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THERMAL PRESSURIZATION AND ANOMALOUS THERMAL EXPANSION OF THE PORE FLUID OF A HARDENED CEMENT PASTE

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ABSTRACT. Temperature increase in a fluid-saturated porous material in undrained condition leads to pore pressure increase. This phenomenon of thermal pressurization is studied experimentally for a saturated hardened cement paste. The measured value of the thermal pressurization coefficient is found equal to 0.6MPa/°C. The experimental observation that this coefficient does not change with temperature between 20°C and 55°C is attributed to the anomalous thermal behaviour of cement paste pore fluid. It is shown that the thermal expansion of the cement paste pore fluid is higher than the one of pure bulk water and is much less sensitive to temperature changes. This anomalous thermal behaviour is due to the confinement of the pore fluid in the very small pores of the microstructure of the cement paste, and also to the presence of dissolved ions in the pore fluid.

1. Introduction

Temperature increase in saturated porous materials in undrained condition leads to volume change and pore fluid pressure increase. This thermal pressurization of the pore fluid is due to the discrepancy between the thermal expansion coefficients of the pore fluid and of the pore volume. This increase of the pore fluid pressure induces a reduction of the effective mean stress, and can lead to shear failure or hydraulic fracturing. This phenomenon is important in petroleum engineering where the reservoir rock and the well cement lining undergo sudden temperature changes. This phenomenon is also important in environmental engineering for radioactive (exothermal) waste disposal in deep clay geological formations as well as in geophysics in the studies of rapid fault slip events when shear heating tends to increase the pore pressure and to decrease the effective compressive stress and the shearing resistance of the fault material (Sulem *et al*. 2007). The values of the thermal pressurization coefficient, defined as the pore pressure increase due to a unit temperature increase in undrained condition, is largely dependent upon the nature of the material, the state of stress, the range of temperature change, the induced damage. The large variability of the thermal pressurization coefficient reported in the literature for different porous materials with values from 0.01MPa/°C to 1.5MPa/°C (see Ghabezloo and Sulem (2008) for a review) highlights the necessity of laboratory studies.

It is known that the thermal expansion of water, when confined in vey small pores of nanometre size, is higher than that of bulk water. This phenomenon is showed experimentally by Derjaguin *et al*. (1986) who studied the thermal expansion of water in nanopores of silica gel (5nm) and observed that it is anomalously higher than that of bulk water. Their results also show that the rate of increase of the thermal expansion of confined water with temperature is smaller than the one of bulk water. The ratio of the thermal expansion of confined water to that of bulk water decreases with temperature and for temperatures higher than 70°C no more difference is observed between the thermal expansion coefficients. Xu *et al*. (2004) also studied the thermal expansion and viscosity of water and salt solutions in porous silica glasses with two different pore sizes and found that the thermal expansion of water in smaller pores (5.0nm) is higher than that in larger pores (7.4nm).

The aim of this paper is to study the phenomenon of thermal pressurization for a fluid-saturated hardened cement paste. An experimental program of drained and undrained heating tests is performed and the tests results are critically discussed. The anomalous thermal behaviour of cement paste pore fluid is back analysed from the results of the undrained heating test.

2. Theoretical background

A complete derivation of the equations of thermo-poro-elasticity for a saturated porous material and also an extension to account for the effect of non-elastic strains is presented in Ghabezloo *et al*. (2008b). The variation of the pore pressure in undrained condition is given by equation (1) as a function of the variations of the total stress σ, the temperature T and the non-elastic strains ε^{ne}:

$$dp_f = Bd\sigma + \Lambda dT + \frac{d\varepsilon^{ne}}{\left(c_d - c_s\right) + \phi\left(c_f - c_\phi\right)}$$

(1)

where B is the Skempton coefficient and Λ is the thermal pressurization coefficient given by:

$$\Lambda = \frac{\partial p_f}{\partial T} = \frac{\phi\left(\alpha_f - \alpha_\phi\right)}{\left(c_d - c_s\right) + \phi\left(c_f - c_\phi\right)}$$

(2)

c_d is the drained bulk compressibility, c_s is the unjacketed compressibility, c_ϕ is the pore volume compressibility for unjacketed loading condition and c_f is the pore fluid compressibility. α_f and α_ϕ are the thermal expansion coefficients of the pore fluid and pore volume respectively and ϕ is the porosity. The non-elastic strain ε^{ne} can be plastic, viscoelastic or viscoplastic.

