

Influence of chemical degradation on the mechanical behaviour-permeability coupling of an oil well cement paste under temperature

I. Yurtdas

Laboratoire de Génie Civil, GRESPI EA4301, Université de Reims Champagne Ardenne, Rue des crayères, 51687 Reims Cedex, France

S. Xie, J. Secq, N. Burlion, J.F. Shao

Laboratoire de Mécanique de Lille, UMR CNRS 8107, Equipe Mécanique des Géomatériaux Cohérents, Polytech'Lille, Cité Scientifique, 59655 Villeneuve d'Ascq, France

F. Rodot

TOTAL Exploration Production, CSTJF, Avenue Larribau, 64018 Pau Cedex, France

ABSTRACT: In the oil field, cement pastes are used during drilling operations, plugging and/or abandonment of the wells. Therefore, the understanding of the implied phenomena is important from a point of view of durability. This paper deals with the hydraulic behaviour of an oil cement paste submitted to chemical degradation and mechanical loading, under temperature. The obtained results show that even if the porosity of degraded material is higher with regard to sound material, its permeability is lower due to compaction caused by hydrostatic confining pressure. The permeability of the degraded material becomes higher when there is no active confinement. Under creep with weak confining pressure (uncoupled chemo-mechanical test), the permeability of degraded material decreases contrary to sound material, because of the preponderance of the compaction effect with regard to the induced microcracking. Under simultaneous creep and chemical degradation (coupled chemo-mechanical test), the permeability increases due to the dissolved chemical products which leads to the creation of preferential ways for the fluid flow.

1 INTRODUCTION

In the field of nuclear installations, for the storage of radioactive waste, drilling of the oil wells or storage of acid gases in these wells, the knowledge of the hydro-mechanical behaviour of cement-based materials is of great interest. The present study is focused on the oil field where cement pastes are used during drilling operations, plugging and/or abandonment of the wells. These cement pastes could also be used for the re-injection and sequestration of acid residual gases such as CO₂ and H₂S. Therefore, after its set up, the material is subjected to mechanical loading, temperature increase and acid fluids leading to chemical degradation. The study of cement-based material degradation by natural process being very long, it is necessary to use an accelerated degradation process under controlled conditions, an artificial accelerated degradation by ammonium nitrate solution as fluid was selected in this study for acid degradation. Degradation by ammonium nitrate, regarded as the ultimate stage of an acid deterioration, is due mainly to the leaching of the calcium of the main hydration products, which are the portlandite

(Ca(OH)₂) and calcium silicate hydrates (CSH) (Adenot 1992, Carde et al. 1996, Gérard 1996, Torrenti et al. 1999, Le Bellégo et al. 2000, Heukamp et al. 2001, Heukamp et al. 2003, Burlion et al. 2006). The leaching of the first increases macro porosity while the leaching of the second increases micro porosity (Carde et al. 1996). The presence of the aggregates seems to play a great role in the leaching process (Nguyen et al. 2007).

After leaching the short term hydro-mechanical behaviour (multiaxial compression) of cementitious materials, studied in the literature until now at ambient temperature, is deteriorated: loss in strength (Heukamp et al. 2001, Heukamp et al. 2003, Nguyen et al. 2007, Agostini et al. 2007) and Young's modulus (Carde et al. 1996, Gérard 1996, Le Bellégo et al. 2000, Nguyen et al. 2007, Agostini et al. 2007), passage from fragile behaviour to ductile one (Carde et al. 1996, Nguyen et al. 2007, Agostini et al. 2007) or, amplification of material sensitivity with respect to the pore water pressure by the Skempton coefficient increase (Heukamp et al. 2001, Heukamp et al. 2003).

However, few studies only focused on the chemical degradation effect on the long-term behaviour

(creep). These studies, always carried out at ambient temperature, underline the importance of leaching on uncoupled (Bernard et al. 2003) and coupled (Torrenti et al. 2008, Xie et al. 2008) creep. It is obvious that leaching will also modify the transport properties of cement based-materials. For instance, the permeability to gas of mortar of construction increases by two orders with degradation at ambient temperature (Agostini et al. 2007). The permeability measured on samples subjected to creep coupled with chemical degradation decreases with the increase in deviatoric loading for the same confinement (Xie et al. 2008). In contrast, in an oil well, the temperature is much higher than the ambient temperature and will influence the microstructure evolution during the maturation phase of the paste. The aim of this study is then to study the hydraulic behaviour evolution of an oil cement paste at the sound state, chemically degraded state and during chemical degradation under mechanical loading and temperature. The evolution is considered at 90°C, because this temperature is characteristic of the conditions met in some oil reservoir. The use of ammonium nitrate solution accelerates 300 times the process of leaching compared to the pure water effect at ambient temperature (Heukamp et al. 2001). This kinetic factor is amplified by the increase in temperature (Torrenti et al. 1999). In this work, the results for the permeability evolution of hardened cement paste according to the chemical degradation state of material and mechanical loading types are presented and analyzed.

