EFFECT OF MICRO-CRACKING ON WATER RETENTION AND GAS TRANSPORT PROPERTIES OF TWO INDUSTRIAL CONCRETES

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Abstract
In the context of deep underground storage structures for long life radioactive wastes, prior to the final closure of disposal tunnels, the concrete sheath may suffer micro- to macro-cracking. In this framework, the primary goal of the French Nuclear Waste Management Agency (Andra) is to get a good knowledge of the conditions, in which radioactive materials are efficiently isolated from the environment. Therefore, determining water retention and advective transfer properties of micro-cracked and partially water-saturated concrete is a critical issue.

Several methodologies have been developed to create an “intermediate” and an “advanced” damage state, in two different Andra industrial concretes. Gas permeability is used as the privileged tool to assess the actual damage state, because it has shown good sensitivity to micro-crack presence. Our aim is to investigate gas migration properties (gas breakthrough pressure) and critical advective transfer properties (namely suction curves and gas permeability) for both concretes, before and after the dedicated damage procedures.

1. INTRODUCTION
In France, long term repository of high-level and long-life nuclear waste is planned within a highly impermeable and seismically stable geological layer made of claystone, and located in both Haute-Marne and Meuse French Departments. This formation welcomes a full-scale underground research laboratory drilled within clay host rock, and still under construction [1]. Different concrete formulations are used for waste canister covers, or for tunnel backfilling, lining and closure. These are bound to be micro- or macro-cracked due to their contact with the excavation damaged zone (EDZ), located at the tunnel surface.

In such context, for performance and safety assessment purposes, varied damage and failure scenarios are investigated. In particular, on the long term, humid corrosion of copper/steel canisters, coupled to radioactive waste decay and radiolysis of water, may induce
hydrogen gas production [2]. Gradually, hydrogen gas pressure could increase notably, first, inside disposal pits, at the interface between waste metal canisters, concrete covers and plugs, and, subsequently, inside the repository tunnel. Whenever the capillary threshold for gas breakthrough into repository materials is reached, hydrogen gas leakage may occur through the whole structure and penetrate its surroundings.

As reported by [3], gas migration mechanisms related to capillarity involve the creation and propagation of preferential pathways through the water-saturated porous material. Whereas gas entry is reached as soon as gas enters the porous material, breakthrough pressure is reached when gas passes through the whole porous network, either by diffusion or by discontinuous capillary passage (snap off). Later, gas may permeate through the porous medium, when a continuous flow occurs. These phenomena are potentially enhanced by material micro-cracking. Therefore, the aim of the present study is to investigate gas migration properties (gas breakthrough pressure) and critical advective transfer properties (namely suction curves and gas permeability) of two Andra concretes (based on CEMI or CEMV-type cements according to european standards), before and after a dedicated damage procedure aimed at micro-cracking them.

2. EXPERIMENTAL METHODS

Two industrial Andra concrete named “CEM I” and “CEM V” have been used. These are respectively composed of cement powder reference CEM I 52,5 PM ES for “CEM I” concrete and CEM V/A for “CEM V” concrete, mixed with (5-12mm) gravel, (0-4mm) sand, and with a super-plasticizer (Glenium 27, BASF). The water to cement ratio (W/C) is 0.43 for CEM I and 0.39 for CEMV, (see [2] for full formulation data). All samples are cylinders of 37 mm diameter and 30 mm height. The reference dry state is chosen after oven-heating at 65°C until mass stabilization. This drying procedure minimizes concrete alteration and prevent from micro-cracking [2]. However, it does not allow the removal of concrete bound water, within its C-S-H solid phase, which is removed above 105°C [2]. Such water is typically located in nanoscopic pores, from 2 to 30nm.

