for cores in different aqueous solutions during loading phase

Core no.	Brine	Porosity [%]		Yield [MPa]		Bulk modulus [GPa]		Creep stress level [MPa]		Total strain within loading [%]	
Group 1: First phase; Flooding, second phase; Bypass											
SK3	DW	43.90		7.7		1.1		10.5		0.80	
SK8	NaCl	45.10		6.2		0.50		9.4		1.33	
SK2	Na ₂ SO ₄	45.20		4.6		0.32		7.7		2.20	
SK1	MgCl ₂	45.76		5.0		0.71		7.3		1.4	
SK26	CaCl ₂	45.63	Avg. 46.15	5.2	Avg. 4.95	0.52	Avg. 0.54	6.6		0.68	Avg. 0.73
SK28		46.68		4.7		0.55				0.77	
SK16	SSW-1[Mg ²⁺]	47.12		4.7		0.57		7.9		1.16	
Group 2: First phase; Bypass, second phase; Flooding											
SK6	Na ₂ SO ₄	45.1		4.9	Avg. 4.85	0.37		7.7	Avg. 7.65	1.9	Avg. 2.25
SK5		45.4	4.8	7.6			2.6				

SK7	MgCl ₂	45.5		5.7		0.46		8.8		1.82	
SK4	SSW-1[Mg ²⁺]	44.55	Avg. 45.20	5.7	Avg. 4.85	0.64	Avg. 0.5	8.9	Avg. 7.9	0.81	Avg. 1.17
SK11		45.84		4.0		0.36		6.9		1.52	
SK17	SSW	46.01		4.8		0.42		7.4		2.7	

886

887 **Table 3.** Experimental observations for cores in different aqueous solutions during creep stage

Core no.	Brine	Creep stress level [MPa]	Total creep strain [%], end of 1 st phase		Total creep strain [%], end of 2 nd phase		Strain rate [%/time decade], first phase		Strain rate [%/time decade], second phase	
Group 1: First phase; Flooding (a week), second phase; Bypass (a week)										
SK3	DW	10.5	0.15		-		0.06		-	
SK8	NaCl	9.4	1.25		1.33		0.45		0.45	
SK2	Na ₂ SO ₄	7.7	1.83		2.23		1.21		1.21	
SK1	MgCl ₂	7.3	0.84		1.25		0.3		1.7	
SK26	CaCl ₂	6.6	1.05	Avg. 0.93	-		0.35	Avg. 0.45	-	
SK28			0.8		-		0.55		-	
SK16	SSW-1[Mg ²⁺]	7.9	1.84		2.34		1.43		1.43	
Group 2: First phase; Bypass (a week), second phase; Flooding (a week)										
SK5	Na ₂ SO ₄	7.6	1.5		1.72		0.5		2.9	
SK7	MgCl ₂	8.8	1.19		1.27		0.84		0.37	
SK4	SSW-1[Mg ²⁺]	8.9	1.18	Avg. 1.18	2.25	Avg. 2.05	0.46	Avg. 0.46	2.8	Avg. 2.55
SK11		6.9	1.18		1.85		0.46		2.3	
SK17	SSW	7.4	2.00		2.33		2.15		0.85	

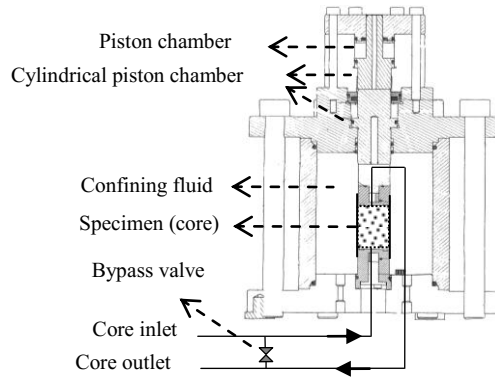
888

889 **Table 4.** Experimental observations for cores: initially saturated and flooded with distilled water
 890 and changed to saline solutions