2 EXPERIMENTAL CAMPAIGN

2.1 Material used and conditioning of samples

The study is conducted on a classical oil cement paste with water by cement ratio $W/C=0.44$ (Yurtdas et al. 2006). A cement of class G and two additives, a dispersing agent and an anti-foamer agent, are used to cast the material.

The samples of dimension $\phi 37 \times 100 \text{ mm}^3$ are initially preserved during 3 days in their mould at a temperature of 100 °C. They are demoulded quickly and still preserved 4 days at 100°C then brought back gradually to 90°C (3°C/day). Afterward, they are preserved in the distilled water saturated with lime at 90°C to reach 1 month of maturation (Fig. 1). Notice that the manufacture conditions of the cement paste in laboratory, like its maturation without pressure, lead to a more important permeability than that met in the oil wells. After the maturation phase, the samples are separated, under temperature, in two series:

- the first series is placed in a neutral fluid (a synthetic fluid of similar composition to the interstitial fluid)

- the second series is subjected to chemical degradation with ammonium nitrate NH_4HNO_3 solution -6 mol/kH₂O- until obtaining complete degradation.

The principle of conditioning of the sound and degraded samples is shown on Figure 2. The samples are kept in an enclosure at $T=90 \text{ °C}$ and the pH is controlled by a probe. The solution is regularly renewed so as to keep as much as possible the same solution effect with respect to the cement paste. The samples of the second series are then placed in distilled water in order to rinse them before carrying out the mechanical tests. The rinsing operation helps to evacuate the disunited solid particles of the sample. In addition, the samples were always preserved under wet conditions in order to prevent the very expansive calcium nitro-aluminate precipitation leading to cracking (Adenot 1992).

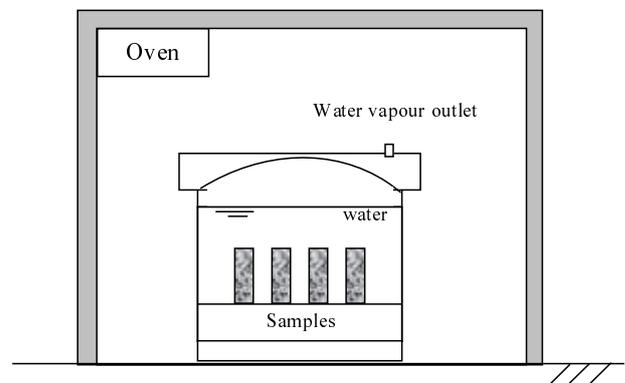


Figure 1. Storage of samples after casting under temperature.

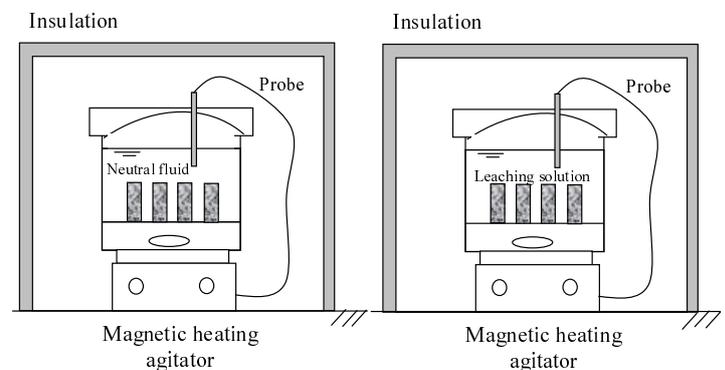


Figure 2. Conditioning of samples in neutral fluid and ammonium nitrate solution under temperature of 90 °C.

