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Influence of chemical degradation on mechanical behavior of a petroleum cement paste

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ABSTRACT

Cement paste used in the Oil Industry is generally subjected to chemical degradation due to flow of acid fluids in various situations. The present study focuses on the evolution of thermo-hydro-mechanical (THM) behavior with chemical degradation of petroleum cement paste. Triaxial compression tests with different confining pressures (0, 3, 10 and 20 MPa) are carried out on a standard oil cement paste in sound state and completely degraded state by ammonium nitrate solution under a temperature of 90 °C. The results obtained show that the material in its initial state exhibits a small elastic phase and a strong capacity of compaction. The mechanical behavior depends on the load induced pore water pressure. Because of the increase in porosity caused by chemical degradation, the mechanical strength (cohesion and friction angle) and Young's modulus decrease. The dependence of mechanical strength and Young's modulus on confining pressure is smaller in the chemically degraded cement paste than in the sound one. In fine, the mechanical behavior of the whole material becomes more ductile. As a result, such effects of chemical degradation should be taken into account when modeling such cement paste materials exposed to such chemical degradations.

1. Introduction

The study of thermo-hydro-chemo-mechanical behavior of cement-based materials is of great interest in various applications, particularly for radioactive waste storage, oil wells exposed to acid gasses sequestration in geological formation like carbon capture and storage. Here we are interested in this topic for possible applications in the Oil Industry. When building a well, cement pastes are largely used in various situations, like cementing casings or plugging a wellbore. They could be also used as barrier for sealing geological sequestration of acid gasses such as CO_2 and H_2S in depleted reservoirs. In such situations, the cement pastes are subjected to mechanical loading, temperature variation, interstitial pore pressure changes and chemical attacks. Therefore, the understanding of different coupling phenomena and appropriate modeling are fundamental to design such structures.

Many works have been devoted to chemical degradation of cement pastes. Among various scenarios, a basic one is the degradation of cement paste by de-ionized or slightly ionized water. The chemical degradation, which is a non uniform evolution process [1–13], mainly comes from the calcium leaching of portlandite ($Ca(OH)_2$) and calcium silicate hydrates (C–S–H): the first dissolves completely while the second decalcifies itself gradually by reduction of C/S ratio in solid phase [1,2]. The portlandite dissolution appears suddenly from a threshold of a calcium concentration in pore water of approximately 21 mmol/l, while the C–S–H dissolution phase begins from a concentration about 19 mmol/l [14]. Here one should notice that the leaching process is also influenced by material composition [12,15]. Such chemical leaching leads to an increase in porosity and thus modifies mechanical and transport properties of the material. Poromechanical behavior, for instance Biot's coefficient, is therefore affected. For instance, there is a decrease in mechanical strength [3,7–9,12] and elastic modulus [3,4,6,12], there is also a transition from brittle behavior to ductile one [3,12], and an amplification of material sensitivity with respect to pore water pressure by the increase in Skempton coefficient [7–9].

Most studies so far were performed at ambient temperature only and under uniaxial compression. The purpose of the present study is to investigate chemical degradation effects on thermo-hydro-mechanical (THM) behavior of an oil cement paste, which means under temperature and under triaxial stress. It is carried out by comparing THM behavior at sound state with that at chemically completely degraded state. This paper will emphasize the study of cement paste mechanical properties. Moreover, the degradation kinetics with real chemical solutions (water for example) is generally low. In order to reduce testing time in the present work, the degradation is obtained by an artificial acceleration procedure using an ammonium nitrate solution NH_4NO_3 with a concentration of 6 mol/l. Such acceleration procedure is based on the assumption that the final consequence of chemical degradation on microstructure modification is the same for

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different solutions; the chemical nature of solution will affect the degradation kinetics only. Indeed, the chemical degradation caused by 6 mol/l ammonium nitrate solution is 300 times higher than that by water at ambient temperature [7]. Moreover, to be close to real borehole conditions, all the studies are performed at 90 °C, a temperature experienced by a number of wells, and under different state of stress. The kinetics of degradation involves initially matter diffusion due to calcium concentration gradient between pore water and aggressive solution, and chemical reactions of dissolution–precipitation. This process is controlled by the slowest phenomenon that is the diffusion process [1,2,7]. According to Fick's laws, the degradation generally follows a linear law of square root of time as long as there is an unaltered zone and the chemical solution composition remains constant. The degradation acceleration is amplified by the temperature increase [5,15,16]. However, it appears that the portlandite solubility decreases when the temperature increases, leading to an earlier attack of the C–S–H [14,17,18]. The calcium proportion passing into the solution increases as soon as the temperature changes from 20 to 50 °C. For temperature ranging between 50 and 85 °C, Kamali et al. [16] reported an increase in kinetics whereas Torrenti et al. [5] did not observe such an evolution.

The present paper is organized as follows: the set up of an experimental campaign is first presented. Last, a comparison of the results obtained on the THM behavior of an oil cement at the sound and completely degraded state is presented and analyzed. The influence of interstitial water pressure on the mechanical behavior (strength, elastic coefficient, and plastic strains) during loading is also presented. Notice that this experimental study has some similarities with those of Heukamp et al. [7,9] and Xie et al. [13] carried out at ambient temperature.

2. Experimental program

We present in this section the experimental program used in laboratory investigations.

2.1. Material composition, samples conditioning and testing

The study was undertaken on a standard oil cement paste with a water/cement (w/c) ratio equal to 0.44. A class G cement and two additives (a dispersing agent and an anti-foam agent) were used to pour the material. Several samples were manufactured. Initially it was envisaged to undertake the experimental study in the following way: after one month of maturation of the samples in lime saturated water at 100 °C, these samples were to be conserved under 100% relative humidity and under nitrogen at 100 °C. However, this protocol of conservation after one month maturation proved to be problematic. Indeed, the samples underwent a severe drying which led to a very important cracking and the samples were not usable any more for the experimental study. This is why the following protocol has been chosen to conduct the study. After casting, the samples, in their mold, were first maintained for 3 days in distilled lime saturated water at 100 °C then removed quickly from their mold and preserved still for 4 days in the distilled lime saturated water at 100 °C. After, the temperature was gradually reduced to 90 °C (3 °C/day) and the samples were kept in the distilled lime saturated water at 90 °C to reach a maturation of one month in total; with this protocol it is aimed to have an optimal maturation in a minimum time. The samples were sliced and rectified under temperature, to have a diameter of 37 mm and a height of 40 mm. They were obtained from the central part of the mold samples. Their homogeneity was controlled by apparent bulk density measurement. These dimensions were selected so as to carry out the measurements within a reasonable period of time, in particular for reaching the equilibrium of pore pressure or steady state during the tests. Note that as we are interested here in the evolution of hydro-mechanical behavior at 90 °C, this evolution integrates possible effects of high temperature during curing process and testing of samples [19,20]. According to Taylor [21], the chemistry of hydration is essentially the same between 25 and 100 °C, but the temperature accelerates the hydration and modifies the volume fractions of different phases. Hydration at higher temperature increases the porosity and results in a more porous and more heterogeneous low density C–S–H but a less porous high density C–S–H [22–24]. These modifications of porous structure due to temperature increase lead to an increase of early age strength and a decrease of long-term strength [19,22].