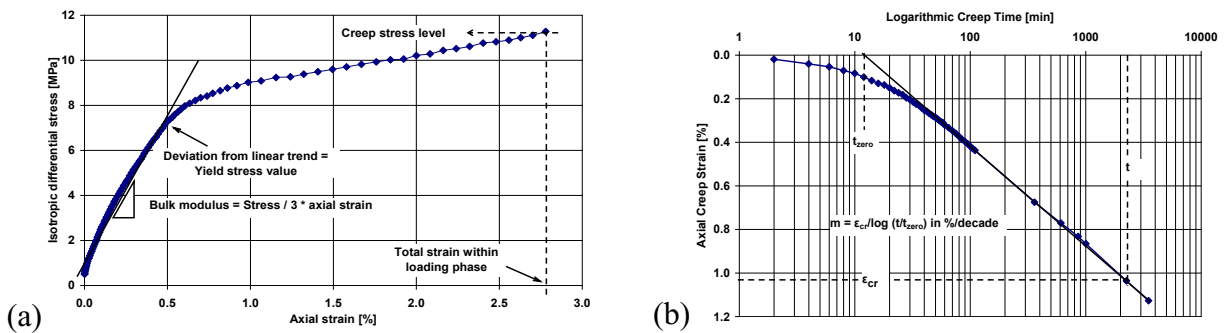
Core no.	Brine (switched within creep phase)	Porosity [%]	Yield [MPa]	Strain rate within flooding DW [%/time decade]	Strain rate within flooding brine [%/time decade]
SK20	DW → NaCl	45.05	6.5	0.22	2.5
SK5A	DW → Na ₂ SO ₄	51.17	6.7	0.5	1.21

891

892



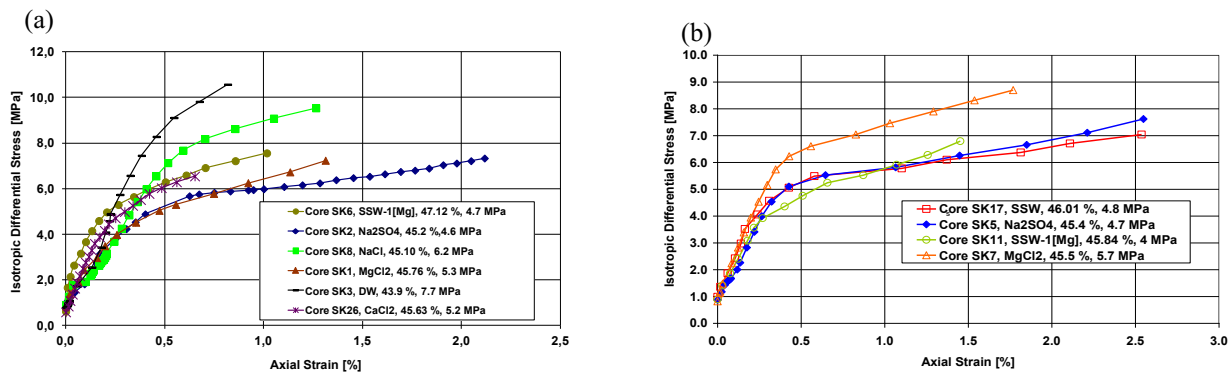
893 **Figure 1.** Schematic illustration of triaxial cell, including flooding and bypass line



894 **Figure 2.** (a) Schematic diagram of hydrostatic loading phase, yield stress value, total strain

895 within loading phase, and creep stress level; (b) Schematic diagram of creep phase in semi-

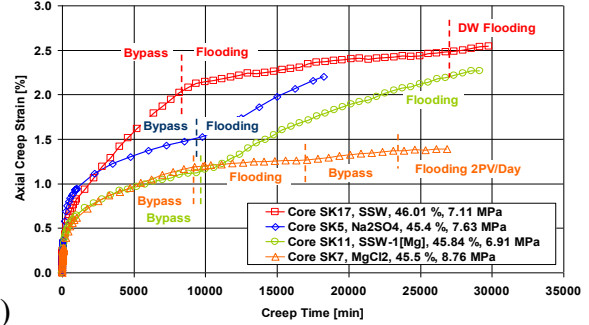
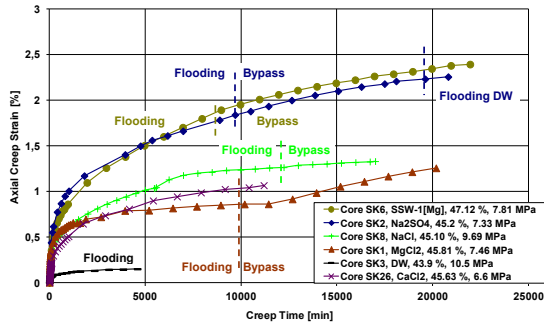
896 logarithmic, creep strain slope (m)