2.2 Experimental device and measurements performed

Permeability measurements of samples under controlled temperature are carried out after obtaining the homogeneous states for sound and completely degraded materials. The picture of Figure 3 shows the evolution of the front of leaching with time of a control sample broken in splitting. It is noted that the front of leaching, followed by the application of phenolphthalein, has reached until the core of the sample. The variation of mass during leaching and rinsing versus time are plotted in Figure 3. The mass

evolution of the three samples is similar and stabilizes at the end of approximately 40 days of leaching. Moreover, the rinsing by distilled water causes an additional loss in mass after leaching, due to the dissolved chemical products. However, this second loss is also stabilized quickly. Approximately 70 days were necessary for the process of leaching and rinsing. The tests are carried out on $37 \times 40 \text{ mm}^3$ cylindrical samples. These samples are obtained, under temperature, from the central part of the samples having initially a height of 100mm. These dimensions are selected so as to carry out the measurements in a reasonable time. Indeed, more the sample is long and more it takes time for the steady state establishment.

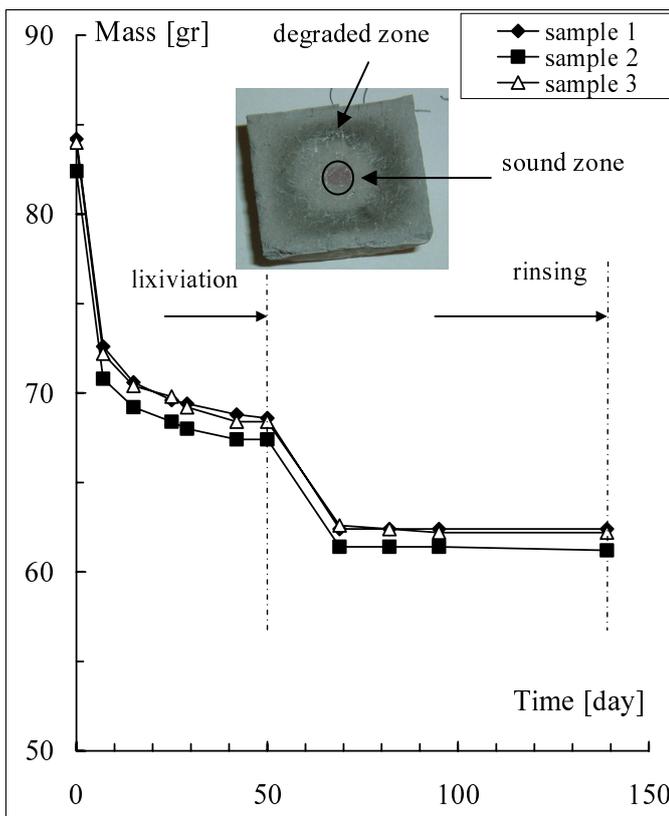


Figure 3. Variation of mass of three samples during lixiviation and rinsing process.

The following tests were carried out in order to understand the permeability evolution according to the material state and loading type:

- permeability measurements on the sound and degraded $37 \times 40 \text{ mm}^3$ cylindrical samples according to the confining pressure ($P_c = 3, 10$ and 20 MPa),
- permeability measurements on the sound, degraded and degrading $37 \times 40 \text{ mm}^3$ cylindrical samples under deviatoric creep with confining pressure of 3 MPa ,
- porosity measurement of the sound and degraded samples.

These tests are performed using an experimental device developed for the present study in the Labo-

ratory of Mechanics of Lille. This one is composed of an auto compensated autonomous triaxial cell, an oven, three pumps for the application of confining pressure, deviatoric stress and for the pore water injection, an overflow allowing to keep the intensity of the pore water pressure at the desired level and an acquisition system allowing in-situ measurements of the axial and radial strains. Figure 4 shows the simplified scheme and the boundary conditions for the permeability tests. Moreover, as the permeability value is influenced by hydrostatic confining pressure, a new device of permeability measurement is conceived in order to obtain the permeability value “without” confining effect. In this device, the sample is placed in cylindrical cell which has a diameter slightly higher than that of the sample. Then, the empty space between the sample and the cell is filled by an adhesive providing the lateral sealing. The effect of the confining pressure on the axial permeability was thus being avoided. It is worth mentioning that carrying out this type of test was particularly difficult. So the following measurement is made to complete permeability measurements:

- Permeability measurement on the sound and degraded $37 \times 40 \text{ mm}^3$ cylindrical samples “without” confining pressure.

The uncoupled creep tests are carried out with a compressive stress equal to 50% of the failure strength for a given confining pressure. However, at the end of the creep test, we increased the loading in order to get more information on the behaviour evolution. In the case of coupled tests, the deviatoric stress is equal to 50% of the failure strength of the sound material and not of the degraded material. In addition, during uncoupled creep tests, the permeability is always determined after deviatoric unloading, in the hydrostatic phase. In the case of coupled creep tests, the permeability is determined in the deviatoric phase.