After the end of the maturation phase, the samples were separated into two series under 90 °C:

- the first series of samples were placed in a neutral fluid (a synthetic fluid which has similar composition to the interstitial fluid) whose composition is given in Table 1,
- and the second series of samples were submitted to chemical degradation with ammonium nitrate (NH_4NO_3) solution until complete degradation; then these samples were rinsed in distilled water before mechanical tests.

To maximize the kinetics of the degradation we have chosen an ammonium nitrate solution with 6 mol/l concentration, which has a pH of about 5. As the volume of the solution is important enough for the quantity of the matter to be degraded, the pH of the solution did not exceed 7.8 during degradation process. Therefore, it has not been necessary to renew the solution because the pH is lower than 9.25 [7]. The degradation of the cement paste by ammonium nitrate leads to the formation of calcium nitrate, a very soluble compound, and to that of calcium nitro-aluminates, a very expansive compound. The precipitation of the latter induces cracks if the samples are not protected from drying [2]. As a result, the samples must be kept in wet conditions.

The uniaxial and conventional triaxial compression tests were carried out respectively on the sound and degraded cement pastes under a temperature of 90 °C. The loading rate of multiaxial tests was 10^{-3} mm/s. Recall that the size of cylinder samples is 37 mm in diameter and 40 mm in height. The values of confining pressure are 3, 10 and 20 MPa and the pore pressure is equal to 2.5 MPa: these values were chosen according to average in situ conditions. Two types of uniaxial compression tests were performed. For the first type, the sample was loaded in uniaxial compression without interstitial pressure until failure (Fig. 1.a). For the second type, the sample was initially subjected to a confining pressure of $P_c = 3$ MPa then to an injection pressure of fluid of $P_i = 2.5$ MPa at the upstream and an outlet pressure of $P_0 = 0$ MPa at downstream; this interstitial pressure gradient was applied for the measurement of initial permeability (Fig. 1.b). Afterwards, the interstitial pressure in the sample was reduced to zero. And finally, similar to the first test, the sample was loaded in axial stress until failure. In such way, the sample used in this second test is subjected to a pre-confining pressure of 0.5 MPa. For the triaxial tests, a constant pore pressure of 2.5 MPa was applied for all confining pressures. The principle of this type of test is schematized on Fig. 1.c: after the application of the desired confining pressure, the fluid is injected into the sample from one side in order to proceed again in permeability measurement. Next, the outlet valve of interstitial fluid was closed to get an increase of pore water pressure up to 2.5 MPa. Then, axial

Table 1
Composition of neutral fluid for 1 kg of de-ionized water at 25 °C (theoretical pH is about 13).

Composition	Quantity (g)
$Al(OH)_3$	7.8
$Ca(OH)_2$	7.4
NaCl	0.3
NaOH	5.93
Na_2SO_4	7.6
SiO_2	1.2

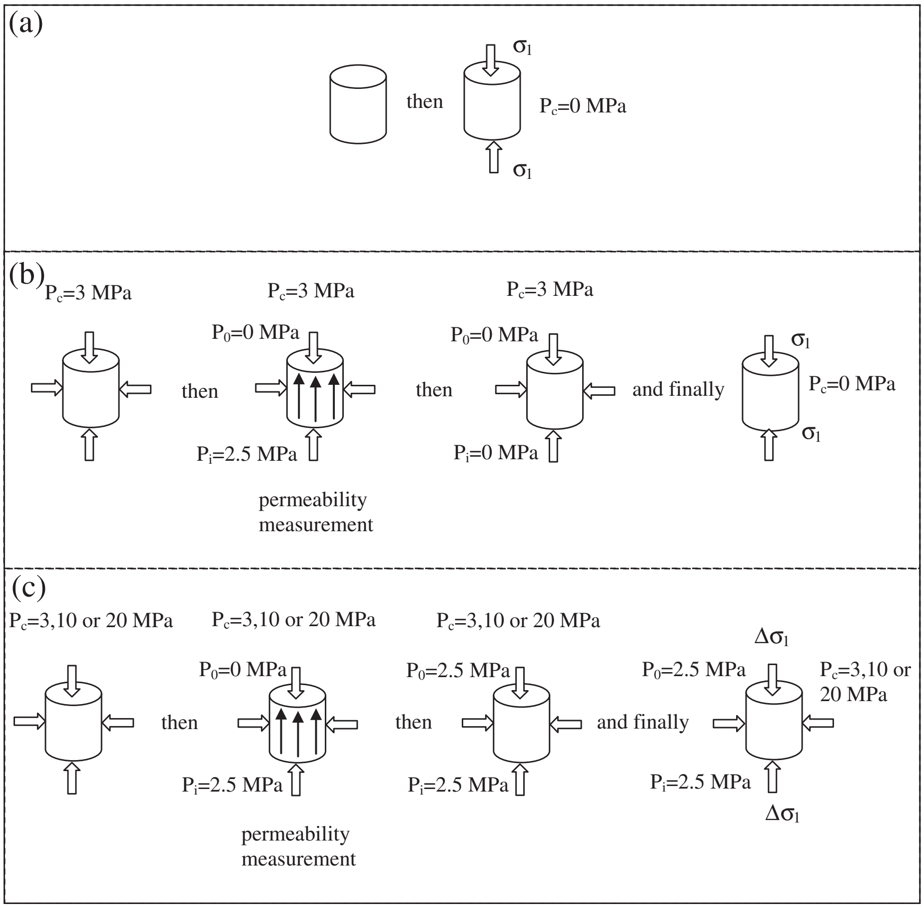

Fig. 1. Schematic representation of various tests.

(deviatoric) stress was applied to the sample until failure, by keeping the pore pressure constant throughout the test. The neutral fluid was used for the tests on the sound samples and the distilled water was used for the tests on the degraded samples.