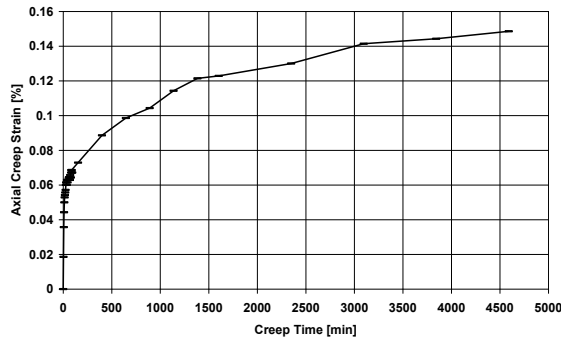
897 **Figure 3.** (a) Hydrostatic compression tests on flooded cores. Legend: brine, porosity, yield

898 stress value; (b) Hydrostatic compression tests on flood-bypassed cores bypassed. Legend: brine,

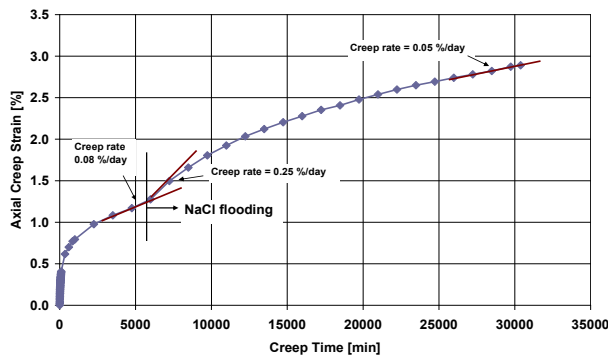
899 porosity, yield stress value



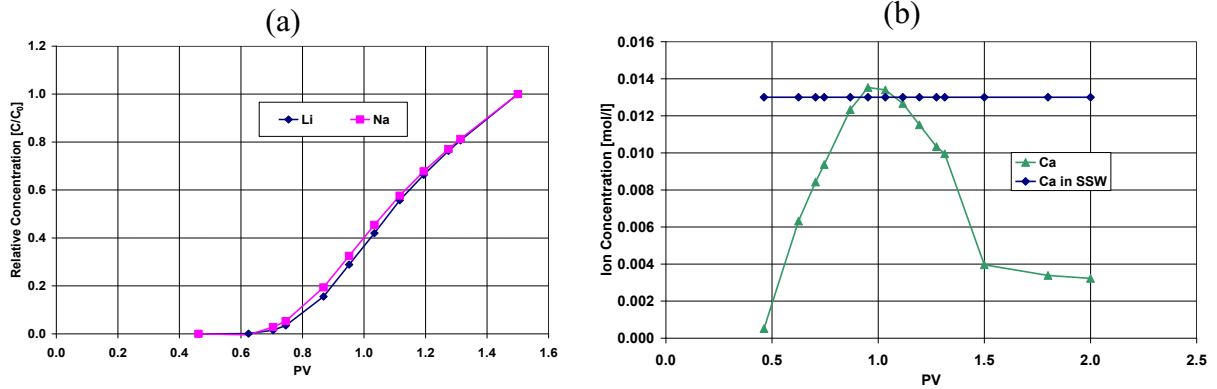
900 **Figure 4.** (a) Axial creep strain vs. creep time, first week saturated and then flooded, Legend:
 901 core number, brine, porosity, creep stress level; (b) Axial creep strain vs. creep time, first week
 902 bypassed and then flooded, Legend: brine, porosity, stress level