The permeability is obtained by the application of the Darcy’s law which requires the establishment of the steady state. After the application of confining pressure, and with (coupled creep tests) or without (hydrostatic tests, uncoupled creep tests) deviatoric stress, the liquid is axially injected from bottom side under a constant pressure equal to 2.5 MPa . The pressure on upper side is equal to the atmospheric pressure P_{atm} (Fig. 4). The axial permeability is easily determined by measuring the flow rate at the exit of the sample.

$$K_i = \frac{\mu Q}{S} \frac{L}{(P_i - P_0)} \quad (1)$$

where K_i is the intrinsic permeability (independent of the injected fluid) [m^2] ($1 \text{ m}^2 = 10^{+12}$ darcy), μ is the dynamic viscosity of the injected fluid [$\text{Pa}\cdot\text{s}$], Q is the liquid flow [m^3/s], L is the length of the

sample [m], S is the cross section surface [m²]. P_i is the pressure of injection [MPa] while P_0 is the pressure of exit and equal to the atmospheric pressure.

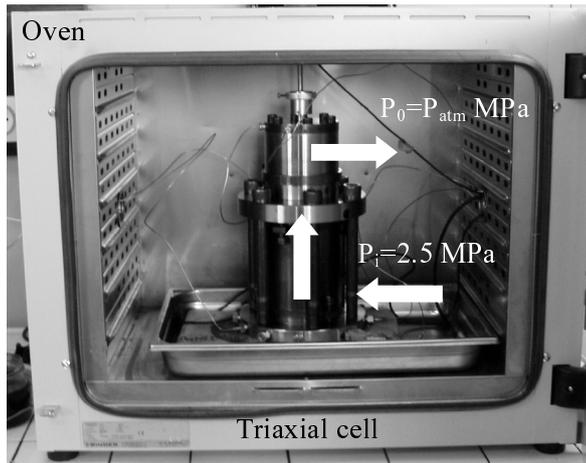


Figure 4. Experimental devices and limit conditions for permeability measurements.

Using this method, the permeability determined directly is considered as intrinsic if the injected fluid is neutral with respect to the cement paste. The fluids used for the measurement of the permeability are the same ones as those in which the samples are conditioned until the moment of tests, namely the neutral synthetic fluid (sound material) and distilled water (degraded material). The synthetic fluid with which the sound state is characterised will have no influence on the permeability value because of its neutral nature. On the other hand, with the use of distilled water the degraded samples are better rinsed before the permeability measurement. The influence of the precipitation of the particles on the permeability and mechanical test is thus minimised. Notice that it is well-known that some interactions exist between cementitious material and injected water and influence the measured permeability (Hooton 1989, Yurtdas et al. 2008). In contrast, in the present study, the influence of this water would be very weak due to the fact that the material is very strongly attacked by ammonium nitrate solution.

3 EXPERIMENTAL RESULTS

3.1 Permeability evolution with and without hydrostatic compression at 90°C

Table 1 gives porosity measurements obtained on the sound and completely degraded samples. The porosity is determined after oven drying at 105°C up to constant weight of the saturated samples (sound samples by neutral water and degraded samples by distilled water). The average material porosity increases from 37% to 56% after degradation (approximately an increase of 50%). The increase comes from principally Ca(OH)₂ decalcification lead-

ing to a macro porosity [4]. Therefore, the strength loss is principally due to portlandite leaching. In addition, the morphology of the CSH being modified by leaching, the ductility of material increases with degradation.

Table 1. Porosity of the sound and degraded materials.

Nb of sample State of material	1	2	Mean value
Sound Degraded	0.34	0.39	0.37
	0.56	0.56	0.56

Figure 5 shows the strains evolutions in the hydrostatic phase for the sound and degraded materials before permeability measurement. For the sound material, an initial tightening phase appears before the elastic phase. After chemical degradation, this elastic behaviour becomes elastoplastic as soon as the confining pressure is equal to 3 MPa. There is also a slight dispersion of the sound material results, due to the variability of cementitious materials. This variability seems to vanish after chemical degradation. It is interesting to observe an important deformation of samples after degradation, especially at high confinement.

