Gas relative permeability of High-performance concrete: effect of water saturation under phase desorption and sorption

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ABSTRACT:
This experimental work investigates the hydraulic behavior of two different high-performance concretes (called CEMI and CEMV), in order to improve the understanding of the effect of water saturation on relative permeability, during sorption and desorption phases.

Each material is put more than 500 days over water or saline solution in order to change its saturation. Nine samples, for each concrete, are tested from saturated to dry state after stabilization in hermetic chambers at different fixed relative humidity: 98, 92, 85, 75, 70, 59, 43, and 11%. An additional sample is tested after drying at 65°C, which is considered as the reference state for gas permeability measurements. The Pulse-Test method, with a static gas pressure of 2MPa and an overpressure of pulse of 0,5MPa, is used to measure effective gas permeability.

Firstly, gas permeability is measured during desorption phase, for each RH, after mass stabilization. Secondly, all samples are dried in an oven at 65°C, and then intrinsic gas permeability is measured. Finally, each sample is put for a second time in the same hermetic chamber in order to be re-saturated at the same RH: it is the sorption phase. For this phase, three tests are done for each sample at three different times. These tests show a hysteretic phenomenon during the concrete imbibition phase. The amplitude of hysteresis decreases with time. Besides, both concrete have very close intrinsic gas permeability, but significantly different effective and relative gas permeability. All the results mean that gas permeability mainly depends on saturation state, whatever the path of saturation, except for the CEM I at the end of the re-saturation process.

1 INTRODUCTION

Concretes have been selected by ANDRA to design the nuclear waste storage. They could be used for tunnels intended for the manufactured barrier system. One of these concrete will be used in storage structures built into an argillite layer at 500m depth. A laboratory has been installed into the same layer, which is designed to study in field and to evaluate the feasibility and safeness for million years. In storage situation, the concrete will be subjected to different stresses (thermic, hydric, mechanical and chemical). During the early stage, the processes associated with the desaturation / resaturation materials, will affect the mechanical behaviour of storage. The process of construction underground will lead to a hydraulic upload in the geology.
layer. After that, the structure is characterized by a period of resaturation, in which the water contained in the layer will flow towards the engineering barrier. These processes will influence the behavior of concrete storage site and will last a period ranging from several thousand to ten thousands years. Hence, studying gas transport through saturated or partially saturated concretes appears to be of crucial interest as there is a lack of data necessary to the numerous numerical modelling which are currently performed to simulate the behaviour of the storage structure. The first objective is the identification of the real relative gas permeability curves for both concretes. The second objective is to evaluate the effect of different water saturations obtained under desorption or sorption. As it is well known, there is generally a strong hysteretic effect on the saturation state depending on whether it is drying or imbibition. Espinosa (2006); Baroghel-Bouny (2007)

2 EXPERIMENTAL METHODE

2.1 Material and sample preparation

Both studied concretes are used by ANDRA to study the feasibility of radioactive waste storage in deep geological formation; their formulation is presented in Table 1. The main difference between the ANDRA concretes is the nature of the cement (CPA-CEM I 52.5 PM ES CP2 and Cement CEM V/A 42.5). Cement CEM I is made of pure Portland clinker, and CEM V/A is constituted of 60% of clinker in mass, 22% of blast-furnace slag, 14% of fly ash and 4% of setting regulator, according to NF EN 196-4 European Standard. (Andra (2001A), and Andra (2001B)). Blast furnace slag and fly ash are pozzolanic additives. Different formulations will lead to different microstructures. Concrete CEM I has a water-to-cement ratio equal to 0.43 whereas CEM V ratio 0.39. Large concrete beams are made and kept in lime-saturated water at a constant temperature of 20°C during six months before use. Concrete samples are cylinders of 37 mm diameter and 30 mm height. They are cored from the same beams after 28 days and rectified to obtain a well adopted geometry of their end surfaces.