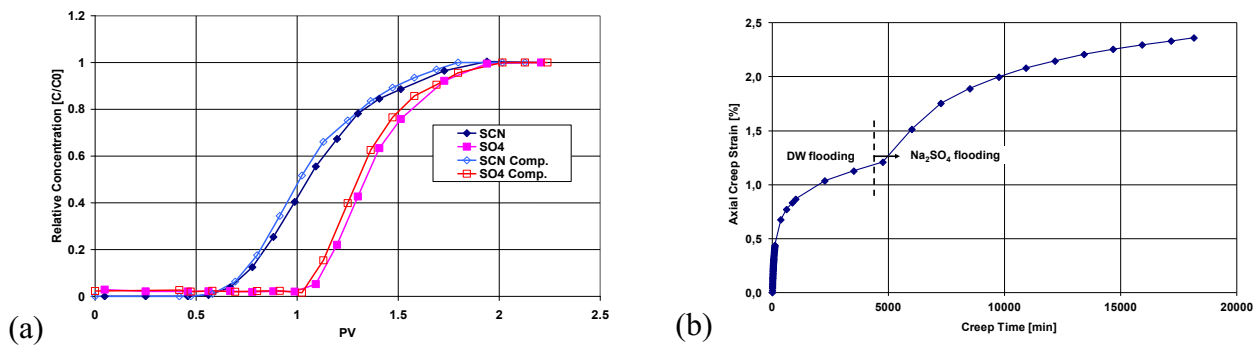
903 **Figure 5.** Axial creep strain vs. creep time for core SK3 flooded with distilled water, Stress level
 904 = 10.5 MPa



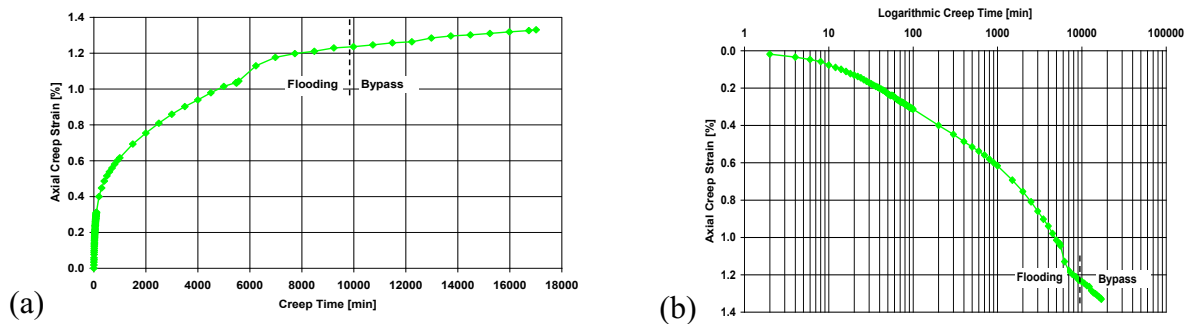
905 **Figure 6.** Axial creep strain vs. creep time for core SK20 flooded with DW followed by 0.657 M
 906 NaCl brine; Stress level = 9.3 MPa



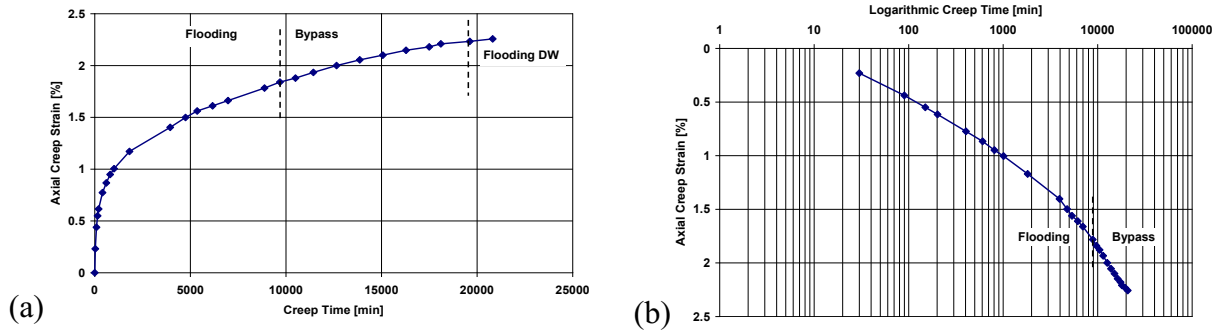
907 **Figure 7.** (a) Relative concentration of Li⁺ and Na⁺ ions at the core outlet, core SK20, flooded
 908 with 0.657 M NaCl. Small area between two cation curves is due to little adsorption of sodium in
 909 the core. (b) Calcium concentration in analyzed effluents after NaCl injection, core SK20