Figure 6 shows the permeability evolution of the sound and degraded material versus confining pressure. The initial permeability values are related to the preparation conditions in laboratory and to the maturation without pressure of the paste. We are interested here mainly in the permeability evolution. The permeability is always measured in the hydrostatic phase. This figure shows that the permeability decreases about 70-80% for two materials with confinement. A similar decrease is also observed with the degradation of material whatever the applied confinement (whereas this degradation considerably increases the porosity). The decrease in permeability with confinement is due to the reduction of the space for the fluid flow and perhaps also to the reduction of the interconnection degree of the porous network. The decrease in the permeability of degraded material compared to sound material comes from the fact that the first contracts more at equal confining pressure. Moreover, if there is no active lateral confining, the axial permeability of degraded material will be higher than that of non degraded material. This was confirmed by the results obtained without confining pressure application: the permeability was $2.0 \times 10^{-17} \text{ m}^2$ and $4.8 \times 10^{-17} \text{ m}^2$ respectively for the sound and degraded material. Therefore, the permeability of the degraded material is 2.4 times higher than that of the sound material.

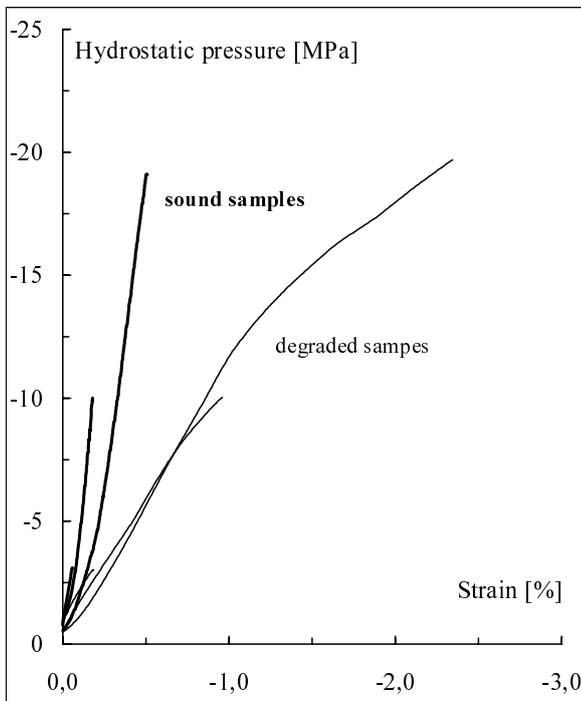


Figure 5. Strains evolution evolution of the sound and degraded samples under 3, 10 and 20 MPa of confining pressure.

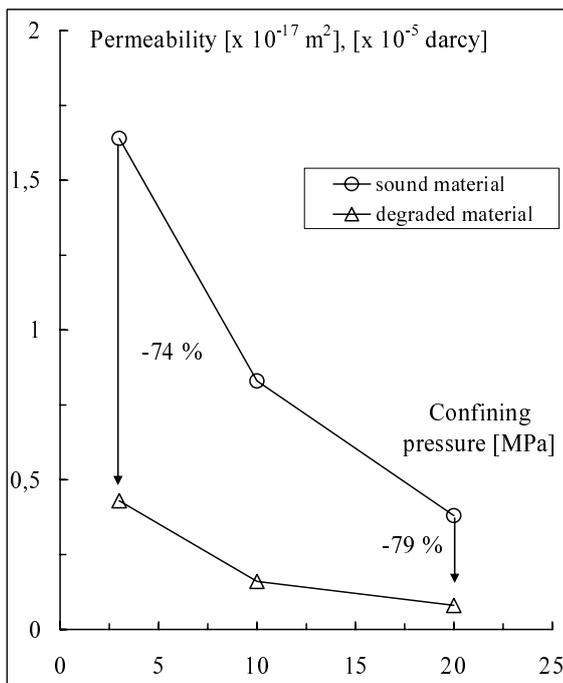


Figure 6. Evolution of the permeability versus confining pressure for the sound and degraded materials.

3.2 Permeability evolution under deviatoric creep with $P_c=3$ MPa at 90°C

3.2.1 Case of uncoupled creep

Figure 7 shows the permeability evolution of a sound sample during a deviatoric creep test with confining pressure $P_c = 3$ MPa. This creep tests is carried out with a deviatoric stress equal to 14.6 MPa corresponding to 50% of the failure strength of a similar sample under identical confining pressure.