Brue et al[2] provides pore size distributions for both CEM I and CEM V concrete pastes by using Mercury Intrusion Porosimetry (MIP), from different batches of concrete than those presented here. Similar data may be found in [4], also on different batches of the same concretes. Depending on the batch used for MIP experiment, pore size distributions vary, yet three distinct peaks are observed. In [2], one is located between 1 and 2 microns, which is attributed to large capillary pores, entrapped air bubbles and/or to micro-cracks (potentially due to sample oven-drying); the second, much smaller, peak is located between 100nm and 1 microm: it is centered around 200nm for CEM I and 400nm for CEM V, and corresponds to capillary pores [1]; the third, greatest peak is centered around 30nm for CEM I and 40nm for CEM V: it is attributed to inter-layer C-S-H porosity. This third peak has greater amplitude for CEMV than CEMI, meaning that CEMV contains more inter-layer C-S-H pores than CEMI. More generally, sorption experiments and hydration numerical modeling show that CEMV contains a greater amount of C-S-H than CEMI concrete.
2.1 Design of a damage methodology

Firstly, a methodology has been designed in order to induce damage, and most probably micro-cracks, in concretes. The aim is to reproduce cracks similar to those occurring in situ. An experimental protocol, named DM1, has been tested on CEM I concrete. It consists in a heat shock on initially fully water-saturated concrete: each sample is submitted to three cycles of freeze/thawing under water (-18°C for 24h followed by 100°C for 30min). Heat shock generates damage only when the material is initially fully liquid-saturated. At the microscopic level, damage is bound to result in an intense micro-cracking of the cement paste, which contributes, in particular, to weaken and separate the interface between paste and aggregate. For each sample, the damage state is assessed using gas permeability in the dry state, inside a conventional triaxial cell. Argon gas is the interstitial fluid.

Table 1. Comparison of (1) gas permeability (minimum value, average value and maximum value for a total of 9 samples) at the dry state and (2) porosity using DM1 and DM3 damage methods

<table>
<thead>
<tr>
<th>Sample type (total of 9 samples for each type)</th>
<th>K (min) in m²</th>
<th>K (average) in m²</th>
<th>K (max) in m²</th>
<th>Average porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intact CEM I</td>
<td>2.73 \times 10^{-18}</td>
<td>4.31 \times 10^{-18}</td>
<td>8.74 \times 10^{-18}</td>
<td>7.59 (± 4.95%)</td>
</tr>
<tr>
<td>DM1 damaged CEM I</td>
<td>2.8 \times 10^{-18}</td>
<td>6.16 \times 10^{-18}</td>
<td>1.10 \times 10^{-17}</td>
<td>7.59 (± 4.05%)</td>
</tr>
<tr>
<td>DM3 damaged CEM I</td>
<td>1.2 \times 10^{-17}</td>
<td>2.01 \times 10^{-17}</td>
<td>2.67 \times 10^{-17}</td>
<td>8.56 (± 5.21%)</td>
</tr>
<tr>
<td>Intact CEM V</td>
<td>3.24 \times 10^{-18}</td>
<td>5.39 \times 10^{-18}</td>
<td>7.26 \times 10^{-18}</td>
<td>12.08 (± 4.04%)</td>
</tr>
<tr>
<td>DM1 damaged CEM V</td>
<td>4.86 \times 10^{-18}</td>
<td>6.44 \times 10^{-18}</td>
<td>8.79 \times 10^{-18}</td>
<td>11.73 (± 5.59%)</td>
</tr>
</tbody>
</table>

For both concretes, nine samples have been prepared in both intact and damaged states (18 in total per concrete), using DM1 damage procedure. Total connected porosity, obtained by the water saturation method, is also provided. For both CEMI and CEMV concretes, the permeability range for intact samples intersects with the permeability range of DM1 damaged material (see Table 1). This means that damage procedure DM1 is insufficient to provide a statistically significant difference in permeability: DM1 method will be considered as an intermediate damage procedure.