Table 1 Composition of concretes

<table>
<thead>
<tr>
<th></th>
<th>CEMI 52.5R</th>
<th>CEM V/A 42.5N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>400</td>
<td>450</td>
</tr>
<tr>
<td>Sand [Limestone 0-4mm]</td>
<td>858</td>
<td>800</td>
</tr>
<tr>
<td>Gravels [Limestone 5-12mm]</td>
<td>945</td>
<td>984</td>
</tr>
<tr>
<td>Superplasticizer [Glenium 27]</td>
<td>10</td>
<td>11.5</td>
</tr>
<tr>
<td>Water</td>
<td>171</td>
<td>176.3</td>
</tr>
<tr>
<td>W/C</td>
<td>0.43</td>
<td>0.39</td>
</tr>
</tbody>
</table>

To obtain partially-saturated samples from an initial fully water-saturated state, saturated saline solution were used. Samples are put in a hermetic vacuum bell jar above saturated solution, until mass stabilization at 22°C (S. Poyet, (2009); Baroghel-Bouny and al (1999)). Relative humidity depends on the used salt. Eight levels of relative humidity: 98, 92, 85, 75, 70, 59, 43 and 11% have been chosen to get desorption and sorption isotherms. Reference dry state is taken after oven-heating at 65°C until constant mass.

2.2 Gas permeability measurement

The technique used was a pulse-test method which is quite usual in our laboratory. The test apparatus is shown in figure 1. The device comprises a triaxial pressure cell, a Gilson pump, a gas injection circuit comprising, an argon supply reservoir, two surge reservoirs R1 and R2, a
For measuring the pressure, a transmitter and a differential pressure indicator for measuring the difference pressure between both sides of the samples. The sample is placed inside the cell and initially subjected to a hydrostatic stress, i.e. a confining pressure $P_c$ (5MPa). A static gas pressure $P_s$ is applied on its upper and lower surfaces, in order to have a uniform pore pressure within the sample, and then an overpressure $\Delta P$, 0.5MPa is applied on one of the sides. Recording the dissipation of overpressure according to time by the help a differential pressure sensor finally leads to permeability.

![Diagram showing experiment and equipment.](image)

The evolution of the differential pressure according to time $\Delta P(t)$ is defined by a simplified exponential expression:

$$P_1(t) - P_2(t) = \Delta P(t) = \Delta P_0 e^{-ct}$$

(1)

With $c$ is defined by:

$$c = \frac{K_{eff} (S_w) A}{\mu h} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) P_f$$

(2)

$V_1$ and $V_2$ are the volume of the reservoir ($V_1=V_2=0.4L$), $A$ is the sample cross section, $h$ is the sample length, $\mu$ is the gas viscosity ($2.2 \times 10^{-5}$ Pa/s) and $P_f$ would be the final pressure. $P_s$ is the initial static pressure. The choice of a high static pressure ($P_s=2-2.2$MPa) can avoid the sample desaturation during permeability test and no significant Klinkenberg effect is to be expected. However $\Delta P$ is small compared to $P_s$. (Loosveldt (2002))

2.3 **Experimental procedure**

There were three steps to conduct this study. The first one was dessaturation process, from saturated state to the partially-saturated state. After, weighing, each sample saturated state was put under rh% as mentioned before. When the mass is stabilized (no more than 0.01g for three days), the effective gas permeability $K_{eff}$ is measured. The second step was drying process, after the effective permeability measurement, the sample is dried at 60°C which leads to its porosity measurement and to the saturation level obtained a rh%:
\[ S_n(rh) = \frac{M_w - M_s(rh)}{M_w - M_d} \]  

(3)

Where \( M_w \) is saturated mass; \( M_s \) is partial saturated mass and \( M_d \) is dried mass.

The intrinsic permeability \( K_{\text{int}} \) is measured with the same procedure as partially saturated samples, and the relative permeability \( K_{\text{rg}} \), for each sample, is deduced from:

\[ K_{\text{rg}} = \frac{K_{\text{eff}}}{K_{\text{int}}} \]  

(4)

\( K_{\text{rg}} \) will vary in the range [0, 1]; 0 for the saturated state and 1 for the dry state. It is generally admitted that the relative permeability does not depend on the saturating liquid nature (Dana et al. (2002)) and is mainly a function of the saturated state \( S_w \) (Abbas (1999)). It should also depend on the gas nature (Skoczylas (1995)). Pure Argon was chosen as a neutral gas.

The third steps was the resaturating process, after the intrinsic permeability measurement, the sample is put at its previous rh% level in order to evaluate the hysteretic effects in the cycle drying-imbibition and to measure its effective gas permeability at this new saturation state. Three measurements were thus performed at different time of imbibition.

