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Issam I. Takla Takla, Yun Jia, Thomas Rougelot, Nicolas Burlion. Influence of pre-carbonation on hydro-mechanical properties of cement paste subjected to leaching. *Materials and structures*, 2022, 55 (4), pp.129. 10.1617/s11527-022-01975-z . hal-04460293

HAL Id: hal-04460293

<https://hal.science/hal-04460293>

Submitted on 15 Feb 2024

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1 **Influence of pre-carbonation on hydro-mechanical properties of cement**
2 **paste subjected to leaching**

3
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10
11 **Abstract**

12 Depleted oil reservoirs have been one of the most practical options for CO₂ sequestration. To ensure the
13 overall sealing performance of oilwell for CO₂ injection, it is necessary to understand the long-term
14 hydro-mechanical behaviour of cement paste used as oilwell casing. In the presence of high CO₂
15 concentration and water, cement paste is firstly carbonated and then may be degraded by carbonic acid
16 in CO₂ storage. The present work aims to experimentally investigate the pre-carbonation effects on the
17 leaching of oilwell cement paste, with special attention to hydro-mechanical properties. By using a
18 series of uniaxial compression tests and triaxial compression tests with permeability measurements,
19 permeability and mechanical properties of sound and pre-carbonated materials, before and after leaching
20 treatment, are measured and analysed. Moreover, the time-dependent behaviour of pre-carbonated
21 material subjected to leaching is studied via a coupled creep test. The obtained results exhibit that after
22 leaching treatment, comparing with the initially sound samples, the pre-carbonated samples exhibit
23 higher mechanical properties, lower permeability, and smaller creep deformation. Therefore, one can
24 conclude that the degradation of mechanical and hydraulic properties induced by leaching is reduced by
25 the pre-carbonation of cement paste and the carbonation has a positive effect against leaching. To verify
26 and understand the macroscopic experimental observations, some micro-indentation tests are performed
27 at a mesoscopic scale and a mineralogy and chemistry analysis are also conducted via SEM-EDS and

28 Raman spectroscopy tests. Experimental investigation, micromechanical analysis and microstructure
29 will advance the understanding of long-term durability of CO₂ geological storage.

30

31 **Keywords:** CO₂ storage; Carbonation; Leaching; Cement paste; time-dependent strain; Permeability;
32 mechanical properties

33

34 **1. Introduction**

35 In order to reduce carbon dioxide CO₂ concentration in the atmosphere, depleted oil and gas
36 reservoirs have been one of the most practical options for CO₂ sequestration due to its numerous
37 advantages, such as high geological stability, absence of leakage paths and availability of
38 infrastructures. In gas and oil exploitations, cement paste is widely used as oilwell casing to isolate the
39 production zones and provide mechanical support. In the oilwell for CO₂ injection, the carbonic acid,
40 which is formed with the dissolution of CO₂ in water, firstly reacts with the portlandite of cement paste.
41 This carbonation process results in the formation of calcite and improves the mechanical and transport
42 properties of cementitious materials [1]. Once the depletion of portlandite is achieved, the carbonic acid
43 induces the leaching of calcite [2]. This leaching process may create mechanical damage and alter
44 transport properties of cement paste, potentially perturbing the storage integrity [2,3,4,5,6,7,8,].
45 Moreover, the geological storage is located at several kilometres beneath the Earth's surface. Under the
46 geothermal gradient, high downhole temperature may induce a further evolution of the hydro-
47 mechanical properties of cement paste [9]. As a result, a long-term integrity and durability of CO₂
48 storage requires a good understanding of the hydro-mechanical behaviour of cement paste subjected to
49 high temperature and two mentioned successive chemical processes: carbonation and then leaching.

50 In the literature, number of experimental tests have been performed to study separately the
51 carbonation or leaching processes of cement-based materials. On one hand, previous studies [10,11,12
52 ,13,14,15,16] exhibit that carbonation induces a decrease in porosity and permeability as well as an
53 increase in mechanical strength. However, very few authors have studied the carbonation process under
54 a high temperature close to the real temperature level of CO₂ storage, just to mention a three. Takla et al.
55 [17] have studied the effect of carbonation on the mechanical and hydraulic behaviour of an oilwell

56 cement paste under high temperature $T=90^{\circ}\text{C}$. They found that with respect to the initially sound
57 material, carbonated samples exhibited a remarkable permeability decrease about one order of
58 magnitude as well as 100% ~150% increase of mechanical strength. Recently, Borje et al. [18] have
59 studied the microstructural changes induced by the carbonation of Portland cement by using different
60 experimental techniques. Wang et al. [Erreur ! Source du renvoi introuvable.] have also studied the
61 carbonation performance and carbon dioxide uptake rate of cement paste in the temperature range
62 (20°C – 300°C). The obtained results demonstrated that carbonation reaction increased obviously with
63 increasing temperature.

64 On the other hand, a large number of experimental studies have been performed to study the
65 leaching of cementitious materials [19,20,21,22,23,24,25,26]. Leaching of cement paste dissolves the
66 solid phases (for instance, portlandite, calcium silicate hydrates, and ettringite etc.) and induces a
67 porosity/permeability increase as well as a reduction of mechanical properties. Moreover, the leached
68 material exhibits a more ductile behaviour than the sound one [23,26]. The leaching kinetics depend
69 strongly on temperature [20]. According to Kamali [Erreur ! Source du renvoi introuvable.], for a
70 cement paste of CEM I type with a water/cement ratio of 0.4, the leaching process was accelerated by a
71 factor of 2.3 when the temperature increased from 25°C to 85°C . However, only one of carbonation and
72 leaching processes has been studied in these research work. To the best of the authors' knowledge, the
73 leaching of pre-carbonated cement-based material under high temperature has not yet been investigated.

74 The present work focuses on the impact of pre-carbonation on the leaching of a cement-based
75 material under high temperature, with special attention to hydro-mechanical properties. In view of this
76 objective, the tested cementitious material is prepared under two carbonation conditions: one group is
77 kept in aluminium sheets to avoid the CO_2 contact (CO_2 -free environment), called “sound samples”; the
78 other ones are exposed to an accelerated carbonation, called “carbonated samples”. After that, some
79 sound and pre-carbonated samples are subjected to leaching. Consequently, four types of cement paste
80 are obtained in the experimental program. Their permeability, failure strength and creep deformation
81 are firstly studied via a series of uniaxial compression test, triaxial compression tests with permeability
82 measurements and coupled creep tests. After that, micro-indentation tests are performed to identify the
83 mechanical properties of studied materials at a mesoscopic scale. Additionally, the chemical and

84 mineral analysis is conducted using SEM-EDS and Raman spectroscopy technology on different types
85 of specimens to verify the theoretical chemical processes and understand the experimental observations.

86

87 **2. Materials and samples preparation**

88 The present study is performed in the framework of the feasibility study of depleted oil reservoirs for
89 CO₂ sequestration, coordinated by *Total* Company. The emphasis focuses on the influence of pre-
90 carbonation on hydro-mechanical properties of an oilwell cement paste subjected to leaching and high
91 temperature.

92 As aforementioned, in the oilwell for CO₂ injection, the hydro-mechanical properties of cement
93 paste will be firstly improved by carbonation and then degraded by further leaching. To reproduce the
94 mentioned chemical reactions in a reasonable period of time, laboratory samples have been prepared in
95 in an accelerated way: carbonation is performed in a climate chamber with a high gaseous CO₂
96 concentration while leaching is realized by using the ammonium nitrate solution. The choice of
97 ammonium nitrate rather than carbonic acid for the leaching is to accelerate the leaching kinetics with
98 almost the same products [27]. Moreover, the adopted temperature of 90°C can also accelerate the
99 leaching kinetics of cement paste. The studied material and sample preparation are presented in this
100 section.