Investigations are currently conducted in order to improve the damage procedure: they led on an improved, more efficient, damage procedure named DM3. It consists, from an initial state at -18°C (min. 30h) in a thermal gradient from -18°C to 200°C in an oven during 2h, then 30min at 0°C in the frozen water. The duration of heating at 200°C (2h) is assumed to be too short to change significantly the concrete microstructure. Only CEM I concrete has been tested by this damage method. DM3 shows a significant increase in dry permeability of concrete samples: the average dry permeability is multiplied by 5 after the damage method (see Table1).
2.2 Measurements at given partial saturation

After maturation, fully water-saturated concrete samples are placed in a RH-controlled atmosphere at a fixed RH value of 100%, 98, 92, 85, 75, 70, 59, 43 or 11% allowed by salt-saturated solutions. Their mass evolution are recorded from the fully water-saturated state (i.e. from saturated mass $m_{sat}$), at a given RH ($m_{eff}$), until drying in the oven at 65°C ($m_{dry}$). For all samples, water saturation ratio $S_w$ is calculated at each RH using the following definition:

$$S_w = \frac{m_{sat} - m_{dry}}{m_{sat} - m_{eff}}$$

At given RH, the bigger the material pores, the lower the saturation ratio $S_w$. Moreover, at given RH, an assessment of the biggest water-saturated pore size is provided by Kelvin-Laplace’s law, by assuming a simplified model of the pore network, as follows. At constant temperature $T$, capillary pressure $P_{cap}$ within the porous material is given by Kelvin’s law [5]:

$$P_{cap} = \frac{\rho_{water}RT}{M_{water}} ln (RH)$$

where $\rho_{water}$ is water mass density (taken at 1000kg/m$^3$), $R$ is perfect gas constant (8.314 J/mol/K), $T$ is temperature (in Kelvin) and $M_{water}$ (taken at 18g/mol) is water molar mass. Using Laplace’s law, capillary pressure is also related to a so-called drained pore radius $r_{drained} = \frac{2\gamma}{P_{cap}}$, where $\gamma$ is water/air surface tension (equal to 73e-3 N/m). If the pore network is represented by an assembly of cylinders of varying radii $r$ placed in parallel, $r_{drained}$ represents the biggest water-saturated pore size: all pore radii bigger than $r_{drained}$ are dry. One should note that these laws assume that the water inside pores is mainly governed by the capillary condensation phenomenon, which is not the case for low values of RH. In such case, adsorption is the predominant phenomenon (a fine water film of varying thickness is adsorbed on the pore surface). This point is not drawn further in this paper because, in the repository context, we specifically investigate high saturation levels.

Gas permeability $K_{gas}$ is measured for each sample at given RH (or $S_w$), under a confinement $P_c$ fixed at 6 or 12MPa (i.e the in situ major stress) (see figure 1). Gas relative permeability is then given as the ratio between gas permeability at a constant RH and dry gas permeability

$$K_{rg} = \frac{K_{gas}(RH)}{K_{gas}(S_{dry})} = \frac{K_{gas}(S_{w})}{K_{gas}(S_{dry})}$$

2.3 Measurements of gas breakthrough pressure (GBP)

When gas is injected on one side of a saturated porous medium, its passage is progressive. When gas pressure reaches the so-called gas entry pressure, gas begins to pass through the material and pushes a small amount of water on the upstream sample side. Experimentally, gas entry pressure is difficult to measure. Rather, gas breakthrough pressure (GBP), defined as the gas injection pressure at which gas is expelled on the sample downstream side, is measured. Firstly, the sample is placed in a triaxial cell (cf. Fig.1) and subjected to a confinement $P_c=5-7$MPa or 12MPa. The sample is saturated with water until full saturation. The full saturation state is achieved when water permeability falls below $10^{-20}$-$10^{-21}$m$^2$. Following this, upstream and downstream pipes are emptied from water (volumes of 5 and 2 cl respectively). Finally, argon gas pressure is increased very slowly on the sample upstream
side (at a rate of 1 to 10 days with an average at 2-3 days between two $\Delta P_{\text{gas}}=0.5 \, \text{MPa}$ steps), until gas presence is detected in the downstream chamber (cf. Fig.1). Gas detection is performed using both a downstream pressure transducer ($\pm 1 \, \text{mbar}$) and a dedicated argon gas detector ($\pm 0.1 \mu\text{l/sec}$).