Like most porous materials, the mechanical behavior of cement paste should be affected by any change in interstitial pressure through poromechanical coupling effects [9,25–29]. The effect of interstitial pore pressure under isotropic loading on the sound cement sample was already studied [29]. In order to highlight such effects on the sound samples under deviatoric loading–unloading, two couples of comparative tests were considered. On one hand, we compared the triaxial compression test with $P_c = 3$ MPa and $P_i = 0$ MPa with that with $P_c = 3$ MPa and $P_i = 2.5$ MPa, to show the effects of interstitial pressure on mechanical responses of cement paste. On the other hand, the triaxial compression test with $P_c = 7.5$ MPa and $P_i = 0$ MPa was compared with that at $P_c = 10$ MPa and $P_i = 2.5$ MPa. Note that these two tests were performed with the same value of effective confining pressure (say 7.5 MPa) in the sense of Terzaghi effective stress concept that was already verified by Heukamp et al. [9] on the chemical degraded samples. Here, the objective was to verify the pertinence of such concept for numerical modeling of poromechanical coupling [26–28] in cement paste. In this study, the test with $P_i = 0$ MPa corresponds to the situation in which the pore pressure of the saturated sample is kept constant at atmospheric condition (through an appropriate drainage system).

The triaxial compression tests were further completed with the measurement of porosity at the sound and completely degraded state. The porosity was determined by drying of initially saturated samples at 105 °C until constant weight. The variation of porosity due to chemical degradation is one of the key parameter to be used in chemo-mechanical modeling.

Fig. 2 shows the evolution of the leaching front with time in a reference (witness) sample broken by splitting test along diameter plane. We can see that the leaching front, viewed through the use of phenolphthalein solution, reached the core of the sample. The mass variation versus time during leaching and rinsing is plotted in Fig. 3. The mass evolution of the three samples is similar and stabilizes after approximately 40 days. This figure also shows that, after leaching, the rinsing by distilled water caused an additional loss in mass, due to the

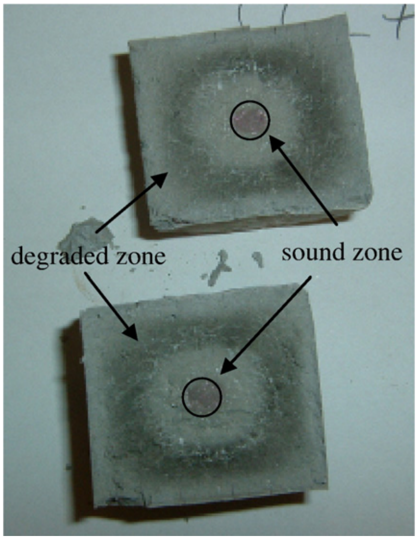

Fig. 2. Example of the leaching evolution on a sample after splitting test.

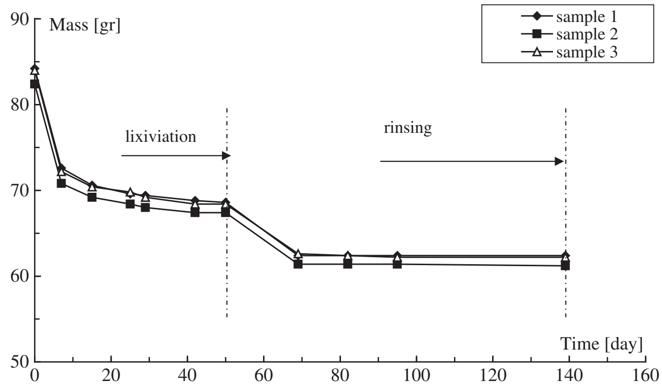

Fig. 3. Mass variation of 3 samples during lixiviation and rinsing process.

removal of dissolved chemical products. However, this second loss is also stabilized quickly.

2.2. Experimental devices and measurement procedure

Uniaxial and triaxial tests with loading–unloading cycles were carried out using an experimental device developed especially in our laboratory for the present study. It was composed of the following components (Fig. 4):

- an auto-compensated and autonomous triaxial cell
- an oven
- three pumps for the application of confining pressure, deviatoric stress and pore water
- an overflow valve allowing to keep the pore water pressure at desired value
- an acquisition system.

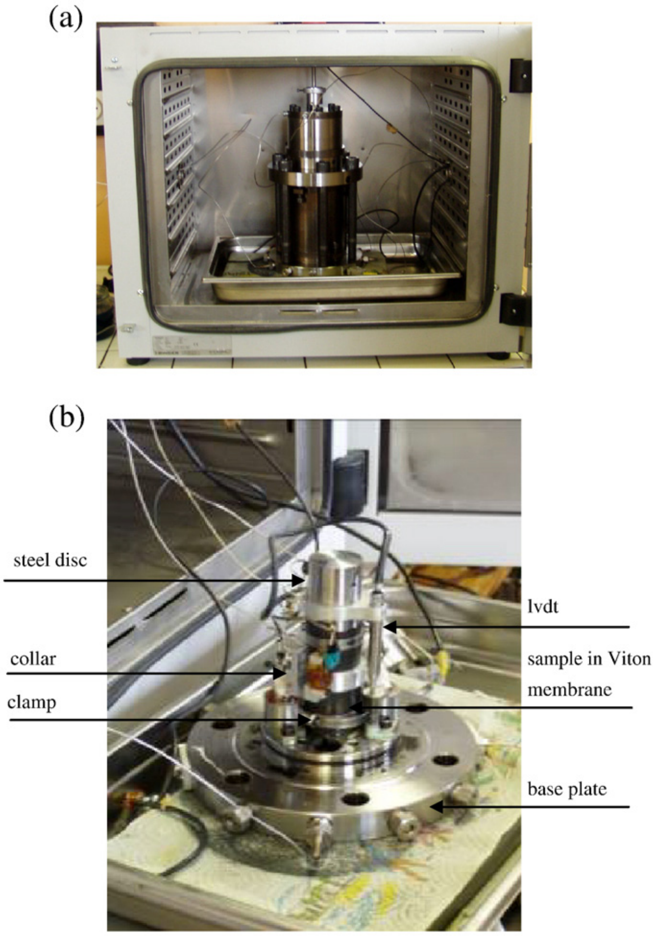

Fig. 4. (a) General view of the experimental device and b) photography of a sample instrumented for the test.

As strain gauges can not be glued on porous cement paste at 90 °C, different measuring techniques are necessary for monitoring the strains. In the present work, the axial strain was measured by LVDT. The radial strains were obtained with the help of a special ring [30] composed of a blade on which were glued strain gauges. The radial strains of sample were translated to flexion displacement of the blade. Fig. 4.b shows the photographic view of an instrumented sample for a triaxial compression test. In order to carry out a rigorous experimental campaign, the same protocol was followed for all tests. We paid a special attention to a uniform distribution of temperature before testing.