101

102 **2.1 Materials**

103 Actually, the studied cement paste is being used as cement casing of oilwells, whose composition has
104 been provided by French company *Total*. It is made with a water/cement ratio of 0.4 and a G class
105 cement commonly used in oil-well industry. The G class cement is defined by American Petroleum
106 Institute (API), in accordance with standard 10A API [28]. Thanks to its special chemical composition,
107 this cement is largely used in the construction of oil wells. Because of the complexity of engineering
108 application and extreme conditions of temperature and pressure that is subjected to, the class G cement
109 is characterized by the constancy of important requirements, such as high durability, fluid loss control
110 and high sulphate resistance, etc...With respect to the composition provided by *Total* (Table 1), all the

111 laboratory samples were prepared in the Laboratory of Mechanics, Multi-physics, Multi-scale
112 (*LaMcube*).

113

Components	Quantity (kg/m ³)
Cement G class	1308.3
Water	578.5
D175 (antifoaming)	5.2
D80 (dispersant)	8.1
Water/Cement ratio	0.4

114

Table. 1 Composition of the studied cement paste

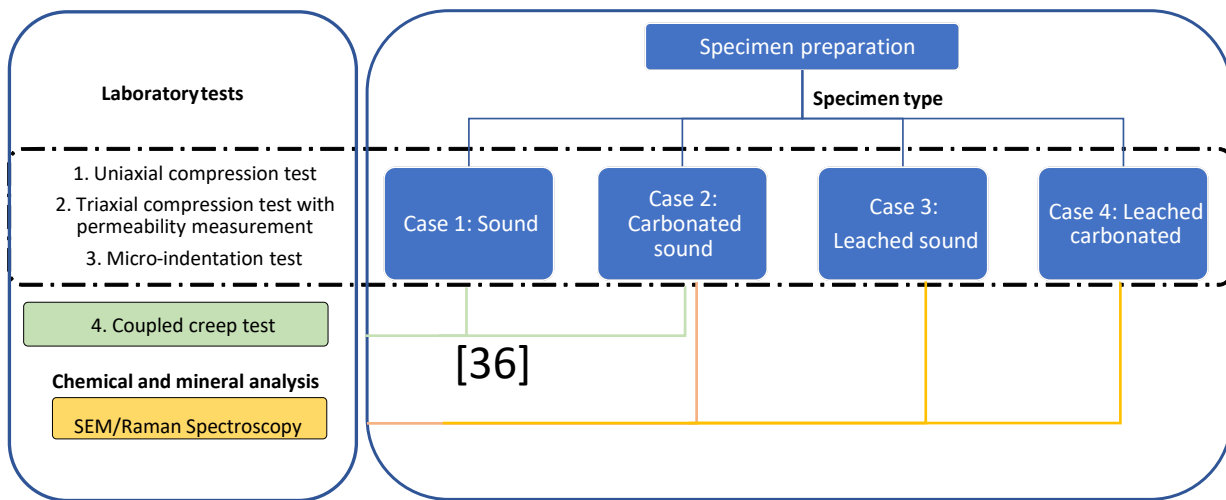
115 Before the sample preparation, 18 preliminary tests using the cement paste samples ($20 \times 20 \times 160$
116 mm^3) have been performed at the temperature of $T=90^\circ C$ to estimate the curing period. As the
117 laboratory samples are conserved in water, the water consumption related to the hydration can be
118 replaced by the entrance of external water. Once the relative mass variation of samples is inferior to 2%
119 during a week, the mass stability is achieved, and a quasi-complete hydration is obtained. As the
120 microstructure of cement paste is almost stabilized, it is possible to suppose that with respect to the
121 post-treatment procedures (i.e. carbonation and leaching processes), the effect of further hydration can
122 be neglected. Therefore, one month of curing period was adopted in the present study while $T= 90^\circ C$
123 was used to reproduce the real temperature level in CO_2 reservoir.

124 After mixing all the components at atmospheric temperature, the cement paste was cast in
125 cylindrical stainless-steel moulds ($\varnothing 36$, $H= 100$ mm). The moulds were kept in distilled water
126 (saturated with lime) at $90^\circ C$ for 3 days. After a rapid demoulding, samples were kept in distilled water
127 at $90^\circ C$ for one month. Consequently, cylindrical cores used for the laboratory tests were cut from the
128 central parts of cured samples ($\varnothing 36$, $H= 100$ mm). Dimension of cores was 22mm in length and 20 mm
129 in diameter.

130 These samples were prepared under two carbonation conditions: one group was protected by
131 aluminium sheets to avoid the CO_2 contact (CO_2 -free environment), called “sound samples”; the other
132 ones were exposed to an accelerated carbonation, called “carbonated sound samples”. After that, some

133 of previous samples (i.e. sound and carbonated sound samples) were subjected to leaching to obtain
 134 “leached sound samples” and “leached carbonated samples”, respectively. In total, four types of cement
 135 paste were investigated in the present work: sound (case1), carbonated sound (case 2), leached sound
 136 (case 3) and leached carbonated (case 4) samples. According to the carbonation and leaching processes
 137 adopted in the samples’ preparation, they will be given in the next sections. A schematic summary of
 138 the specimen categories and different laboratory tests are given in Fig. 1.

139



140

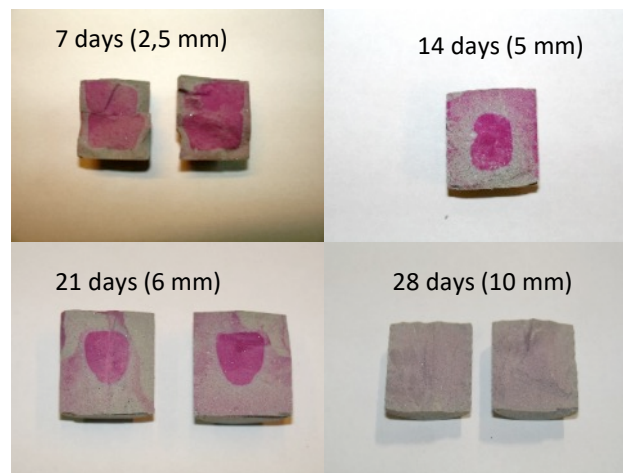
141 Fig 1. Schematic summary of the experimental program

142

143 2.2 Specimen carbonation

144 Inspired by previous research works [29,30,31], the carbonation of sound samples was realized in a
 145 climatic chamber *Binder*[®], under a temperature of 90°C and related humidity of 65%. The adoption of
 146 this relative humidity is to accelerate the carbonation process. As a result, carbonated cement paste,
 147 similar to the in-situ oilwell one, can be obtained within an acceptable period of time (about 28 days). In
 148 the climatic chamber, CO₂ was injected at a rate of 100 cm³/min. At the end of one day, the injected
 149 CO₂ volume was then equal to the chamber volume (0.15 m³) [32]. To compensate the partial
 150 consumption of CO₂ during carbonation and the potential CO₂ leaks in the climatic chamber, the
 151 continuous injection was adopted during the carbonation. Its objective is to obtain the highest CO₂
 152 concentration in the climatic chamber and then maximize the kinetics of carbonation without modifying
 153 the carbonation products [33].