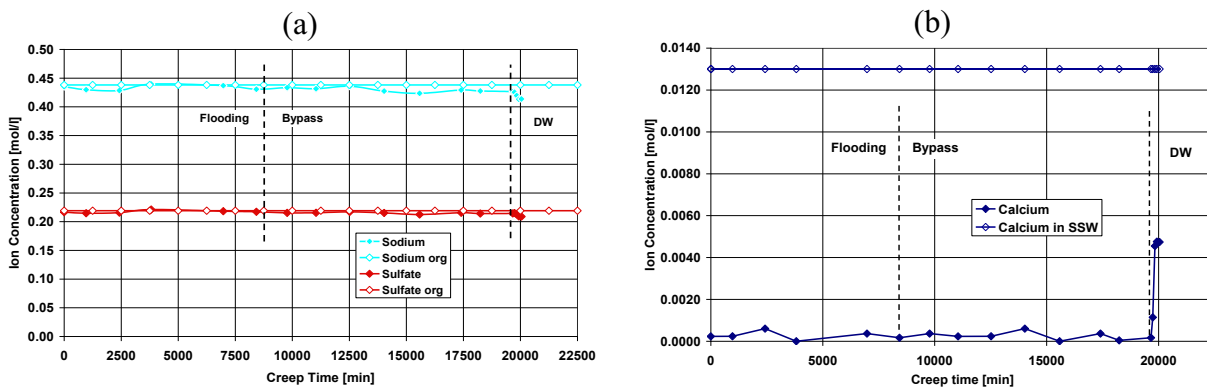
910 **Figure 8.** (a) Relative concentrations of SCN⁻ and SO₄²⁻ at the core outlet, core SK5A, flooded
 911 with 0.219 M Na₂SO₄ brine with tracer Comp.: compacted core after hydrostatic loading. (b)
 912 Axial creep strain vs. logarithmic creep time for core SK5A; Stress level = 8.2 MPa



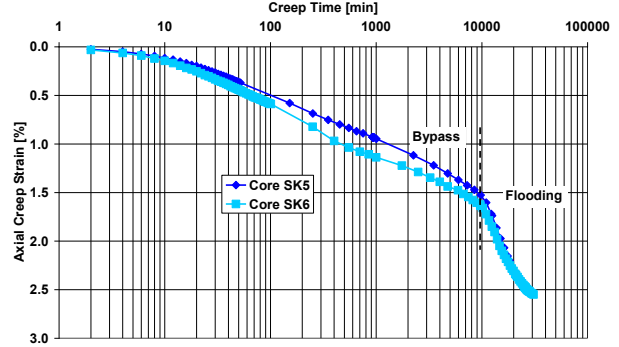
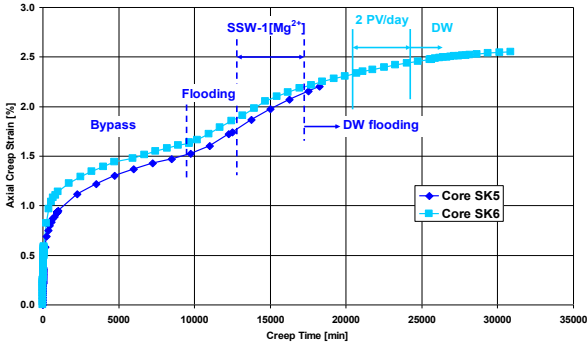
913 **Figure 9.** (a) Axial creep strain vs. creep time for core SK8, Stress level = 9.6 MPa; Saturation
 914 brine: NaCl (b) Axial creep strain vs. logarithmic creep time for core SK8, Stress level = 9.6
 915 MPa; Saturation brine: NaCl