3. Experimental program

In order to evaluate the effect of temperature on the behaviour of hardened cement paste, drained and undrained heating tests are performed and presented in the following. The cement paste was prepared using a class G oil well cement with a water to cement ratio w/c=0.44 and was cured for at least 3 months at 90°C in a fluid which is neutral with respect to the cement pore fluid. More details about the preparation procedure are presented in Ghabezloo *et al*. (2008a). The total porosity of the samples is measured by oven drying at 105°C equal to 0.35. As discussed in Ghabezloo *et al*. (2008a,b) this porosity should not be used in poromechanical calculations because it includes a part of the interlayer porosity of the cement paste. The porosity which should be used in the calculations is the free water porosity. The mercury porosity is measured equal to 0.26 and will be used as an approximation of the free-water porosity of the studied cement paste. The drained and undrained heating tests are performed in a triaxial cell, which is equipped with a heating system that can apply a temperature change with a given rate and regulate the temperature. The details of the triaxial system are presented in Ghabezloo and Sulem (2008).

4. Test results

A drained heating test was carried out under a constant confining pressure of 1.5MPa and a constant back fluid pressure of 1.0MPa. During the test, the temperature was increased from 18°C to 87°C at a rate of 0.08°C/min and the drained thermal expansion coefficient was evaluated as the slope of the temperature-volumetric strain response, equal to $6\times10^{-5}(°C)^{-1}$.

The phenomenon of thermal pressurization was studied in an undrained heating test under a constant isotropic stress equal to 19MPa. After the saturation phase, the confining pressure was increased up to 19MPa in drained condition at a rate of 0.025MPa/min. Then, the temperature was increased at a rate of 0.1°C/min and the pore pressure change was monitored during the test. As in a triaxial device the pore pressure cannot exceed the confining pressure, the heating phase was stopped when the pore pressure reached the confining pressure and the temperature was then decreased. The test results are shown on Figures (1) and (2) where the measured pore pressure and volumetric strain are plotted versus the temperature change. As seen in Figure (1), the pore pressure increases and then decreases almost linearly with temperature during the heating and cooling phases. For a pore pressure close to the confining pressure, the pressurization curve becomes almost horizontal. This phenomenon is due to the leakage of pore fluid between the sample and the rubber membrane when the difference between the confining pressure and the pore pressure is too small. Similarly, the pore pressure reduction is delayed at the beginning of the cooling phase. The measured volumetric strains, presented in Figure (2), show the expansion and the contraction of the sample during the heating and cooling phases respectively. The undrained thermal expansion coefficients for the heating and cooling phases are found respectively equal to $9.6\times10^{-5}(°C)^{-1}$ and $1.2\times10^{-4}(°C)^{-1}$. As expected, these values are greater than the measured drained thermal expansion coefficient.