154 During the carbonation, at predefined intervals, one of the samples was taken out the climate
155 chamber and split along its longitudinal axis. Phenolphthalein solution was then sprayed onto its surface
156 area to determine the carbonation depth. Four different samplings are given in Fig.2 (7, 14, 21 and 28
157 days). One observes that the pink colour disappears progressively with time, indicating that the
158 carbonation front gradually penetrates towards the centre of sample. This observation is due to the fact
159 that phenolphthalein changes into pink in the non-carbonated zone (i.e., sound zone) while it remains
160 transparent in the carbonated zone where pH is smaller than 9. For a given moment, four measurements
161 of carbonation thickness were taken on each edge of sample and the mean value was used as the
162 carbonation depth (Fig. 2). After 28 days exposure, no pink colour was observed in the sample,
163 indicating that pH of the whole sample was smaller than 9. Assuming that $\text{pH} < 9$ represents a
164 complete/quasi-complete carbonation, carbonated sound samples (case 2) were obtained at the end of 28
165 days.
166



167
168 Fig.2 Evolution of carbonation front in the carbonated sound samples (case 2)
169

170 2.3 Specimen leaching

171 In the present work, the same leaching processes were applied on two categories of laboratory samples
172 at different carbonation states: initially sound samples (case 1) and carbonated sound samples (case 2).
173 To determine the leaching front in these two materials, two indicators have been used in the present
174 work: Phenolphthalein solution for initially sound material and darker grey colour for pre-carbonated
175 material.

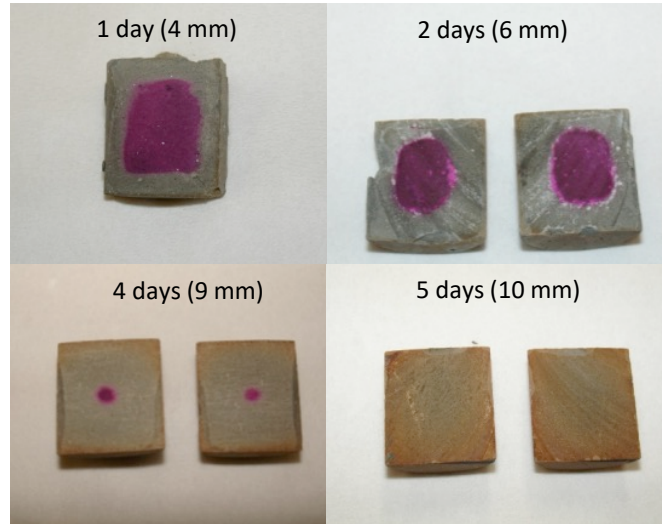
176 The samples were placed in a cooking vessel of 5 litres and leached in an ammonium nitrate
177 solution at 90°C. The initial concentration of the ammonium nitrate solution was 6 mol/l, which wasn't
178 renewed during leaching. For a cooking vessel, a maximum of 20 samples could be contained to
179 guarantee a sufficient concentration of leaching solution. The leaching process of laboratory samples is
180 given as follows. Firstly, the salt of ammonium nitrate is mixed in distilled water in the cooking vessels
181 and then kept 24 hours under ambient temperature. The prepared ammonium nitrate solution is then put
182 in the oven at 90°C for 24 hours in order to attain the same temperature as the laboratory samples.
183 Afterwards, the samples (conserved initially at 90°C) are put in the cooking vessels installed in the oven
184 at 90°C, for leaching process.

185 For each group, after a certain reaction time, one of sample was split and examined to identify the
186 leaching depth. The leaching of initial sound samples is firstly presented. The freshly split surface was
187 sprayed with the phenolphthalein solution. After a few seconds, two distinct zones could be observed: a
188 pink colour was observed in the sound zone and a grey colour was presented in the degraded zone. This
189 observation can be explained by the fact the phenolphthalein remains transparent in leached zone, in
190 which pH is less than 9. The evolutions of leaching front in leached sound sample are given in Fig. 3a at
191 four degradation times (i.e, 1, 2, 4 and 5 days). It is observed the leaching area increases progressively
192 with time (Fig. 3a). When no pink colour is observed in the whole sample (Fig. 3a), a complete or
193 almost complete leaching is achieved and the leached carbonated samples (case 3) are obtained at the
194 end of 5 days.

195 For pre-carbonated samples, as their pH is smaller than 9, phenolphthalein cannot be used as a
196 good indicator of leaching. However, one observes that the pre-carbonated cement paste progressively
197 becomes darker with the advancement of leaching front. Therefore, once the light grey zone disappears
198 in the whole sample (Fig. 3b), it's considered that the pre-carbonated sample is complete/quasi-
199 complete leached. As a result, the leached carbonated samples (case 4) are obtained after 10 days of
200 leaching treatment. By comparing the leaching kinetics in cases 3 and 4, one observes that the leaching
201 of pre-carbonated material needs much more time than that of the sound one, even up to two times: the
202 sound samples are almost completely leached at the end of 5 days while the leaching of carbonated

203 samples is relatedly slow and lasts up to 10 days. Consequently, the pre-carbonated cement paste (case
204 2) is more resistant to leaching than the initially sound one.

205

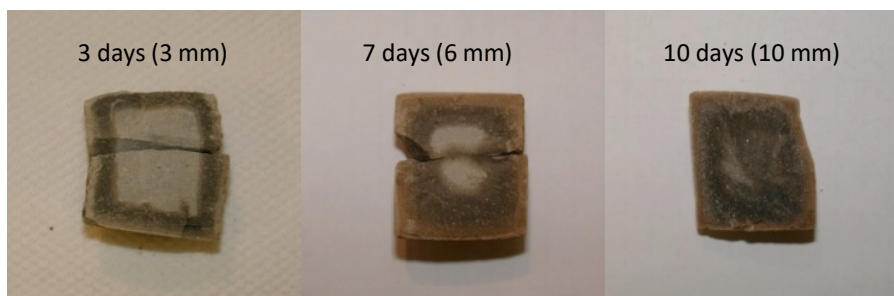


206

207

208

(a)



209

210

(b)

211

Fig.3 Evolution of leaching front in two leached samples:

212

(a) leached sound samples (case 3); (b) leached carbonated samples (case 4)

213

214

3. Experimental setup for laboratory tests

215

216

217

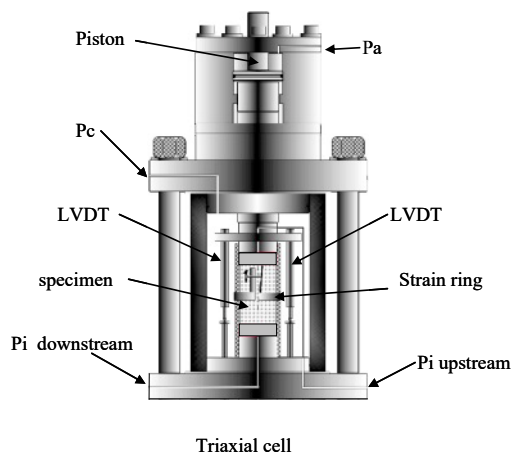
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219

In order to study the effects of carbonation on the permeability and mechanical characterises of oilwell cement paste subjected to leaching and high temperature, four categories of samples obtained in the previous section were used to perform four types of laboratory tests: uniaxial compression tests, triaxial compression tests accompanied with permeability measurements, micro-indentation tests and coupled creep test. Additionally, by using SEM-EDS and Raman spectroscopy technology, the mineralogy and

220 chemistry was also conducted on three categories of samples (cases 2,3 and 4). Different types of
221 laboratory tests performed on different categories of samples are summarised in Fig 1.

222 All the tests (except micro-indentation tests) were carried out by using an auto-compensated and
223 auto-equilibrium triaxial cell system (Fig. 4). It is composed of a conventional triaxial cell and two fluid
224 reservoirs which control the water pressure, respectively, on the lower and upper sides of sample. The
225 axial displacement is measured by two LVDT in the cell while the lateral strain is measured with a
226 strain ring. The confining pressure, deviatoric stress and fluid injection pressures (upstream and
227 downstream) are, respectively, measured by four pressure sensors. The cell is installed in an oven,
228 where a temperature of 90°C is kept.



237
238 Fig. 4 Schema of triaxial cell system

239
240 As the processes of uniaxial compression test are well known, only the triaxial compression tests
241 accompanied with permeability measurement, the coupled creep test and the micro-indentation tests are
242 presented in detail in this section.