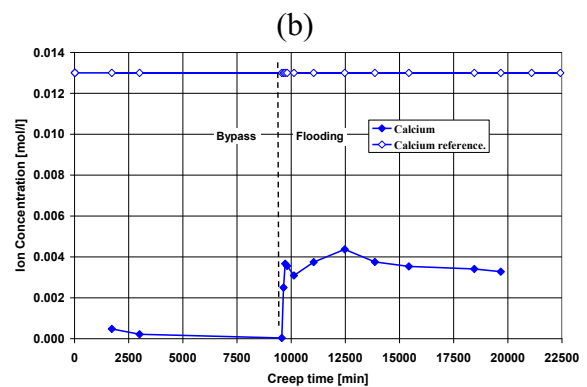
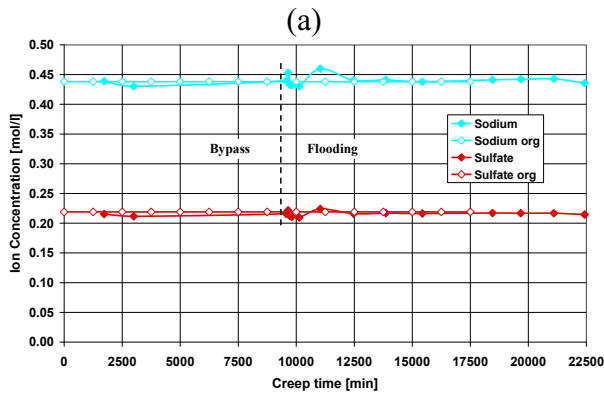
916 **Figure 10.** (a) Axial creep strain vs. creep time for core SK2; Stress level = 7.4 MPa; Saturation
 917 brine: Na₂SO₄ solution (b) Axial creep strain vs. logarithmic creep time for core SK2; Stress
 918 level = 7.4 MPa; Saturation brine: Na₂SO₄ solution



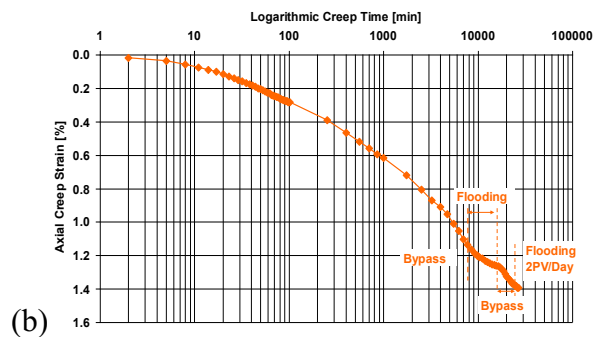
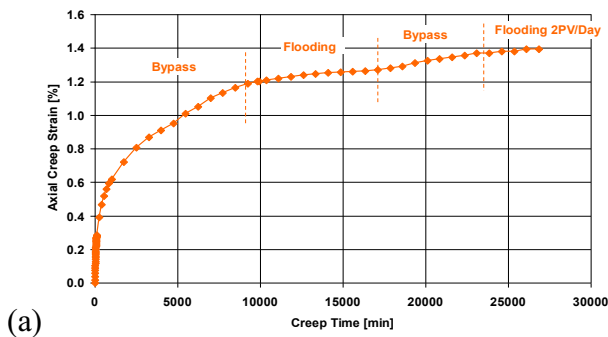
919 **Figure 11.** (a) Chemical analysis result for Na⁺ and SO₄²⁻ ions in sampled effluent of core SK2
 920 flooded with 0.219 M Na₂SO₄. The original concentrations (sodium org, sulfate org) are included
 921 for comparison; (b) Chemical analysis result for Ca²⁺ ions in sampled effluent of core SK2
 922 flooded with 0.219 M Na₂SO₄. The concentration of calcium in SSW is included for comparison.