The measured pore pressure in the undrained heating test should be corrected for the effect of the dead volume of the drainage system of the triaxial cell, as presented by Ghabezloo and Sulem (2008). This correction was performed here and the thermal pressurization coefficients for heating and cooling phases are measured respectively equal to 0.62MPa/°C and 0.57MPa/°C.
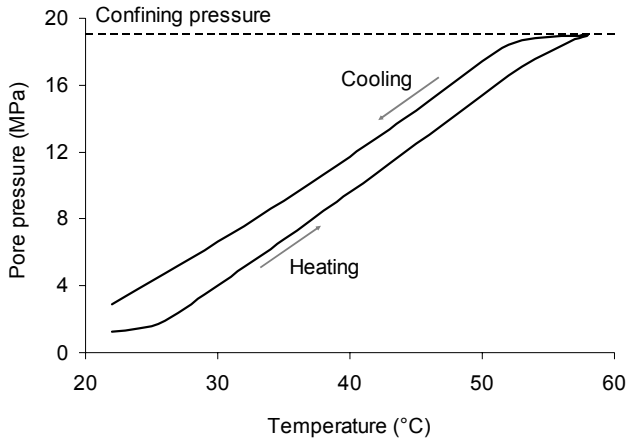
Figure 1. Undrained heating test, temperature-pore pressure response.
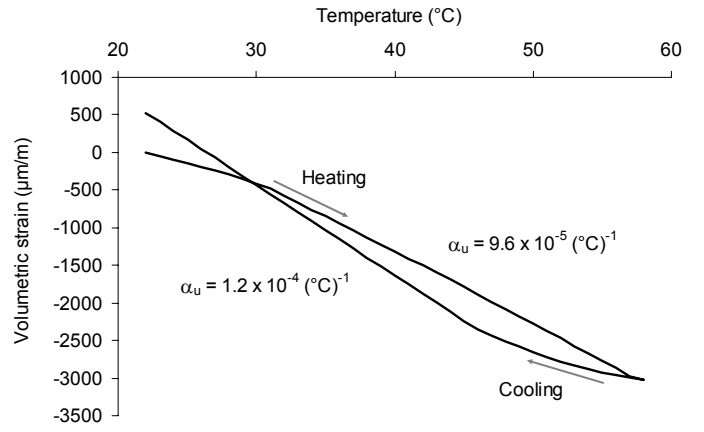

Figure 2. Undrained heating test, temperature-volumetric strain response.

5. Discussion of the results

In the above experimental results, it is observed that the thermal pressurization curve during heating and cooling is almost a straight line so that the thermal pressurization coefficient of the hardened cement paste can be considered as constant, equal to 0.6MPa/°C. It has been checked that this value is retrieved when the test is repeated. From equation (2) we can see that the thermal pressurization coefficient Λ depends on the physical properties of water and on the thermal and mechanical properties of the porous material considered. Stress and temperature dependency of these parameters can thus lead to a variation of the thermal pressurization coefficient with the temperature and the level of stress. This temperature and stress dependency of the thermal pressurization phenomenon is showed experimentally for a granular rock by Ghabezloo and Sulem (2008). The thermal expansion coefficient of water varies significantly with temperature. The experimental study of Ghabezloo (2008) and Ghabezloo et al. (2008a) has shown the stress and temperature dependent character of the mechanical properties of the hardened cement paste. Then one can ask the question why is it found that the thermal pressurization coefficient is constant during the undrained heating test?

One possible explanation can be found in the anomalies of the thermal expansion of cement paste pore fluid, as presented by Valenza and Scherer (2005). They evaluated the permeability of the hardened cement paste using two different methods: thermopermeametry and beam bending. According to these authors, the comparison of the measurements using these methods showed that to bring the two measurements into agreement, the pore fluid in the fine pores of the hardened cement paste should have a thermal expansion coefficient about one and a half times larger than the one of the bulk liquid. The possible effect of the anomalies of thermal expansion of cement paste pore fluid on our test results can be investigated in a back-analysis of the performed undrained heating test. In this test the confining pressure remains constant, $d\sigma=0$, so that $d\sigma_d=-dp_f$. The back analysis can be done using the following equation from the theory of poroelasticity:

$$\alpha_f dT = \alpha_\phi dT - \frac{1}{\phi}\left(d\varepsilon + \alpha_d dT\right) + dp_f\left(c_f - c_\phi\right) \tag{3}$$