244 3.1 Triaxial compression tests with permeability measurement

245 As indicated by Total, mean stress in an oilwell may be up to 20MPa. Therefore, confining pressure in
246 the range of 0 MPa to 20 MPa is adopted to investigate the hydro-mechanical behaviour of cement paste
247 under different levels of mechanical loading. In this section, four categories of cement paste (i.e. sound,

248 carbonated, leached sound and leached carbonated samples) are studied under four different confining
249 pressures P_c (0, 3, 10 and 20 MPa).

250 Before the realisation of triaxial compression tests with permeability measurements, one group of
251 preliminary permeability tests have been conducted on four initially sound samples (case 1) under
252 $P_c=3\text{MPa}$. A mean value of permeability of $1.1\times 10^{-18}\text{ m}^2$ was obtained with a standard deviation of
253 $0.2\times 10^{-18}\text{ m}^2$ (minimal value: $9.6\times 10^{-19}\text{ m}^2$, maximal value: $1.4\times 10^{-18}\text{ m}^2$). One can observe that the
254 dispersion of experimental results is extremely limited. Moreover, the permeability measurements take a
255 long period of time, even up to 14 days. Therefore, only one permeability measurement has been
256 performed for a given confining pressure. The experiment set up of triaxial compression tests
257 accompanied with permeability measurement under the confining pressure $P_c=3\text{MPa}$ is presented as
258 follows:

- 259 I. The sample was firstly put in a sheath of *Viton*® synthetic rubber and placed in the cell. The
260 strain ring and LVDT were installed. The cell was heated up to 90°C during 24h in order to get
261 a homogenous temperature in the cell.
- 262 II. The sample was firstly subjected to an initial hydrostatic stress phase with a given confining
263 pressure $P_c=3\text{MPa}$. Meanwhile, the fluid pressure of upstream reservoir was rapidly set to 2.5
264 MPa while the atmospheric pressure was kept in downstream area. The permeability was then
265 measured after getting a stable flow.
- 266 III. The valve of fluid exit was turned off to get a homogenate interstitial pressure (2.5MPa). A
267 deviatoric stress was then applied and increased until the failure of studied sample to determine
268 the triaxial compressive strength.

269 The permeability measurement was also performed under other confining pressures (0, 10 and 20MPa).
270 By applying the Darcy's law, the permeability of studied material can be obtained by using the
271 volumetric flow [17].

272

273 **3.2 Coupled triaxial creep tests**

274 The creep test aims to study the evolution of time-dependent deformation of pre-carbonated cement
275 paste during the leaching and $T=90^\circ\text{C}$. To reduce the duration of laboratory test and get a first sight on

276 the long-term deformation behaviour of studied material, an accelerated way is adopted in the present
277 study: the ammonium nitrate (accelerated leaching) is used for leaching while a high deviatoric stress of
278 35 MPa is applied on the sample. This deviatoric stress is equal to 50% the failure strength of a
279 carbonated sample at $P_c = 3$ MPa and very close to the failure strength of a leached carbonated sample at
280 the same confining pressure.

281 In the triaxial creep test, one pre-carbonated sample (case 2) was installed in the same cell used
282 for triaxial test (Fig. 4). The evolutions of axial deformation were recorded by two LVDT until the
283 sample failure (about 2500 hours). At the beginning of the laboratory test, the sample was subjected to
284 a hydrostatic stress of 3 MPa. After that, the deviatoric stress increased to 35MPa. While the mechanical
285 loading was kept constant, the NH_4NO_3 solution (6 mol/l) was injected in the upstream reservoir with a
286 fluid pressure of 2.5 MPa while an atmospheric pressure was found at the downstream side of studied
287 sample. Moreover, in order to illustrate the influence of pre-carbonation on the time-dependent
288 mechanical characteristics of cement paste subjected to leaching, this test will be compared with another
289 creep test performed on sound sample [34].

290

291 **3.3 Micro-indentation tests**

292 Micro-indentation is an appropriate and non-destructive method to identify the mechanical properties of
293 geomaterial. In order to identify the material property at mesoscopic scale and verify the experimental
294 results obtained on macroscopic scale (i.e. in uniaxial and triaxial compression tests), a series of micro-
295 indentation tests were performed on these four types of cement paste.

296 A *Micrope*® indentation system was used in the present work. It is composed of a loading frame
297 and a data acquisition system. The piston motor allows to ensure an exceedingly small load speed (about
298 $1\ \mu\text{m}/\text{min}$). The applied force is measured by a force sensor while the displacement is measured by two
299 LVDT. Based on the preliminary tests, the round punch of 1 mm diameter is adopted with respect to the
300 size of cement paste components.

301 The tested samples ($\varnothing 20$, $H = 22\ \text{mm}$) were prepared under ambient temperature. The middle of
302 the sample was cut transversely by a wire saw machine, parallel to its end-surfaces. To get a good
303 parallelism between two extremities, a polishing machine, composed of a rotating disc with sandpaper

304 (P800), was used. The obtained cross-section was mounted in a special mould and placed on the rotating
305 disc. Two extremities of sample were then rectified while the parallelism was checked by using a
306 vernier calliper. Finally, test points were chosen on two main axes of examined sample (Fig. 5).

307 The micro-indentation tests are presented in detail as follows. For a given cement paste, a series
308 of preliminary tests were firstly realized to identify the yield strength of studied material. After that, an
309 elastic test was then performed with the application of a mechanical load, which was smaller than the
310 yield strength. Finally, the value of Young's modulus was calculated by using the slope of unloading
311 line [35]. However, due to the heterogeneity of cementitious materials, a large degree of scatter may be
312 observed in the measurements [36]. In view of this, for a given distance with respect to the sample
313 centre, four measurement points are chosen to insure the reliability of experimental results (Fig. 5).

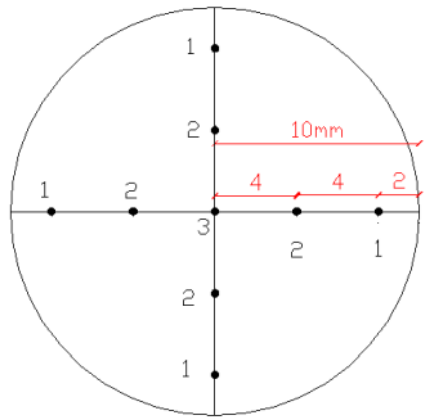


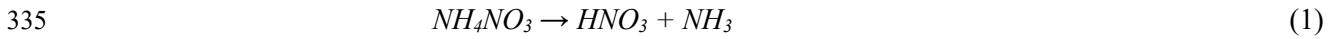
Fig. 5 Test points on the cross-section of sample

4. Results and discussions

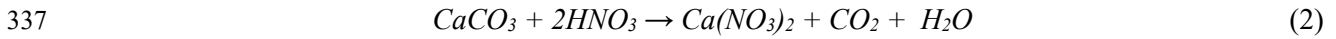
324 The obtained experimental results are analysed and discussed in this section. A series of chemical
325 equations are firstly presented to analyse the expected leaching effects on the evolution of composition
326 of sound and pre-carbonated materials. Moreover, SEM-EDS and Raman spectroscopy results provide
327 the additional information on the composition of the studied cement paste, in accordance with chemical
328 equations. Finally, the effects of pre-carbonation on the permeability and mechanical (instantaneous or
329 delayed) properties of cement paste subjected to leaching are discussed.