During a creep test, when the applied stress leads to reach the failure of the sample, the curve of creep shows three distinct phases according to time: a first phase where the velocity of strain decreases and tends towards a stabilization (primary creep), a second phase characterized by a constant velocity (secondary creep), and finally, a third phase for which the velocity increases very quickly and the sample is broken (tertiary creep). For the sample studied here, only the first two phases of creep could be observed after the application of a stress equal to 50% of deviatoric strength. Even after the application of deviatoric stress equal to 80% of the failure strength, the passage to the third phase of creep does not appear. Thereafter, the sample is broken by stress increase. Notice that the failure strength of the sample shown on Figure 7 is higher of 21% than that of a sample which is not submitted to creep. This amplification of strength can be explained by a progressive compaction of the sample during creep. However, a regular increase in the permeability is observed: its value, initially equal to $0.7 \times 10^{-17} \text{ m}^2$ ($= 0.7 \times 10^{-5}$ darcy), reached $4.8 \times 10^{-17} \text{ m}^2$ ($= 4.8 \times 10^{-5}$ darcy) after the end of 80% loading application. This increase can be explained by the creation of new microscopic cracks, which would also favor the connection of the initial porous network. Thus, there is a deterioration of material by induced microcracking.

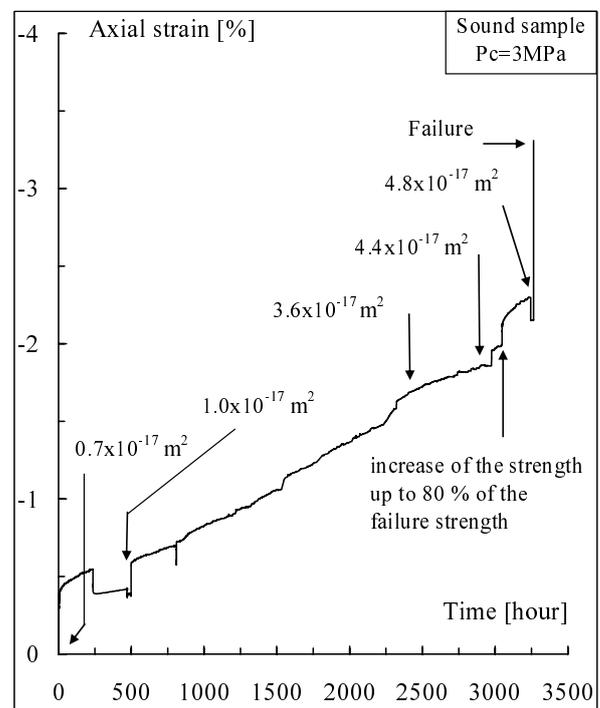


Figure 7. Evolution of the permeability of a sound sample versus time under deviatoric creep at $P_c=3$ MPa.

Figure 8 illustrates the permeability evolution of a completely degraded sample. Like the sound sample, it is initially loaded with a constant deviatoric stress equal to 50% of the failure strength, that is to say 7.5 MPa with $P_c = 3$ MPa. Then, as the strains of

creep tended towards an asymptote, the pressure applied was increased up to 80% of the breaking strength. This last increase led the sample to the failure. There is a stiffening of material during loading, due to compaction. The fluid flow becomes difficult through the porous network.

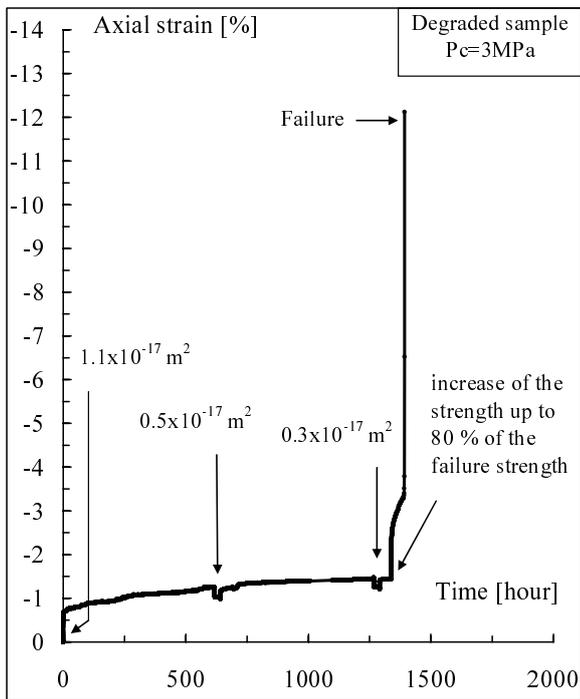


Figure 8. Evolution of the permeability of a degraded sample versus time under deviatoric creep at $P_c=3$ MPa.

3.2.2 Case of coupled creep

A coupled creep test is carried out in a different way compared to an uncoupled creep test: after the set up of the sample in the triaxial cell, the permeability to the neutral fluid is measured after the application of the hydrostatic pressure. Then, the deviatoric stress of creep is applied and the ammonium nitrate solution is injected continuously into the sample. As it was indicated previously, the deviatoric stress is equal to 50% of the failure strength of sound material. However, the failure strength of the sound material will approach progressively to that of degraded material during the action of the chemical solution. In other words, with degradation, the stress applied will not be any more equal to 50% of strength, but will tend towards a higher % of failure strength.