The analysis is done here for the cooling phase where the creep effects are of less importance. Based on the results of Ghabezloo et al. (2008a) we take c_ϕ=0.06GPa^{-1}. We take also $\alpha_d=\alpha_\phi$=6×10^{-5}(°C)$^{-1}$ and ϕ=0.26. The result of the back analysis is shown in Figure (3) along with the evolution of the thermal expansion coefficients of pure bulk water and of 0.5mol/l NaOH bulk solution. We observe that the thermal expansion of cement pore fluid is larger than the one of pure bulk water which is compatible with the results of Valenza and Scherer (2005). We also observe that the rate of increase of the thermal expansion of cement pore fluid with temperature is lower than the one of pure bulk water. This is compatible with the experimental results of Derjaguin et al. (1986) and Xu et al. (2004) as mentioned in the introduction. On the other hand, this lower rate of increase with temperature is probably also due to the presence of dissolved ions in cement pore fluid. It is well-known that the presence of ions in water can influence its thermal expansion. Comparing the thermal expansion of pure bulk water with the one of 0.5mol/l NaOH bulk solution, we can see that the presence of ions increases the thermal expansion coefficient and decreases its rate of change with temperature. Assuming that the thermal expansion of the cement pore fluid in bulk condition is equal to the one of 0.5mol/l NaOH bulk solution, we can evaluate the effect of the anomaly of pore fluid thermal expansion as the ratio between the thermal

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expansion of the (confined) pore fluid and the one of the bulk fluid. This ratio reflects the effect of cement pore structure on the thermal expansion of pore fluid and is almost independent of presence of dissolved ions. This is presented in Figure (4) where a good accordance with the experimental results of Xu *et al.* (2004) is observed. This clearly shows the effect of cement pore structure on the anomaly of the thermal behaviour of the cement paste pore fluid.
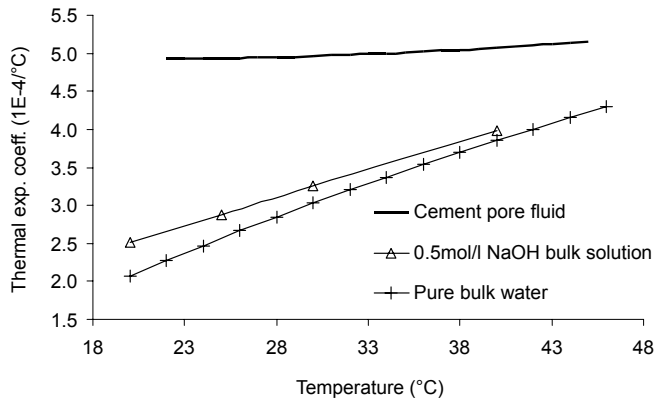

Figure 3. Evaluated thermal expansion coefficient of cement pore fluid compared with the thermal expansion of pure water, and of 0.5 mol/l NaOH solution.
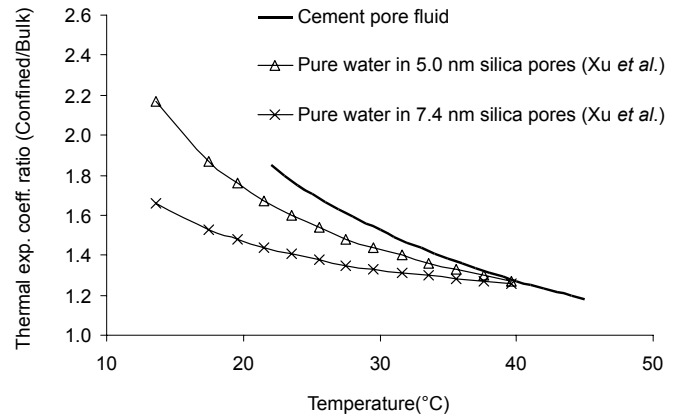

Figure 4. Anomaly of the thermal expansion of cement pore fluid compared with pure water confined in silica pores of different size.

6. Conclusions

The effect of undrained heating on induced pore fluid pressurization and volumetric change is studied experimentally for a fluid-saturated hardened class G cement paste which is prepared with w/c=0.44 and hydrated at 90°C. The thermal pressurization coefficient of the studied cement paste is measured equal to 0.6MPa/°C and is constant between 20°C and 55°C. It could be expected that this coefficient varies with temperature due to the variations of the thermal expansion of water with temperature. The back analysis of the results showed that this phenomenon may be attributed to the anomalies of the thermal expansion of cement paste pore fluid. The evaluated thermal expansion coefficient of cement pore fluid is larger than the one of pure bulk water and its rate of increase with temperature is smaller. These anomalies are mainly due to the thermal behavior of water when confined in small pores and also to the presence of dissolved ions in the cement paste pore fluid.

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