330 In the literature, the leaching of cementitious material has been largely discussed as well as the
331 carbonation of cementitious material. However, the leaching of carbonated cementitious material under

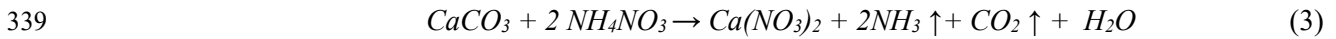
332 high temperature has been little investigated. In the laboratory tests, the use of concentrated ammonium
333 nitrate solutions is an accelerated method to reproduce the degradation of cement-based materials by
334 carbonic acid. The dissolution of ammonium nitrate can be written as:



336 The calcium carbonate reacts with nitric acid and forms calcium nitrate:

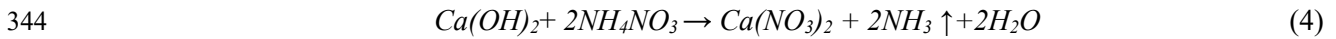


338 Therefore, the general equation for the leaching of carbonated cement paste can be written as follows:



340 The calcium nitrate $Ca(NO_3)_2$ is a soluble hygroscopic salt in the monohydrated state $Ca(NO_3)_2.H_2O$,
341 which is transformed into anhydrous form $Ca(NO_3)_2$ under high temperature.

342 On the other hand, the leaching of sound cement paste in ammonium nitrate induces a drop of pH
343 and a decomposition of portlandite as well as a creation of the salt of calcium nitrate:



345 By comparing the equations (3) and (4), the leaching of sound cement paste (Eq. 4) concerns principally
346 the leaching of portlandite while in the carbonated sample, it is the calcium carbonate that is dissolved.
347 As the solubility of portlandite is of three orders of magnitude bigger than that of calcite, the leaching of
348 portlandite is easier than that of calcium carbonate. This phenomenon can be used to explain the
349 different in the leaching kinetics of sound and pre-carbonate cement pastes (Fig. 3). Additionally, one
350 observes that the same chemical products are obtained in the samples with and without pre-
351 carbonations. To confirm the previous results, SEM, EDS and Raman spectroscopy tests are also
352 realized to analyse the evolutions of microstructure, chemistry and mineralogy.

353

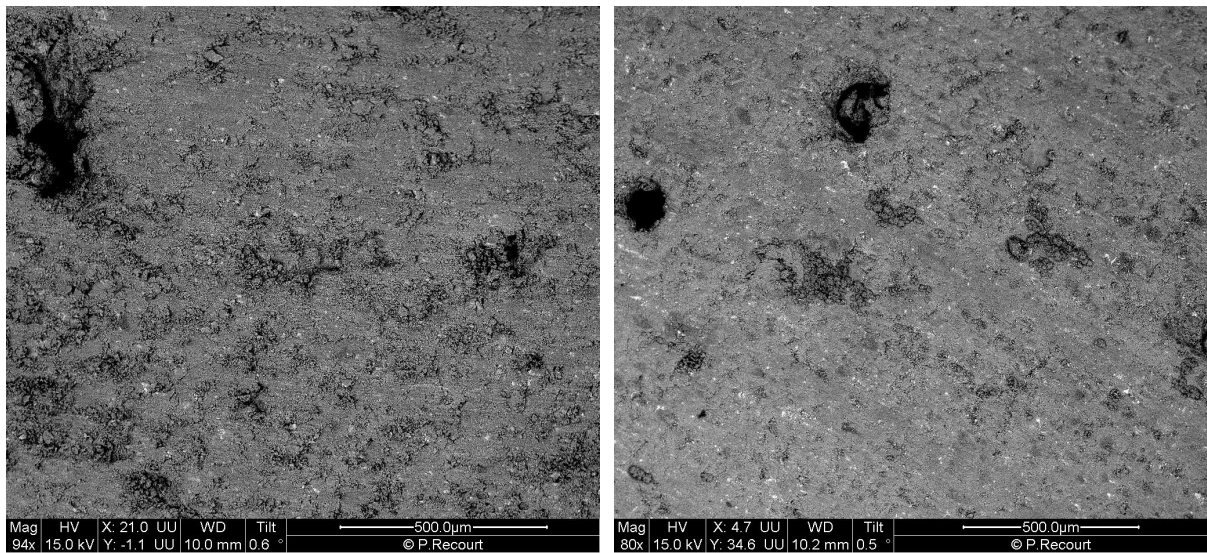
354 **4.1 Microstructure, chemistry and mineralogy analysis**

355 The SEM images have been performed on two leached samples: a leached sound sample (case 3) after 5
356 days of leaching and a leached carbonated sample (case 4) after 10 days of leaching (Fig.1). According
357 to the position of leaching front (Fig. 3), similar leaching levels are attained in these two samples. By
358 using a metal lathe (turning machine), two samples were cut to obtain a fresh plane surface. After that,
359 the obtained specimens were firstly examined by environmental SEM (Fig. 6). One observes that the

360 leached carbonated sample is more porous than the leached sound one. A preliminary conclusion will
361 then be drawn: the pre-carbonation exhibits a protective effect against leaching at the micro-structure
362 level.

363 After that, Energy-dispersive X-ray spectroscopy (EDS) is performed to investigate the relative
364 constitution of two leached materials (cases 3 and 4). For each sample, 3 or 4 measures have been
365 performed at different locations by using different measurement sizes. The atomic percentages of
366 different components are given in table 4. The standard deviation is also calculated to exhibit the
367 variability of measurements. Even though EDS may be not sufficiently accurate to provide a
368 quantitative proportion of light elements, the difference between two types of samples can still be
369 observed by comparing the obtained carbon element. For instance, a quasi-negligible quantity of carbon
370 (smaller than 1%) is observed in the leached sound sample (case 3) while the leached carbonated sample
371 (case 4) presents about 6% of carbon. As calcium carbonate is the unique component in the cement
372 paste containing the carbon element, one can conclude that there are still some calcium carbonates in the
373 leached carbonated sample (case 4). Moreover, by comparing the nitrogen (N) quantity in two samples,
374 it is noted that the quantity of calcium nitrate salt $Ca(NO_3)_2$ in the leached carbonated sample (Case 4) is
375 slightly lower than that in leached sound material (Case 3). This phenomenon may be related to the low
376 precision of SEM-EDS in the quantification of light elements (such as, N) and a more quantitative
377 technique (for instance: Rama spectroscopy) will be required for the further confirmation. In conclusion,
378 these observations tend to exhibit that calcium carbonate has not been totally consumed in the leached
379 carbonated sample (case 4) and will be further verified by using Raman spectroscopy.

380



382 (a)

382 (b)

383

Fig. 6. SEM images of two leached samples:

384

(a) leached sound sample; (b) leached carbonated sample

385

	Chemical element	C	N	O	Mg	Al	Si	S	Ca	Fe
Leached Sound sample (case 3)	Mean value (%)	0.75	11.91	65.02	0.70	1.03	4.74	1.21	13.85	0.79
	Standard deviation	0.55	1.13	2.06	0.17	1.02	1.05	1.66	1.25	0.82
Leached carbonated sample (case 4)	Mean value (%)	5.76	10.02	63.31	0.68	0.64	3.94	0.85	14.20	0.61
	Standard deviation	0.31	0.49	0.26	0.06	0.06	0.15	0.09	0.22	0.03