The permeability is measured continuously, without deviatoric unloading, and with ammonium nitrate solution. It is clear that the permeability thus measured is not intrinsic being given the interaction between the interstitial fluid and material, but it is characteristic of the evolution of the microstructure according to time. Figure 9 shows the permeability evolution versus time during a coupled creep test with $P_c = 3$ MPa. The coupled test makes it possible to study the material evolution from sound state to degraded one. Figure 9 shows that the sample breaks after only approximately 22 hours under the influ-

ence of the chemical degradation by the acid fluid percolation. This result shows a strong coupling between creep and chemical degradation, which is also observed on a concrete sample of construction cured and tested at ambient temperature under uniaxial creep (Torrenti et al. 2008). However, the strains evolve much slower during their test. This comes mainly from the fact that our samples are very porous in sound state due to the maturation and conservation under the temperature of 90 °C. There is also an acceleration effect of the degradation process under high temperature during the test.

As the failure strength of the sample, loaded with 50% of the failure strength of sound material, approaches progressively to that of a degraded sample during degradation, it is normal that the sample breaks under creep loading. A second test carried out showed a similar tendency to the first test. Figure 9 shows that after the ammonium nitrate solution injection the permeability first decreases very slowly (from $0.73 \times 10^{-17} \text{ m}^2$ to $0.72 \times 10^{-17} \text{ m}^2$) certainly due to the deviatoric loading application. Afterward, it increases when the ammonium nitrate solution effect begins to be important leading to progressive decalcification of the cement paste. This permeability evolution remains weak in the absolute, because a part of the porosity increase due to the action of ammonium nitrate is compensated by the progressive compaction of material.

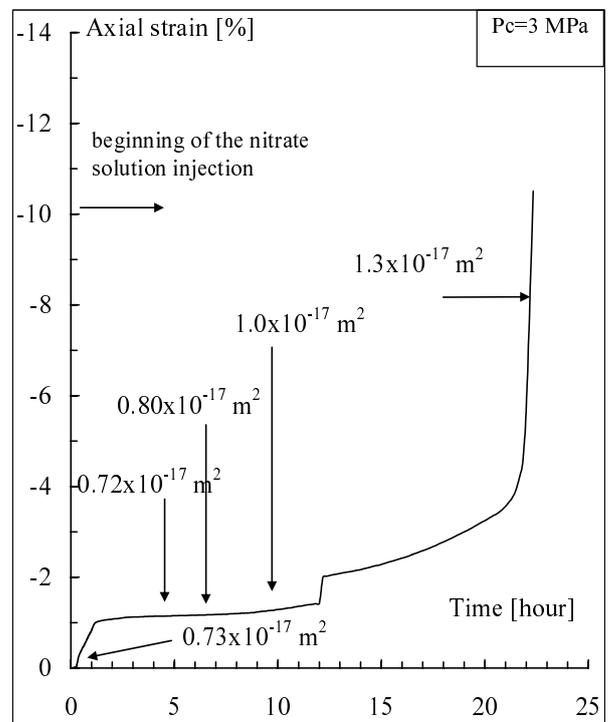


Figure 9. Evolution of the permeability of the first sound sample versus time under deviatoric creep at $P_c=3$ MPa and chemical degradation.

After carrying out each test, the tested sample is divided into two or several pieces by splitting under a very weak load, and then impregnated of phenol-

phthalein, in order to understand the way in which the flow of ammonium nitrate circulates through the sample. The phenolphthalein remains colourless on the degraded part, and becomes pink on the sound part of the sample. The examination of the sample put in light the creation of the preferential ways of flow through the sample, at least for 3 MPa confining pressure.

4 CONCLUSIONS

The objective of this work was to highlight the permeability evolution of an oil cement paste under thermo-hydro-mechanical loading coupled to chemical degradation. Thus, the permeability decreases with the increase in the confining pressure, for the sound or completely degraded cement paste. Moreover, it is observed that the permeability is lower for degraded material, whatever the confinement. The decrease in the permeability with confining pressure is due to the reduction of the fluid flow space and the interconnection degree of the porous network, by compaction. Chemical degradation leads to decalcification of the solid matrix, which becomes contracting under triaxial compression. However, as expected, the measurement of the permeability without active confinement showed that the permeability of the degraded material is higher.