3. Experimental results and analysis

In this section the main results from the experimental testing are presented and discussed. The emphasis is put on the effects of chemical degradation on physical properties and mechanical behaviors of the oil cement paste.

3.1. Variation of porosity due to chemical degradation

Table 2 shows the porosity values obtained on the sound and completely degraded cement pastes. The chemical leaching leads to a 50% porosity increase. Such an increase is also reported by other authors [3,9,13]. In addition, as the process of leaching is not a homogeneous process, there is creation of a calcium loss gradient from outside surfaces of the sample towards its interior core. This process leads to an evolution of porosity in the sample: the greater the calcium loss the more the porosity increases. It becomes progressively uniform when the sample is completely leached. Carde and François [31] compared the leaching of a portland cement paste with the leaching of a cement paste containing 30% of silica fume in cement weight (the silica fume can considerably reduce the portlandite content by pozzolanic reaction). They observed that 2/3 of the porosity increase was due to the portlandite leaching and 1/3 to the CSH leaching in the case of a standard portland cement.

3.2. Chemical degradation effect on uniaxial mechanical behavior

In Fig. 5, we show the evolutions of axial and radial strains during uniaxial compression tests for a sound and a degraded sample. The behavior of both cement pastes is characterized by a small elastic response domain and a very large plastic phase. The results given in Fig. 5 clearly highlight that the chemical degradation leads to a drastic decrease of the uniaxial failure strength, from 29 MPa to 11 MPa. This decrease of mechanical strength is correlated with the considerable porosity increase (see Table 2). Moreover, due to high porosity and ductile behavior, the oil cement paste both in the sound and degraded states exhibits essentially compressive plastic volumetric strain. Fig. 5 shows that for a given stress the axial strain of the sound sample is higher than that of the degraded sample. As this did not seem logical, a second test of uniaxial compression was carried out on a degraded

Table 2
Porosity of the cement paste at the sound state and the degraded state.

Number of sample	1	2	Average [%]
Sound state	0.34	0.39	0.37
Degraded state	0.56	0.56	0.56

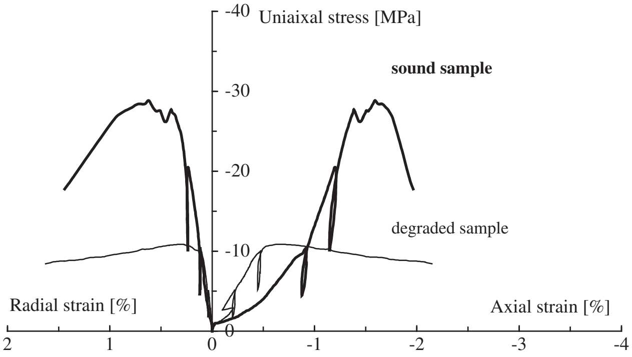

Fig. 5. Stress–strain curves of the sound and degraded cement pastes in uniaxial compression test ($P_c = 0$ MPa, $P_i = 0$ MPa).

sample. This one, with failure strength of 11.5 MPa, perfectly showed that the axial strain is higher for the degraded sample and not for the sound sample (the radial strain could not be measured because the special ring did not function during the test) for a given stress. The classical volumetric dilation in brittle cement-based materials is not observed. The loading–unloading cycles show large variation of elastic modulus or stiffness due to mechanical compaction of the material; the ratio of current modulus to the initial one is about 9 for the sound sample and 24 for the degraded sample (see also Fig. 11). Finally, there is a transition from brittle failure (with very pronounced post-peak regime and splitting of sample) in sound cement paste to ductile failure (smooth peak stress and onset of shear strain bands) in the degraded cement paste.

Fig. 6 shows the evolution of axial and lateral strains under uniaxial compression for the sound and degraded samples after an effective pre-confining pressure. The LVDT in triaxial cell did not function during the test, so the strain value of the sound sample reported here was obtained by an external LVDT that follows the deviatoric loading piston, and thus reveals the compacting elastic–plastic behavior of the sample. We can see that the mechanical responses shown in Fig. 6 are overall similar to those given in Fig. 5. However, the pre-confined samples have a slightly higher strength; this can be attributed to the volumetric compaction due to the preliminary confining pressure of 3 MPa and pore pressure of 2.5 MPa.

The decrease of uniaxial compressive strength due to chemical degradation was also reported in other works [2,3,7,12,32]. Moreover, they showed a more ductile behavior [3,12] and reduction of elastic domain [32]. The work of Carde et al. [3] also allowed distinguishing the portlandite and C–S–H decalcification effects on the mechanical behavior. These authors concluded that for a total decrease of 76% in uniaxial strength, 70% comes from portlandite leaching and only 6% from the CSH decalcification. As the CSH leaching increases the micro-porosity, its influence on the failure strength remains moderate compared to the portlandite leaching which induces a macro-porosity [3]. Therefore, the portlandite leaching is the main cause of the deterioration of uniaxial strength and Young's modulus, the leaching effect by reduction in C/S ratio remaining secondary in the case of a classical portland cement paste. However, the influence of the decrease in C/S ratio on strength becomes important when there is no longer portlandite in cement-based materials (as in the case of the cement paste containing silica fume for instance), even if this material preserves overall its main properties [3].

3.3. Chemical effect on hydrostatic compression behavior

The mechanical behavior of oil cement paste under hydrostatic compression is presented in Fig. 7 for the sound state and degraded state. This loading phase is performed before the deviatoric phase in triaxial compression tests with confining pressures of 3, 10 and 20 MPa. For sound cement paste, the stress–strain curve is characterized by a nonlinear concave part at the beginning of loading, followed by a quasi linear elastic part. Such a nonlinear phase is related to progressive closure of initial microcracks or very plate pores. After chemical degradation, the mechanical behavior of the cement paste becomes elastoplastic as soon as the confining pressure is equal to 3 MPa. Note that there is significant scatter in the experimental results for the sound cement paste. Moreover, the samples seem to have higher initial slopes with low confining pressure. As a limited number of samples are tested here, it is difficult to know the exact reasons. However, this scattering can be due to the variability of cement-based materials and the experimental artifacts. This variability seems to be largely reduced after the chemical degradation. It is important to note that the deformability of the degraded cement paste is much higher than the sound one for all the levels of stress. Under higher hydrostatic stress, for instance 20 MPa, there is an acceleration of strain rate, which is related to pore collapse in the degraded cement paste [13]. The volumetric strains go from −0.23%, −0.54%, and −1.51% for the sound samples to −0.53%, −2.88%, and −6.68% for the degraded samples respectively at 3, 10 and 20 MPa of confining pressure. The volumetric strain difference between the sound and degraded cement pastes reaches 440% when the confining pressure is equal to 20 MPa.