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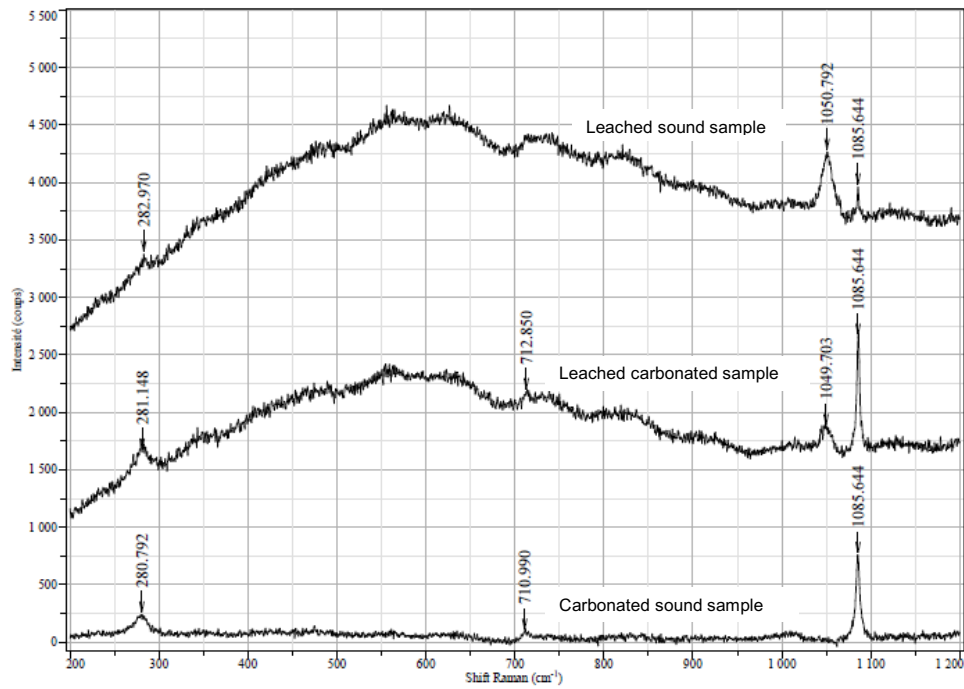
387 Table. 2 Atomic percentage of different components in two leached samples

388

389 As the Raman spectroscopy is well known to be capable of identifying the evolution of mineral
390 composition in cement paste, it is used here to study the effect of pre-carbonation on the leaching of
391 cement paste. In this section, three types of samples (cases 2, 3 and 4) are studied by Raman
392 spectroscopy analysis (Fig. 7). The carbonated sound sample (case 2) will be firstly studied and
393 compared with two leached cases (cases 3 and 4). In the carbonated sample (case 2), the calcium
394 carbonate is clearly observed with three peak values of 280.79, 710.99 and 1085.64 cm^{-1} while no
395 calcium nitrate peak is observed due to the absence of leaching. On the other hand, the calcium nitrate
396 peaks are clearly observed in two leached samples without or with pre-carbonation (cases 3 and 4).
397 Moreover, after leaching, the calcium nitrate peak in the initially sound sample (about 1050.79 cm^{-1}) is
398 slightly greater than that of pre-carbonated sample (about 1049.70 cm^{-1}). These observations allow us to
399 confirm the chemical discrepancies between two types of leached samples (Cases 3 and 4): more
400 calcium nitrate salt is created in the leached sound sample (case 3). The mineralogy and chemistry
401 analysis can help us understand the influence of pre-carbonation on the permeability and mechanical
402 characteristics of cement paste subjected to leaching, which will be presented in the next section.

403

404



405
406 Fig. 7 Raman test performed on carbonated sound, leached sound and leached carbonated samples

407
408 **4.2 Permeability and compression strength**

409 To understand the influence of pre-carbonation on the leaching process of the studied cement paste,
410 permeability and compression strength of four types of cement paste will be studied in this section.

411 The permeability values are given in Table 3. In each case, the influence of confining pressure on
412 the permeability evolution of cement paste is also analysed. In general, one observes that the
413 permeability of studied material decreases when the applied confining pressure increases. For instance,
414 in pre-carbonated samples, a permeability decrease of one order of magnitude is observed when the
415 confining pressure increases from 3 to 20MPa. This observation is in accordance with previous works
416 [37]. Although only one sample is tested in the present study, the results of permeability could still be
417 considered as a complementary indicator for the evolution of microstructure.

Case	Sample type	Pc=3MPa (m ²)	Pc=10MPa (m ²)	Pc=20MPa (m ²)
1	Sound	K=1.6×10 ⁻¹⁸	K=1.5×10 ⁻¹⁸	K=1.1×10 ⁻¹⁸
2	Carbonated sound	K=4.9×10 ⁻²⁰	K=1.3×10 ⁻²⁰	K=8.8 ×10 ⁻²¹
3	Leached sound	K=3.0×10 ⁻¹⁷	K=1.4×10 ⁻¹⁷	K=3.3×10 ⁻¹⁸
4	Leached carbonated	K=3.3×10 ⁻¹⁸	K=1.3×10 ⁻¹⁸	K=9.0×10 ⁻¹⁹

418

Table. 3 Permeability for different types of cement paste

419
420 The leaching effects on the permeability of non-carbonated samples (cases 1 and 3) are then
421 studied. The permeability of leached sound sample (case 3) is approximately one order of magnitude
422 higher than that of sound sample (Case 1). For instance, under the confining pressure $P_c=3\text{MPa}$, the
423 permeability of the leached sound sample (case 3) is equal to $K=3.0\times 10^{-17}\text{ m}^2$ while a permeability value
424 of $K=1.1\times 10^{-18}\text{ m}^2$ is obtained in the sound sample (case 1). On the other hand, the leaching effects on
425 two carbonated samples (cases 2 and 4) show that the permeability of leached carbonated sample (case
426 4) is approximately two orders of magnitude smaller than that of leached sound sample (Case 2). For
427 instance, under the confining pressure $P_c=3\text{MPa}$, the permeability of the leached carbonated sample
428 (case 4) is equal to $K=3.0\times 10^{-18}\text{ m}^2$ while a permeability value of $K=4.9\times 10^{-20}\text{ m}^2$ is obtained in the
429 carbonated sound sample (case 2).

430 The influence of carbonation on the permeability of leached cement paste is also studied by
431 comparing the permeability values of two leached samples (cases 3 and 4). The permeability value of
432 the leached sound sample (case 3) is about 10 times greater than that of the leached carbonated sample
433 (case 4). For instance, under $P_c=3\text{MPa}$, $K=1.1\times 10^{-17}\text{ m}^2$ in case 3 while $K=1.1\times 10^{-18}\text{ m}^2$ in the case 4.
434 After the leaching treatment, the permeability of pre-carbonation cement paste is always smaller than
435 that of initially sound one: at least one order of magnitude under low confining pressure ($P_c=3$ and
436 10MPa) and a factor of 4 under $P_c=20\text{MPa}$. Therefore, one observes that the permeability decrease
437 induced by the leaching is reduced by the pre-carbonation of cement paste.

438 Finally, the permeability values obtained on sound (case 1) and leached carbonated (case 4)
439 samples are compared. One observes that the permeability values obtained in two cases are very close
440 to each other and depend on the confining pressure. Under $P_c=3\text{Mpa}$, permeability of sound material
441 (case 1) is twice that of the leached carbonated one (case 4) while almost the same values are obtained
442 in these two cases under $P_c=10\text{MPa}$. Under $P_c=20\text{MPa}$, the permeability of case 1 is even smaller than
443 that of case 4. One can observed that the effects of carbonation, which induces a decrease of
444 permeability, are not totally cancelled by the leaching process. Again, this observation confirms the
445 protective effect of the pre-carbonation against leaching of cement paste, in terms of permeability.