3. RESULTS AND DISCUSSION

3.1 Desorption isotherms and gas relative permeability

Figure 2 plots the first desorption isotherms (RH, $S_w$) for intact and damaged CEM I and CEM V concretes. Desorption isotherms of CEM V concrete overlap for intact and damaged material, which means that there is no effect of our damage methodology DM1 on CEM V concrete. However, for CEM I concrete, this figure shows a significant effect of the damage procedures. Based on Van Genuchten’s model [6], Fig.2 shows that desorption isotherms are quite similar for DM1 and DM3 damaged concrete even if the damage state is intermediate for DM1 and more advanced for DM3 as measured by gas permeability (see Table 1). At given relative humidity RH, the water saturation ratio $S_w$ of intact material is significantly higher than the micro-cracked one.

![Figure 2](image)

Figure 2. The first desorption isotherms of CEM I (left) and CEM V (right)
Figure 3 plots suction curves for intact and damaged CEM I and CEM V concretes. For CEM I concrete, and for a given saturation ratio $S_w$, Fig. 3 shows that the capillary pressure of intact CEM I concrete is higher than that of the damaged one, whatever the damage procedure. Using Laplace’s law to relate $P_{\text{cap}}$ to the drained pore radius, this means that at given $S_w$, the drained pore radius is greater for micro-cracked concrete, as compared to intact material. For DM1 procedure, this occurs although porosity values are unchanged by the damage procedure (see Table 1). This testifies of an increase in the size of water passages due to freeze/thaw cycles. The DM1 damage method created micro-cracks, which are sufficient to drain further the sample after damage, yet not to increase its porosity significantly. Otherwise, for DM3, the average porosity value is significantly increased from 7.59% to 8.56%. This means that micro-cracks represent a significant volume or that DM3 procedure creates connections with initially occluded pores.

Based on Fig. 3, it is also observed that suction curves of intact and damaged CEMV overlap. In terms of suction curve, the damage procedure has no effect on CEMV concrete. The pore distribution of CEMV, which is different from the pore distribution of CEMI [2], may be the cause of the insensivity of CEMV to freeze/thaw cycles. Indeed, MIP analysis (not shown here, see [2]) shows that CEMV presents a greater amount of finer pores (below 6nm, i.e. within the C-S-H) as compared to CEMI concrete. CEM I porosity is more of capillary size (with peak pore sizes at 30nm) although CEM I porosity is smaller than that of CEM V. This difference in pore network microstructure is due to pozzolanic additions in CEMV, which promote reactions enhancing C-S-H formation at the expense of portlandite [5]. This reduces the proportion of capillary pores and induces a refinement of the CEM V pores. On another hand, the freezing procedure at -18°C is sufficient to damage the pore network of CEM I concrete but not of CEMV due to porosity refinement in this latest case. In order to damage CEMV concrete, the freezing procedure should be performed at lower temperatures, around -78°C at least, which is a temperature at which the more numerous C-S-H nano-pores can freeze [7]. This microstructural difference between CEMI and CEMV materials is also illustrated by comparing the suction curves of both concretes. At a given water saturation level, in the intact state, the capillary pressure of CEMV is higher than that of CEMI. Using Laplace’s law, this means that the drained pore radius is greater for CEMI, as compared to CEMV concrete, i.e. that CEMI pore size distribution is coarser than CEMV.

![Figure 3. Suction curves for CEM I (on the left) and CEM V concretes (on the right)](image-url)
Figure 4 shows gas relative permeability v.s water saturation for CEM I and CEM V concrete:

Despite this difference in suction curves, the relationship between $K_{rg}$ and $S_w$ is similar for each concrete whatever its damage stage (DM1 and DM3 procedures). This is interesting for modelling purposes, since only one fitting curve is necessary for both concretes and whatever their damage state. These curves have been obtained from an initially fully-saturated state, i.e. these are related to first desorptions. For each concrete, the differences between Van Genuchten-Mualem’s model [8] curves, fitted for the different damage states, are due to the lack of experimental points for low $S_w$ values. This is especially true for CEM V concrete for which the lowest water saturation value is about 0.5. Differences between damaged or intact states, could be significant if sorption or sorption/desorption cycles were considered. This will be the subject of further investigations.

