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

I. Yurtdas [a,b], S.Y. Xie [b], N. Burlion [b], J.F. Shao [b,*], J. Saint-Marc [c], A. Garnier [c]

[a] LGC, GRESPI EA4301, Reims, France
[b] LML, UMR8107 CNRS, Villeneuve d'Ascq, France
[c] CST, TOTAL, Pau, France

## ARTICLE INFO

## 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.

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## 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

* Corresponding author.
E-mail address: jian-fu.shao@polytech-lille.fr (J.F. Shao).

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 |