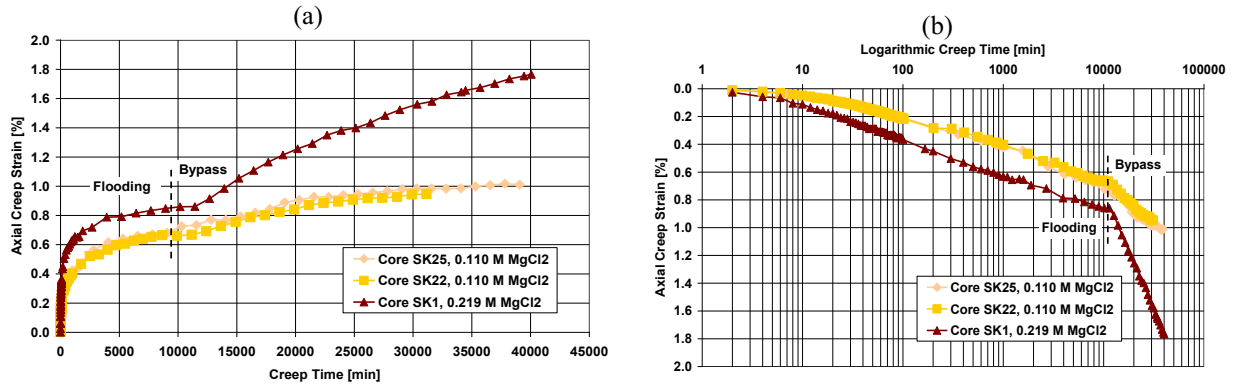
923 **Figure 12.** (a) Axial creep strain vs. creep time for cores SK5 and SK6; Stress level = 7.6 and
 924 7.5 MPa; (b) Axial creep strain vs. logarithmic creep time for core SK5 and SK6; Stress level =
 925 7.6 and 7.5 MPa.



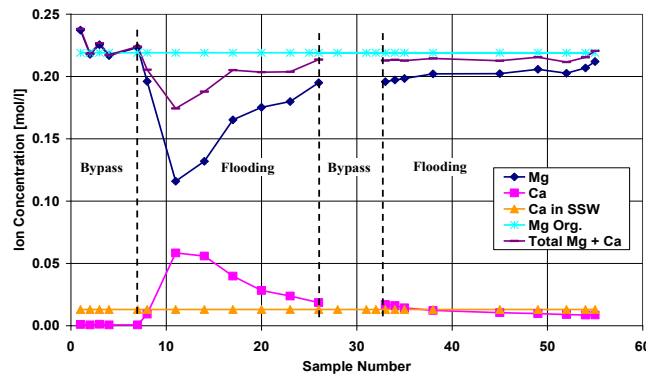
926 **Figure 13.** (a) Chemical analysis result for Na^+ and SO_4^{2-} ions in sampled effluent of core SK6
 927 flooded with 0.219 M Na_2SO_4 . The original concentrations (sodium org, sulfate org) are included
 928 for comparison; (b) Chemical analysis result for Ca^{2+} ions in sampled effluent of core SK6
 929 flooded with 0.219 M Na_2SO_4 . The concentration of calcium is included for comparison.



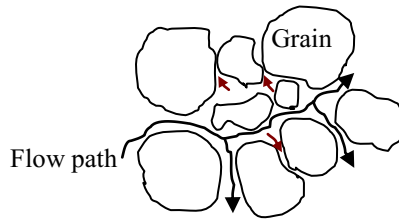
930 **Figure 14.** (a) Axial creep strain vs. creep time for core SK7; Stress level = 9.2 MPa; Saturation
 931 brine: MgCl₂ solution (b) Axial creep strain vs. logarithmic creep time for core SK7; Stress level
 932 = 9.2 MPa; Saturation brine: MgCl₂ solution