3.4. Influence of chemical leaching on triaxial compression

Three triaxial compression tests were carried out respectively on the sound and degraded cement pastes with confining pressures of $P_c = 3$, 10, and 20 MPa and pore pressure of $P_i = 2.5$ MPa. The stress–strain curves obtained from these tests are presented respectively on Figs. 8, 9 and 10. As in uniaxial compression tests, there is a drastic

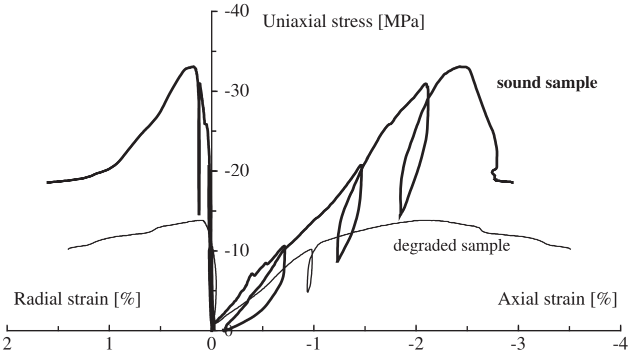

Fig. 6. Stress–strain curves of the sound and degraded cement pastes in uniaxial compression test after a pre-confining (first $P_c = 3$ MPa, $P_i = 2.5$ Pa then $P_c = 0$ MPa, $P_i = 0$ MPa).

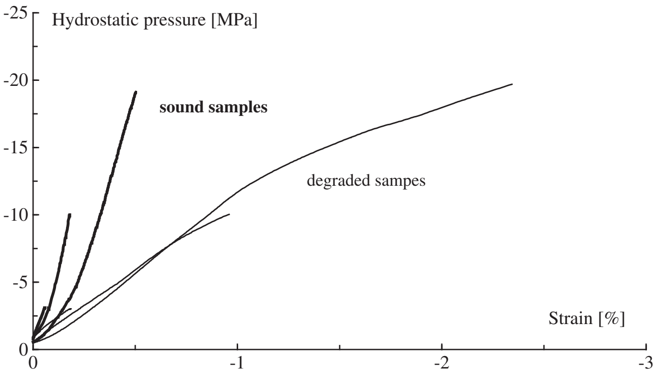

Fig. 7. Comparison of strain evolutions between the sound and degraded cement pastes at 3, 10 and 20 MPa of confining pressure.

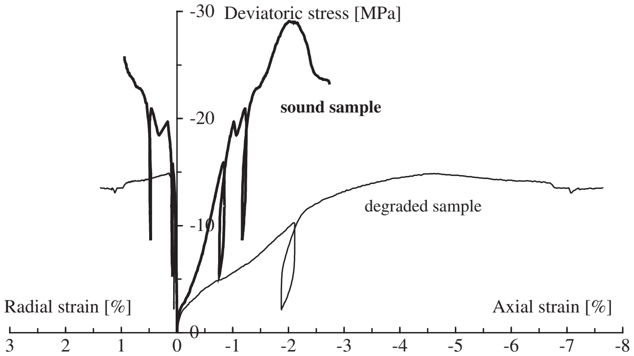

Fig. 8. Stress–strain curves of the sound and degraded cement pastes in triaxial compression test ($P_c = 3$ MPa and $P_i = 2.5$ MPa).

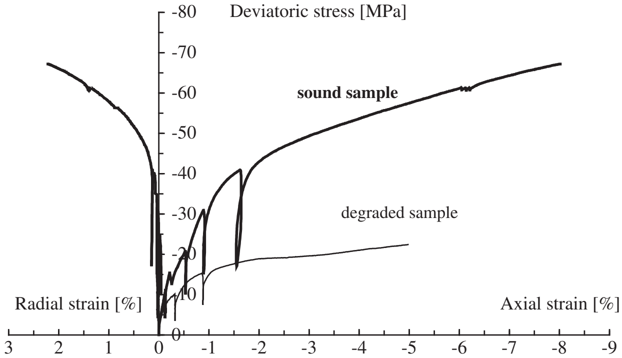

Fig. 10. Stress–strain curves of the sound and degraded cement pastes in triaxial compression test ($P_c = 20$ MPa and $P_i = 2.5$ MPa).

decrease in mechanical strength with chemical degradation. Due to the confining effect, there is a larger elastic range in the sound cement paste when the confining pressure reaches 10 MPa (Figs. 9 and 10). However the effect of confinement on the elastic response is attenuated for the degraded cement paste. Further, even with the more significant elastic deformation in the sound cement paste, the plastic deformation remains dominant compared to the elastic one for both materials.

Fig. 11 gives the evolution of the ratio of current elastic modulus during loading–unloading cycles (E) to initial elastic modulus (E_0) versus normalized accumulated plastic strain. This one is defined as the irreversible axial strain at each cycle divided by the axial strain at peak stress (or by maximum strain when there is no peak as was the case for high confinement). The results show that there is large increase of initial elastic modulus in the sound cement paste with confining pressure. Further, the elastic modulus increases with the cumulated axial strain at low confining pressures (0 and 3 MPa). However, this modulus decreases during unloading–reloading process at high confinement (10 or 20 MPa). On the other hand, the elastic modulus of the degraded cement paste also increases with unloading–reloading cycles, and its evolution is larger than that of the sound material. This is probably due to the fact that large plastic volumetric compaction is produced in the chemically leached material during triaxial compression tests. Indeed, it is interesting to notice that even the elastic part of the radial strain remains always tensile due to positive Poisson's ratio, the total radial strain in such tests can become compressive (having the same sign than the axial strain) due to very large compressive plastic deformation under triaxial compressive loading. Similar compressive deformations have also been reported for ordinary cement-based materials at ambient temperature [33,34]. Such large compressive deformation makes very delicate the measurement of radial strain by the specific strain ring. Indeed, such specific ring is designed mainly for the measurement of expansive strain. When the compressive lateral strain becomes too large, there is loss of contact between the sample and ring. As a consequence, the lateral strain in the test with 20 MPa confining pressure was not correctly measured. The strong compacting nature of the cement paste is also highlighted by the photography of tested samples (Fig. 12). One can see that the compaction under high confining pressure is intensified by the chemical degradation. Notice that even if the strains of the sound sample seem to be higher than that of the degraded sample during the deviatoric phase (Fig. 10), the latter has higher strains due to creep undergone at the time of hydrostatic phase during the time of permeability measurement and of the establishment of uniform pore pressure. Finally, it is also useful to notice that the classical failure mode (characterized by peak stress) is observed only in the tests with low confining pressure (lower than or equal to 3 MPa). Otherwise, the material failure is characterized by a ductile mode due to diffuse microcracks and pore collapse.