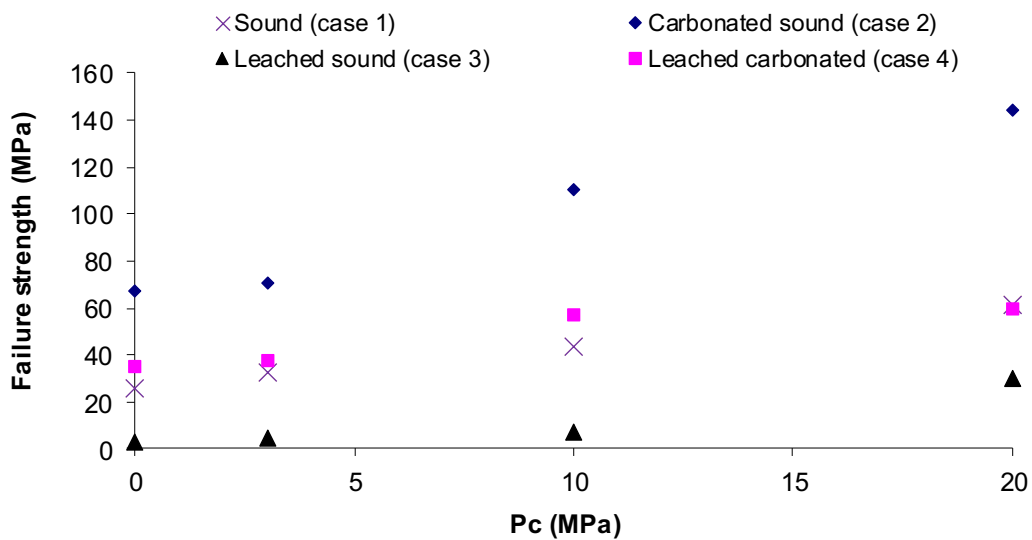
446

447 **4.3 Compression strength**

448

449 The obtained compression strength on four categories of samples is compared in Fig. 8. By
450 comparing the results obtained in the samples with (cases 1 and 2) and without (cases 3 and 4) leaching,
451 one observes that the leaching processes induce a decrease of material strength. For instance, by
452 comparing the cases 1 and 3, a decrease of about 77% is observed in the leached sound samples (case 3)
453 with respect to the sound samples (case 1). Moreover, according to the carbonated samples (cases 2 and
454 4), a decreasing order of 55% is obtained in leached carbonated samples (case 4) versus the carbonated
455 sound samples (case 2). One can observe that the decrease of mechanical strength created by the
456 leaching is also weakened by the pre-carbonation of cement paste. The same remark is drawn by
457 comparing the results of leaching sound (case 3) and leaching carbonated (case 4) samples: the failure
458 strength of leached sound sample is about 79% of that of leached carbonated sample. Again, it is
459 observed that the leaching effects of cement paste is offset by the carbonation.

460 Based on the SEM and Raman spectroscopy analysis, the observed difference between leached
461 sound sample (Case 3) and leached carbonated sample (Case 4) can be explained by the fact that
462 calcium carbonate in the carbonated sample has not been totally consumed by leaching (Table 2).
463 Therefore, a bigger mechanical strength and a smaller permeability are observed in the leached
464 carbonated sample (case 4) with respect to the leached sound sample (case 3).



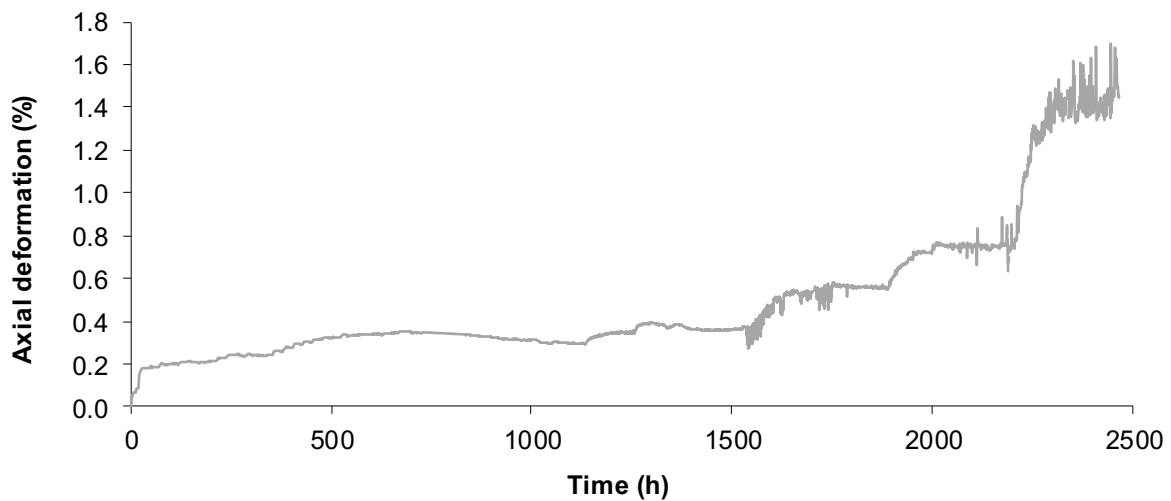
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466 Fig. 8 Evolution of compression strength in function of applied confining pressures

467

468 4.4 Creep deformation

469 As the long-term durability of oilwell also requires a good understanding of the effects of pre-
470 carbonation on the time-dependent behaviour of cement paste during leaching, a coupled creep test is
471 performed on the carbonated sound sample (case 2) with the injection of ammonium nitrate solution (6
472 mol/l). The evolution of axial deformation is shown in Fig. 9. The zero time corresponds to the
473 beginning of chemical fluid injection.



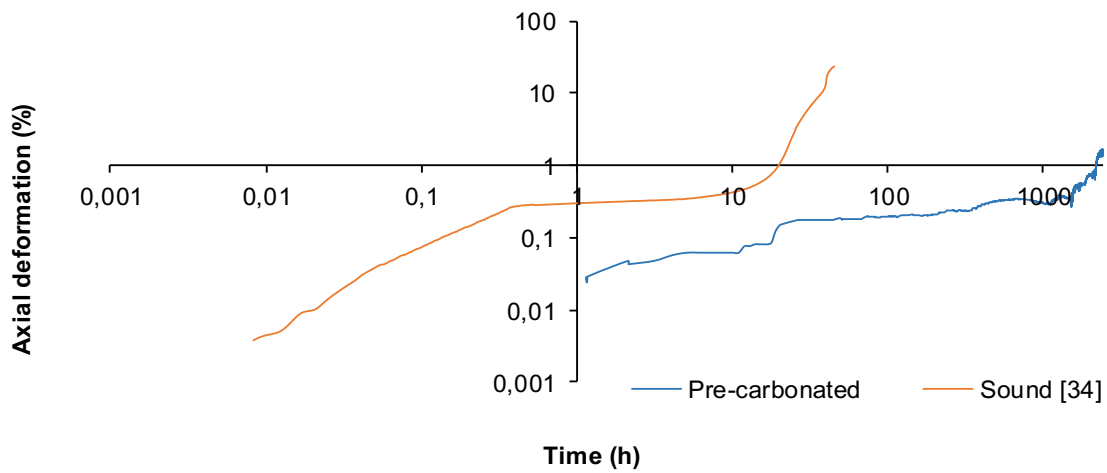
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475 Fig. 9 Evolution of axial deformation over time ($P_c = 3$ MPa, $T = 90^\circ\text{C}$) for a pre-carbonated sample
476 subjected to leaching

477 In the test, due to the injection of chemical fluid, the measured axial deformation increases
478 progressively with the degradation of cement paste. After 1500 hours, a rapid increase of axial
479 deformation is observed as an important part of sample is degraded. Afterwards, the deformation
480 continues to increase until the sample failure, which is characterized by a rapid increase of deformation.
481 These observations are related to the fact that leaching creates an increase of porosity and a decrease of
482 compressibility of studied material. Once the incompressibility becomes small enough, a sample
483 compaction occurs and then a sudden change of axial deformation takes place. The sample failure is
484 observed at 2500 hours.

485 In order to illustrate the effect of pre-carbonation on the creep behaviour of cement paste during
486 leaching, the above test should be compared with the same test performed on initially sound material.