3 RESULTS

3.1 Desorption phase and Drying phase

The desorption curves are plotted in figure 2 in which can be seen a strong difference between both materials. What is firstly remarkable is the very high remaining saturation level for CEMV at a very low relative humidity (\( S_w = 72\% \) at rh=43\% and \( S_w = 53\% \) at rh=11\%). If we assume that Kelvin-Laplace relation applies for the smallest pores, such results mean that 70\% of the water lie in the pores whose radius is less than 1nm! This kind of calculation is mostly qualitative as it is well known that the status of confined water in the nanoporosity is adsorbed water, strongly bounded to the pore wall (Baron (1982)). The porosity is calculated after drying phase, they are 8.3\% for the CEM I and 10.3\% for the CEM V concrete. This means that the porous structure of the CEMV is much thinner than those of CEMI. In fact the CEMV cement contains pouzzolanic species which on the long term results in a more divided porosity (Lobet (2003)).

![Figure 2: Desorption curves for both concretes.](image)
3.2 Sorption phases

All dry samples were re-saturated at the same rh% for around 500 days to achieve mass stabilization for both concrete. Saturation during the imbibition phases can be observed in figure 3 (CEMI) and 4 (CEMV). The gas permeability was measured for each sample at different time. A strong hysteretic behaviour is present for two concretes mostly under the different relative humidity levels. At rh98% the CEMI recover to the saturation level obtained for desorption phase, but the CEMV stabilizes at a saturation below the level obtained during desorption. The maximal difference saturation between desorption – sorption is seen on intermediate range of relative humidity between 11 and 70%.

Figure 3: Desorption – sorption curves at different imbibition times for CEMI

Figure 4: Desorption – sorption curves at different imbibition times for CEMV

3.3 Gas relative permeability

Figures 5 and 6 present the evolution of relative permeability at different saturation reached either on a desorption phase or on one of the three sorption phases ($K_{rg}(1)$ in the figures) or sorption ($K_{rg}(2)$, $K_{rg}(3)$ and $K_{rg}(4)$ in the figures). It appears that a longer waiting time can reduce the amplitude of hysteretic in saturation. The phase of capillary condensation is much
longer than the phases of drying with predominance of evaporation and liquid flow at the beginning. For concrete CEM I, and between 0 to 50% water saturation, gas relative permeability variation only depend on saturation. Over 50%, a little divergence appeared. The gas permeability obtained in the sorption phase seems to be progressively higher than that obtained in desorption when saturation increase, even if at same saturation, the hydraulic clog is not effective in sorption phase like desorption phase. However, for CEM I, at the last point (Sw=73%), the relative permeability in sorption is higher than in desorption at same saturation. It could be due to micro-cracking induced by drying. (CHEN and al (2010)) To verify this assumption a complementary test was performed on the last sample of CEM I (Sw=73%). The table 2 shows the permeability evolution according to confining pressures. It clearly shows a decreasing of permeability due to increasing confining pressure; the result is significant to show a real micro-cracks effect.
Table 2: Variation of effective permeability with confining pressure – CEM I at rh98%

<table>
<thead>
<tr>
<th>Pc</th>
<th>5MPa</th>
<th>10MPa</th>
<th>15MPa</th>
<th>20MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{eff}} \left(10^{19}\right)$</td>
<td>1.9</td>
<td>1.88</td>
<td>1.27</td>
<td>0.9</td>
</tr>
</tbody>
</table>

4 CONCLUSIONS

The results have shown that the concrete CEM V has porosity slightly larger than the CEM I, but with a much thinner structure. This concrete presents saturation level much higher than for CEM I at a same relative humidity. At rh=11% this concrete still has a saturation nearly 60%. A strong hysteretic effect on the water saturation under relative humidity has been confirmed during desorption phase then in sorption phase. As time passed, this hysteretic effect decrease, moreover at the highest relative humidity the CEM I concrete goes back to its initial saturation value (saturation obtained for desorption); the CEM V concrete has a similarly behavior.

The relative gas permeability of CEM V concrete is only dependant on the water saturation during desorption phase and sorption phase. This character is of crucial importance as regards numerical modelling of gas flow in the storage structure as one has just to take into account the saturation level without any hysteretic effect on permeability. Between 0%~50% saturation, the CEM I concrete has a behavior without hysteretic like CEM V. Over this saturation, the relative permeability is higher during the sorption phase than for desorption phase. Attempt to confirm this difference by effect micro-cracks has not given clear evidence. At this stage no satisfactory justification can explain these experimental results.

5 REFERENCE


Andra (2001B), Choix des formulations de bétons de référence, Document interne Andra n° C RP 0 LER 01-004/A, 2001 (in French).