3.5. Analysis of mechanical strength and elastic modulus

Fig. 13 shows the evolution of deviatoric failure strength (peak stress) versus effective confining pressure for the sound and degraded cement pastes. Classically, the deviatoric failure stress increases with confining pressure due to internal friction. However, the increase of strength with effective confining pressure is attenuated by chemical leaching, going from 133% to 99%. This is correlated with the porosity increase of the degraded samples. Further, it seems that for the degraded cement paste, the deviatoric failure stress reaches an asymptotic value after some threshold of confining pressure. Moreover, the failure strength of the sound and degraded samples

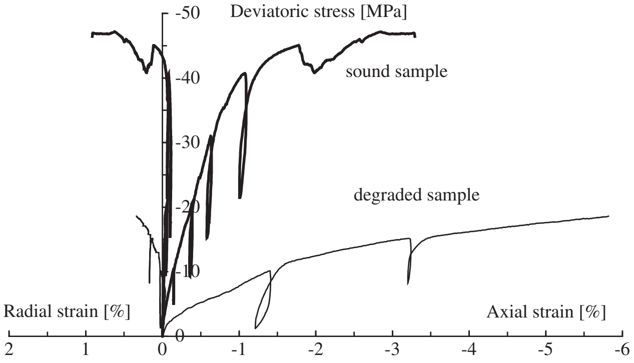

Fig. 9. Stress–strain curves of the sound and degraded cement pastes in triaxial compression test ($P_c = 10$ MPa and $P_i = 2.5$ MPa).

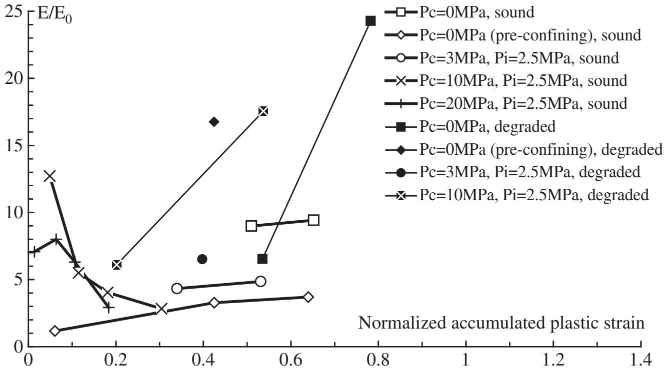

Fig. 11. Evolution of the ratio of current elastic modulus (E) to initial elastic modulus (E_0) versus normalized accumulated plastic strain for different confining pressures.

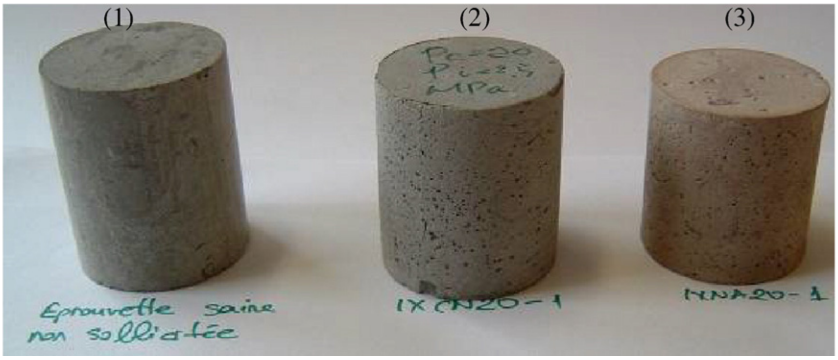

Fig. 12. Photography of 3 cement paste samples: (1) sound non tested, (2) sound and tested at $P_c = 20$ MPa and $P_i = 2.5$ MPa, and (3) degraded and tested at $P_c = 20$ MPa and $P_i = 2.5$ MPa.

slightly increases after pre-confining (●, ▲) due to preliminary compaction of material.

Ulm et al. [8] and Heukamp et al. [9] also reported the same evolution of deviatoric strength with degradation in drained condition on a classical cement paste with $w/c = 0.5$ at ambient temperature. However, these authors [7–9] observed that the deviatoric strength of degraded cement or mortar remains constant with the increase of confining pressure in undrained condition. This comes from the fact that the friction coefficient becomes almost zero in undrained condition. The degraded material is more sensitive to pore pressure than the sound material due to the increase of Skempton coefficient [7,8,35]. The amplification of the material's sensitivity to pore pressure depends on two consequences of chemical damage: increase in porosity and decrease in the ratio of solid to fluid compressibility. The first is mainly due to the portlandite leaching while the second, also called intrinsic chemical damage, is due to the reduction in C/S ratio and has a dominating effect [7,8].

The evolution of initial elastic modulus of the sound and degraded cement pastes versus effective confining pressure is presented in Fig. 14. The values of the elastic modulus are obtained after the beginning of loading, before the loading–unloading cycle. The value of elastic modulus reported in this figure for the degraded cement paste under uniaxial compression is that obtained from the second test (see Section 3.2). Like failure strength, the elastic modulus decreases with degradation. Moreover, the elastic modulus or more exactly elastic stiffness increases with confining pressure, especially for the sound samples. The elastic modulus of the degraded samples determined from uniaxial compression tests with pre-confinement (▲) is slightly higher than that of the sample without pre-confinement (Δ). As indicated earlier, the strain of the pre-confined sound sample is obtained by an external LVDT, so the corresponding value of the sound sample is not reported in this figure to avoid any possible erroneous interpretation. However, the pre-confined sound sample should also have higher initial elastic modulus compared to the sample without pre-confining. This shows the effect of compaction due to pre-confinement on initial elastic modulus. The decrease in elastic modulus of the degraded material compared to the sound one is also reported in the literature at ambient temperature [2–4,6,12,32,36]. Notice that it was not possible to measure the evolution of Poisson's ratio with confinement because of the strongly compacting nature of the cement paste.

The classic Drücker–Prager criterion [37] to describe the failure surface of oil cement paste is expressed by the following form [9]:

$$f = \sqrt{J_2} - \alpha\sigma_m' - k = 0, \tag{1}$$

where J_2 is the equivalent stress (second invariant of deviatoric stress tensor), σ_m' is the effective mean stress; α and k denote respectively the coefficient of friction and cohesion of material. The values of these two parameters can be determined by drawing a failure surface in the $\sqrt{J_2} - \sigma_m'$ plane. This is done for the sound and degraded cement pastes in Fig. 15 and Table 3. One can clearly see that the chemical degradation causes a significant modification of the failure surface. The cohesion and friction coefficient decrease by 33% and 63% respectively with the chemical degradation.