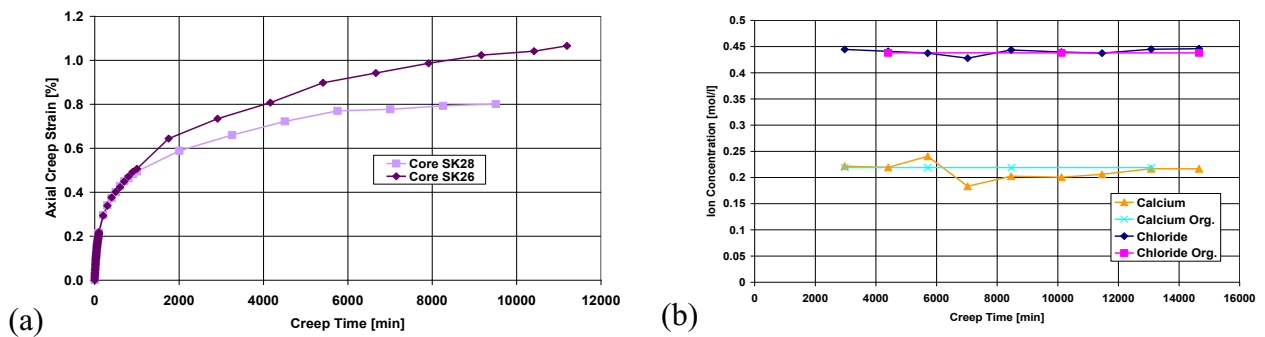
933 **Figure 15.** (a) Axial creep strain vs. creep time for core SK1, SK22, and SK25; Stress level =
 934 7.4, 11, and 10.1 MPa ; (b) Axial creep strain vs. logarithmic creep time for core SK1, SK22, and
 935 SK25; Stress level = 7.4, 11, and 10.1 MPa



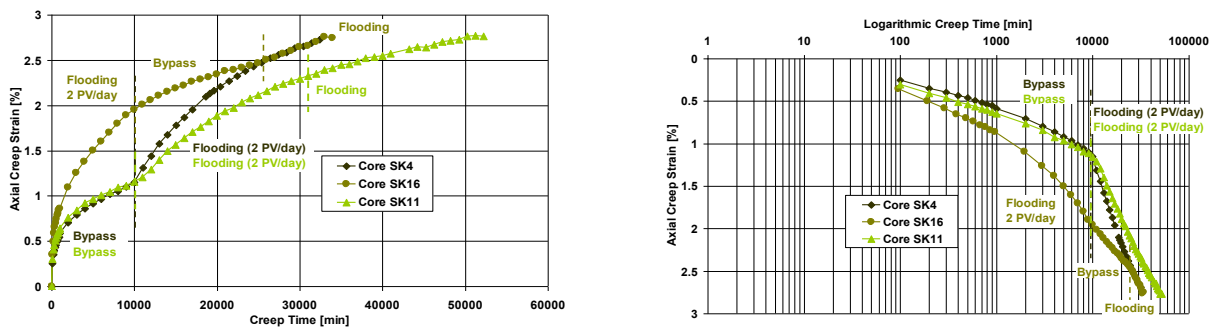
936 **Figure 16.** Concentration of Mg²⁺ + Ca²⁺ ions in the sampled effluents of core SK7, flooded with
 937 0.219 M MgCl₂; Org.: Original concentration



938 **Figure 17.** Schematic illustration of the flow path of $MgCl_2$ brine in chalk; Black arrows;
 939 flooding pathway, brown arrows: probable pathways within the bypass period



940 **Figure 18.** (a) Axial creep strain vs. creep time for cores SK26 and SK28; Stress level = 6.6
 941 MPa; (b) Concentration of Ca^{2+} and Cl^- in sampled effluents (sampling started from beginning of
 942 creep stage), core SK26, flooded with 0.219 M $CaCl_2$. Org.: Original concentration



943 **Figure 19.** (a) Axial creep strain vs. creep time for cores SK4, SK16, and SK11; Stress level = 9,
 944 7.9 and 6.9 MPa; Saturation brine: seawater without magnesium ($SSW-1[Mg^{2+}]$); (b) Axial creep
 945 strain vs. logarithmic creep time for cores SK4, SK16, and SK11; Stress level = 9, 7.9 and 6.9
 946 MPa. Saturation brine: seawater without magnesium ($SSW-1[Mg^{2+}]$)