Permeability measurements during uncoupled creep tests reveal also interesting phenomena. For a confinement of 3 MPa, the permeability, measured at various time, increases for sound material, due to induced microcracking and its propagation. However, it decreases for degraded material because of dominating effect of the compaction with regard to induced microcracking.

In the case of coupled (chemo-mechanical) creep tests, for a confinement of 3 MPa, the permeability increases showing a strong coupling between creep and chemical degradation. This increase is explained by the dissolved products and the creation of porosity due to the chemical attack.

ACKNOWLEDGEMENTS

The present study is part of a global project of Control of Residual Gases that TOTAL SA carries out in its fight against the climatic warming. The authors gratefully acknowledge TOTAL EP to have entrusted this study to the Mécanique des Géomatériaux Cohérents team of the Laboratory of Mechanics of Lille, as well as the permission to publish these results.

REFERENCES

- Adenot, F. 1992. *Durabilité du béton : caractérisation et modélisation des processus physiques et chimiques de dégradation du ciment*. Orléans: Thèse de doctorat de l'Université d'Orléans (In French).
- Agostini, F., Lafhaj, Z., Skoczylas, F., Loodsveldt, H. 2007. Experimental study of accelerated leaching on hollow cylinders of mortar. *Cement and Concrete Composites* 37: 71-78.
- Bernard, O., Ulm, F.-J., Germaine, J.T. 2003. Volume and deviator creep of calcium-leached cement-based materials. *Cement and Concrete Research* 33: 1127-1136.
- Burlion N., Bernard D., Chen D. 2005. X-ray microtomography: application to microstructure analysis of cementitious material during leaching process. *Cement and Concrete Research* 36: 346-357.
- Carde, C., François, R., Torrenti, J. -M. 1996. Leaching of both calcium hydroxide and C-S-H from cement paste : modelling the mechanical behavior. *Cement and Concrete Research* 26: 1257-1268.
- Gérard, B. 1996. *Contribution des couplages mécanique - chimie- transfert dans la tenue à long terme des ouvrages de stockage de déchets radioactifs*. Cachan : Thèse de doctorat de l'ENS de Cachan et de l'Université Laval (in French)
- Heukamp F.H., Ulm F.-J., Germaine J.T. 2001. Mechanical properties of calcium-leached cement pastes: Triaxial stress states and the influence of the pore pressure. *Cement and Concrete Research* 31, 767-774.
- Heukamp F.H., Ulm F.-J., Germaine J. T. 2003. Poroplastic properties of calcium-leached cement -based materials. *Cement and Concrete Research* 33, 1155-1173.
- Hooton, R.D. 1989. What is needed in a permeability test for evaluation of concrete quality. *Mat. Res. Soc. Symp. Proc.*, 137: 141-149.
- Le Bellégo C., Gérard B., Pijaudier-Cabot G. 2000. Chemo-mechanical effects in mortar beams subjected to water hydrolysis. *Journal of Engineering Mechanics* 126: 266-272.
- Nguyen, V.H., Colina, H., Torrenti, J.-M., Boulay, C., Nedjar B. 2007. Chemo-mechanical coupling behaviour of leached concrete Part I: Experimental results. *Nuclear Engineering and Design* 237: 2083-2089.
- Torrenti, J.-M., Didry, O., Ollivier, J. -P., Plas, F. 1999. *La dégradation des bétons : couplage fissuration-dégradation chimique*. Paris: Hermès (in French).
- Torrenti, J.-M., Nguyen, V.-H., Colina, H., Le Maou, F., Benboudjema F., Deleruyelle, F. 2008. Coupling between leaching and creep of concrete. *Cement and Concrete Research* 38: 816-821.
- Xie, S.Y., Shao, J.F., Burlion, N. 2008. Experimental study of mechanical behaviour of cement paste under compressive stress and chemical degradation. *Cement and Concrete Research* 38: 1416-1423.
- Yurtdas, I., Xie, S., Secq, J., Burlion, N., Shao, J.-F., Sibai, M. 2006. *Etude expérimentale du couplage entre le comportement thermo-hydro-mécanique et la dégradation chimique d'une pâte de ciment pétrolier*, Lille: Rapport final, étude n°LML-MGC-03-03/A Total-LML phase 1 (in French).
- Yurtdas, I., Burlion, N., Skoczylas, F. 2008. Comportement différé des mortiers soumis au séchage et effet induit sur la perméabilité. *European Journal of Environmental and Civil Engineering* 12: 701-721 (in French).