### 3.2 Gas Breakthrough pressure (GBP)

For GBP assessment, six samples have been tested:
- For CEM I concrete: one intact sample and two DM1 “micro-cracked” ones
- For CEM V concrete: one intact and one DM1 ‘damaged’ sample

Each test requires a two-month experiment at least, with a preliminary month for obtaining full water saturation.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Confining pressure Pc(MPa)</th>
<th>Water permeability Kw(m²)</th>
<th>P (water injected) (MPa)</th>
<th>GBP (MPa)</th>
<th>Gas passage ? GBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intact CEM I 1</td>
<td>5</td>
<td>3,9e⁻²¹</td>
<td>2</td>
<td>4</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td></td>
<td></td>
<td>4,5</td>
<td>Possibly</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td></td>
<td></td>
<td>5,2</td>
<td>yes</td>
</tr>
<tr>
<td>DM1 damaged CEM I</td>
<td>5</td>
<td>8,77e⁻²¹</td>
<td>5</td>
<td>0.3</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Both intact concretes have similar intrinsic water permeability on the order of $10^{-21}\text{m}^2$. For all samples, either sound or damaged, see Table 2, water permeability is as low as $8,7\times10^{-21}$ down to $6\times10^{-22}\text{m}^2$, which is attributed to full water saturation.

First results show that gas pressure increases systematically on the downstream sample side whatever the upstream gas pressure value (given our manometer accuracy). Simultaneously to downstream pressure increase, one observes water expelled on the downstream side and no argon is detected. For higher upstream gas pressure values, water expulsion is followed by a mix of water and argon, and then by argon only, mainly in a discontinuous manner: gas is accumulated in the downstream chamber when the downstream valve is closed, yet, when opening the downstream valve, no more gas is detected after a few seconds of gas detector use. This discontinuous passage is attributed either to diffusion or discontinuous capillary breakthrough (snap-off). Then, for sufficiently high upstream gas pressure values, gas finally passes continuously, so that gas permeability may be assessed. For the CEM I and CEMV samples tested here, no such gas pressure could be reached, due to the fact that either available gas pressure values were limited to those below confinement ($P_c=12\text{MPa}$), or that this point was not investigated further. This is currently under way.

Nevertheless, when considering GBP as corresponding to discontinuous gas passage, a significant effect of the DM1 damage procedure is noted for CEMI, with a decrease of GBP from 5MPa (intact sample) down to 0.5-1MPa (damaged samples) (see Table 2). Table 2 shows that intact ‘CEMV 1’ has a GBP higher than 9MPa and DM1 damaged ‘CEMV 1’ present a GBP of 5.2MPa, which is similar to that of sound CEMI concrete, but very lower than that of intact CEM V. A further GBP test will be conducted on a DM3 damaged CEM I concrete. GBP is very sensitive to the damage procedures.

4. CONCLUSION

This contribution characterizes the effect of micro-cracking, induced by two dedicated damage procedures (DM1 and DM3), on the hydric and hydraulic behaviour of partially-saturated industrial concretes. Suction curves show that the size of water passages is increased for CEM I concrete after three freeze/thaw cycles (DM1 procedure), while no total porosity increase is detected: the volume of created damage is negligible as compared to total connected porosity. The damage induced by DM3 procedure increases the total connected porosity while desorption isotherms are still similar to that obtained with DM1 method. On the opposite, suction curves of CEM V concrete overlap independently of its damage state, which means that the DM1 procedure has not been efficient on this frost-resistant material. Otherwise, gas relative permeability vs. water saturation level curves overlap, whatever the concrete or the damage state considered. Furthermore, gas breakthrough pressure (GBP) is observed as the discontinuous or excessively slow passage (below 0.1µl/sec) of gas through the sample. GBP decreases significantly after damage by 3 freeze/thaw cycles for CEM I (from 5MPa down to 1MPa) but also for CEM V (from up to 9MPa to 5MPa).
interpretation is that our DM1 damage procedure, have a noticeable effect on CEM I and CEM V concrete in terms of GBP.

Therefore, even if suction curves and gas permeability are potentially good indicators of a concrete damage state, gas breakthrough pressure appears to be a more sensitive indicator. Nevertheless, to be fully conclusive (and in particular, statistically significant), these results will be confirmed by further research.

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REFERENCES