As Xie et al. [13] carried out a study more or less similar on the same cement paste of the present study at ambient temperature (20 °C) it would be useful to make some comparisons in order to understand the effect of elevated temperature on mechanical behavior. Recall that these authors carried out the tests on the sound samples after 28 days of maturation in lime saturated water at 20 °C while the tests on the degraded samples were performed after about two years of leaching with 6 mol/l ammonium nitrate solution. Table 3 shows that the porosities of the sound samples at ambient and elevated temperatures are almost identical while some difference of porosity is measured after chemical degradation. As the mechanical

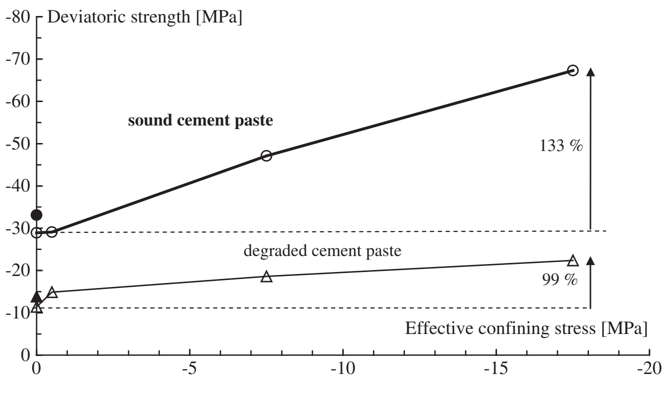

Fig. 13. Multi-axial strength evolution of the sound and degraded cement pastes versus effective confining pressure.

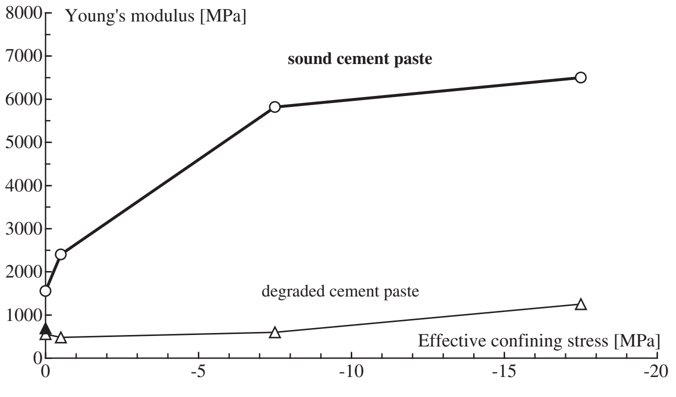

Fig. 14. Young's modulus evolution of the sound and degraded cement pastes versus effective confining pressure.

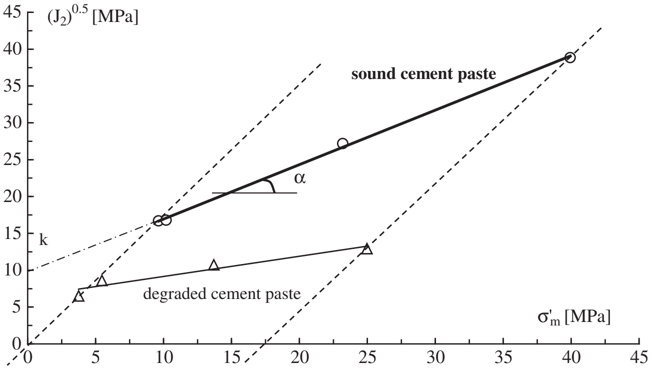

Fig. 15. Representation of failure surface for the sound and degraded cement pastes.

tests at ambient temperature were not carried out under the same experimental loading conditions as in the present study, only general trends can be compared. Both studies show a similar evolution of deviatoric failure with effective confining pressure between 3 and 10 MPa. However, the deviatoric strength of the sound samples at 90 °C increases more quickly than the samples at ambient temperature under higher effective confining pressures, for 17.5 MPa. There is also an increase of deviatoric strengths for the degraded samples with confinement, but the deviatoric strength of samples at 20 °C is very low, which can be certainly explained by a higher level of degradation. Indeed, recall that the leaching process at 90 °C was finished at 50 days, once the loss in mass of samples due to leaching tends towards stabilization (Fig. 3). Although the rate of calcium leaching increases with temperature, i.e. 2.8 times when the temperature goes from 20 to 85 °C [5], the degradation level of samples under ambient and elevated temperatures is quite different. Like deviatoric strengths, the initial elastic moduli also increase with confinement, especially that of the sound samples. However, the initial elastic modulus of the sound samples at 90 °C is lower than that of the sound samples at 20 °C for a given effective confining pressure. On the other hand, even if there is a large difference between the multi-axial strength, the elastic modulus of the degraded samples at elevated temperature is slightly higher than that of the degraded samples at ambient temperature for a given effective confining pressure.

To complete the comparison, Table 3 presents the friction coefficient and cohesion according to material state and conditioning temperature. It can be seen that contrary to cement paste at 90 °C, the friction coefficient slightly increases whereas the cohesion becomes close to zero after degradation of cement paste at ambient temperature due to higher leaching level. Moreover, elevated temperature leads to higher friction coefficient but lower cohesion for the sound cement paste. After chemical leaching, the tendency is reversed. The deterioration of those two coefficients after chemical degradation was also reported by Heukamp et al. [7,9] and Ulm et al. [8] on a cement paste at ambient temperature. They observed also a very low cohesion after degradation.

The comparison of results shows that elevated temperature seems not to have detrimental effect on the multi-axial strength of the sound cement paste studied here but it deteriorates the elastic modulus for all the confining pressures considered here. These results seem to be a little bit different with those generally reported in literature showing large effect of elevated temperature on mechanical properties of cement pastes. However, it seems necessary to distinguish the effect of elevated temperature from that of hydration during maturation process. The elevated temperature can indeed deteriorate the mechanical properties of mature materials [19,38]. However, the deterioration in some cases may be due to the expansion [38] and evaporation of the internal water of material leading to nucleation and growth of microcracks [19,38]. There can be also thermal origin micro-cracking which comes to be added to the previous one. However, as the conditions of maturation and of testing under temperature as well as the composition of materials reported in the literature are very different from those of the present study, it is difficult to make a direct comparison between our results and those from the literature. Moreover, as the duration of leaching is not identical in the present study and in that carried out by Xie et al. [13], it is also difficult to give definitive conclusions concerning the effect of elevated temperature on the mechanical properties of the degraded cement paste. Additional tests performed on the sound and degraded cement pastes under identical experimental conditions (only the temperature is changed) are still necessary.