487 As this test has been conducted in our laboratory, the triaxial creep test performed by Yurtdas et al. [34]
 488 is used for the comparison. In the present work, we have used the same material and experimental
 489 conditions (leaching processes and mechanical loading) as them [34]. Meanwhile, the applied
 490 deviatoric stress is equal to 50% failure strength of studied materials before leaching. Therefore, they
 491 have adopted a deviatoric stress of 16 MPa (50% of the failure strength of sound material at $P_c=3$ MPa
 492 and $T=90^\circ\text{C}$) while in the present work, the deviatoric stress of 35MPa (50% of the failure strength of
 493 pre-carbonated material at $P_c=3$ MPa and $T=90^\circ\text{C}$) is used.



494
 495 *Fig. 10 Evolutions of axial deformation in coupled creep tests for the pre-carbonated and sound*
 496 *samples [34] during leaching*

498 The evolutions of axial deformations in pre-carbonated and sound samples are analysed (Fig.10).
 499 One can observe that the leaching of carbonated cement paste is 55 times slower than that of sound
 500 material: the total leaching of a pre-carbonated sample takes 2470 hours while it takes only 45 hours for
 501 a sound sample. Moreover, in the sound sample, more important deformation is observed at the end of
 502 leaching test: the sound sample is broken with an axial deformation of 24% while a maximum axial
 503 deformation of 1.5% is obtained in the pre-carbonated sample. Again, the carbonation exhibits a
 504 positive effect against leaching, regarding the time-dependent behaviour of cement paste: with respect
 505 to the sound sample, a smaller leaching rate and a small axial deformation are observed in the pre-
 506 carbonated sample.

507

508 **4.5 Young's Modulus**

509 In the present work, a series of micro-indentation tests have been performed to identify the hardness
510 evolution of studied cement paste. According to a given distance from surface (i.e. 2, 6 and 10mm),
511 four measurements are performed for each type of cement paste. One observes that the obtained values
512 are very close to each other with a variation coefficient smaller than 9%. The low variability of
513 measurements confirms the reliability of experimental program as well as a good sample preparation.
514 The mean values are presented in Fig. 11.

515 By comparing the obtained results of cases 1 and 2 (Fig. 11), it is observed that the carbonation
516 induces an increase of Young's modulus. On the other hand, the leaching induces a stiffness decrease of
517 order 63% by comparing the samples of Cases 1 and 3. These observations are coherent with the
518 previous research [38,39]. Finally, the comparison of two leached samples (Cases 3 and 4) exhibits that
519 after leaching, the stiffness of initially sound material is about 80% lower than that of pre-carbonated
520 sample. Once again, it is observed that the carbonation exhibits a good protection of studied material
521 against leaching. Moreover, the results obtained in micro-indentation tests confirm, at the mesoscopic
522 scale, the experimental results of permeability and mechanical strength obtained at the macroscopic
523 level.

524 As this study focuses on the related values of Young's modulus obtained on different types of
525 samples, the values of Young's modulus obtained by micro-indentation tests will not be compared with
526 those obtained by other methods in the literature.

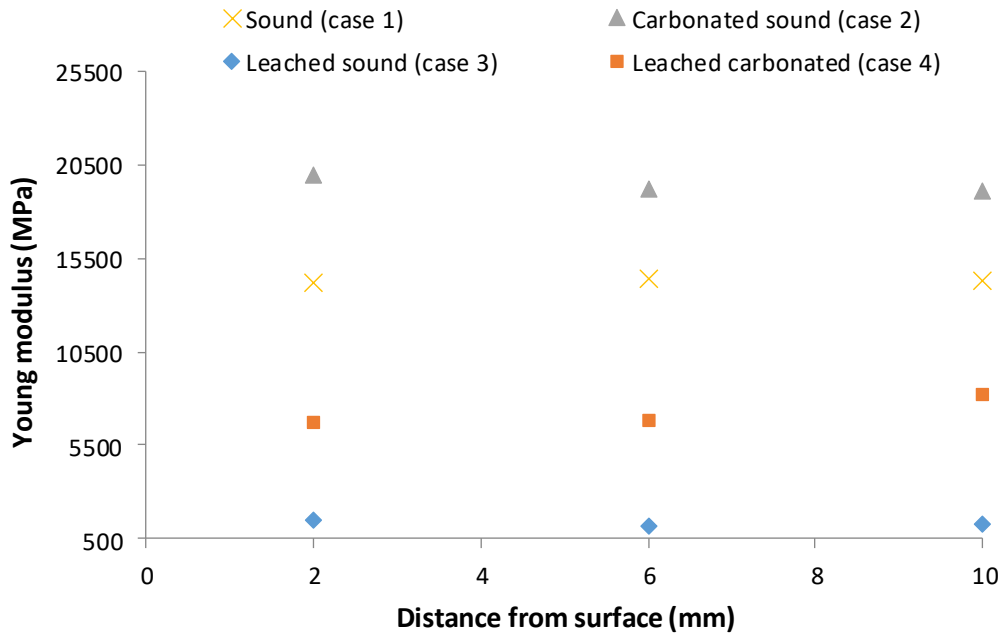


Fig.11 Values of Young's modulus obtained on four types of cement paste

528

529 5. Conclusions

530 In the present work, a series of experiment tests have been performed to characterize the effects of pre-
 531 carbonation on the hydro-mechanical properties of a G class cement paste subjected to leaching and
 532 high temperature $T=90^{\circ}\text{C}$. Based on the experimental observations, the following conclusions can be
 533 obtained:

- 534 • SEM images show that after leaching, the initially sound material is more porous than the pre-
 535 carbonated one. EDS and Raman spectroscopy analysis exhibit that after leaching, the initially
 536 sound and pre-carbonated materials have the same chemical components. Moreover, their
 537 chemical proportion are very similar except the carbon (C), since calcium carbonate in the pre-
 538 carbonated sample has not been totally consumed by leaching.
- 539 • For the leaching kinetics, the leaching of pre-carbonated material is at least one order of
 540 magnitude slower than that of sound material. This observation can be explained by the fact that
 541 the solubility of portlandite presented in sound material is about three orders of magnitude
 542 bigger than that of calcite in pre-carbonated one. As a result, comparing with the initially sound
 543 material, a smaller axial deformation is created during the leaching of pre-carbonated material
 544 in the coupled creep test.

- 545 • According to the permeability, after leaching treatment, the pre-carbonated cement paste is
546 about one order of magnitude lower than that of initially sound material. This observation is due
547 to the fact that the permeability evolution depends strongly on the initial carbonation state of
548 sample, which controls the porous network (quantity, diameter and connectivity of pores).
- 549 • For the mechanical strength and Young's modulus, the Young's modulus of leached sound
550 sample is equal to 79% of that of leached carbonated one while the failure strength of leached
551 sound sample is about 80% of that obtained on the leached carbonated sample. The compression
552 strength of leached carbonated sample is almost equal to that of initially sound one. The
553 Young's modulus obtained at the macroscopic level is confirmed by the experimental results of
554 micro-indentation tests, performed at the mesoscopic level.

555 In conclusion, a pre-carbonation plays a positive role against the leaching of cementitious material
556 in view of the long-term durability of oilwell. In the near future, analysis of microtopography will
557 be performed on different types of cement paste to analyse the dependence of permeability on the
558 microstructure of studied materials. Experimental investigation, micromechanical analysis and
559 microstructure will advance the understanding of long-term durability of CO₂ geological storage.

560

561 **Acknowledgments**

562 The authors gratefully acknowledge Total for entrusting this study to the Coupled Thermo-Hydro-
563 Mechanical-Chemical (THMC) team of the *Laboratory of Mechanics, Multi-physics, Multi-scale*
564 *(LaMcube)*, Lille - France, and for the permission to publish these results.

565

566 **Compliance with Ethical Standards:**

567 Funding: This study is funded by Total.

568 Conflict of Interest: The authors declare that they have no conflict of interest.

569

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