Table 3
Porosity, friction coefficient and cohesion according to material state and conditioning temperature (results at 20 °C from Xie et al. [13]).

Material		Porosity [%]	Friction coefficient (α)	Cohesion (k) [MPa]
20 °C	Sound	0.36	0.51	14.36
	Degraded	0.60	0.63	0.49
90 °C	Sound	0.37	0.74	9.56
	Degraded	0.56	0.27	6.41

3.6. Effect of pore pressure

For constitutive modeling of oil cement paste, it is also important to investigate coupling between pore pressure and mechanical behavior. In Fig. 16, we compare the axial strains obtained from two triaxial compression tests with a confining pressure of 3 MPa: the first one performed on a saturated sample with constant pore pressure of 2.5 MPa and the second one on a saturated sample but without pore water pressure that can be generated for example by a pump ($P_i = 0$ MPa). The failure stress and elastic modulus decrease respectively by 28% and 56% between the first and second tests. This means that the mechanical behavior of cement paste depends not only on total stress but also on pore pressure; there is then poromechanical coupling in elastic and plastic behaviors. Another important point in these results is that the failure stress obtained in the second test (on the sample that is saturated but without pore water pressure) is higher than that expected (according to the theoretical failure surface) for a confining pressure of $P_c = 3$ MPa but rather close to that for $P_c = 4$ to 5 MPa corresponding to a failure strength of 40 MPa (see Fig. 13). This increase in mechanical strength can be explained by a relative drying of the sample [25,26,34,39] before being tested under 90 °C. Therefore, the mechanical behavior of oil cement paste is also dependent on water saturation degree.

To investigate more precisely the pore pressure effects on mechanical behavior, we present here the comparison between two other triaxial compression tests in Fig. 17. The first one is performed with confining pressure of $P_c = 10$ MPa and pore water pressure of

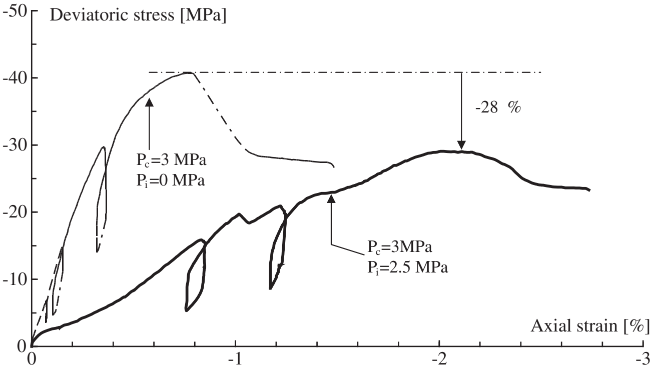

Fig. 16. Effect of interstitial pressure on elastic–plastic behavior (sound cement paste).

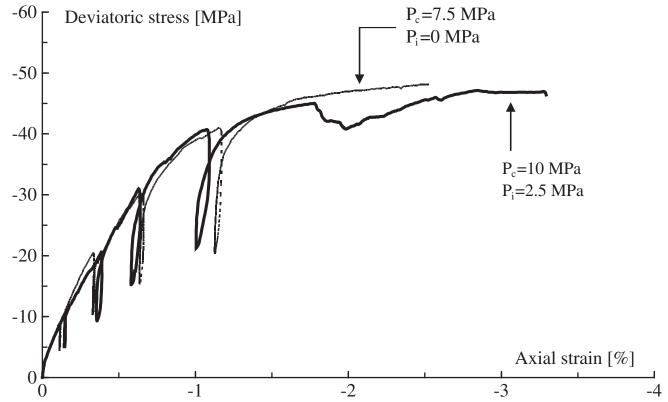

Fig. 17. Effect of interstitial pressure on elastic–plastic behavior (sound cement paste).

$P_i = 2.5$ MPa and the second one with $P_c = 7.5$ MPa and pore water pressure of $P_i = 0$ MPa. In other words, the two tests have the same value of effective confining pressure in the sense of Terzaghi effective stress [28]. We can see that at the first view there is no noticeable difference in mechanical behavior between the two tests. This means that the mechanical behavior of the sound oil cement paste seems to be controlled by the effective confining pressure in triaxial conditions. Finally, it is useful to point out that in this analysis, the sample in the second test is assumed fully saturated. If this is not the case, the mechanical behavior of oil cement paste would depend on saturation degree as mentioned above. Heukamp et al. [9] obtained the same result on the degraded cement paste by showing that Terzaghi effective stress controls the stress–strain behavior (during loading and at failure). The validity of the effective stress concept during the entire loading is attributed by the authors to the incompressibility of the solid matrix. In the case of a completely degraded material the solid phase compressibility can be neglected compared to the high compressibility of the degraded skeleton. In the case of the sound cement paste, the elastic strains should be governed by the Biot effective stress. Assuming that the elastic strains are very small, the test results mean that the solid matrix of the sound cement paste is plastically incompressible [40].

4. Conclusions

The purpose of the experimental study presented in this paper is to investigate influences of chemical degradation on the mechanical and poromechanical behavior of a standard oil cement paste. The chemical degradation process was accelerated by using an ammonium nitrate solution (NH_4NO_3). The degradation of the cement paste is mainly due to the dissolution of portlandite and the decalcification of CSH, leading to a significant increase of total porosity varying from 37% to 56%. A series of uniaxial and triaxial compression tests have been performed on the sound and fully degraded cement pastes. The basic mechanical behavior of the sound oil cement paste is characterized by a small elastic behavior phase and very large plastic deformation. Moreover, the material exhibits a strong capacity of compaction due to plastic collapse of pores. Like most frictional materials, the mechanical behavior of oil cement paste is also dependent on confining pressure. The chemical degradation strongly affects the mechanical properties of cement paste. The uniaxial compression strength is reduced by 61% varying from 29 MPa to 11.3 MPa. The cohesion and friction coefficient decrease by 33% and 63% respectively with the chemical degradation. Pre-confinement of the sample results in a stiffening effect and this is more significant for the degraded cement paste. In the same way, the chemical leaching is also responsible for degradation of the elastic properties. Moreover, the chemically leached cement paste exhibits a much more significant volumetric compaction due to pore collapse, observed by strain measurement and observation of the tested samples. A preliminary study showed also a strong sensitivity of the oil cement paste to water saturation degree and its mechanical behavior is controlled by the effective confining pressure.

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