Influence of temperature and composition upon drying of concretes

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ABSTRACT: The French long-term repository for intermediate level/long lived nuclear wastes consists in a network of underground concrete tunnels in deep geological medium. Various loadings will occur during the repository service-life. Among the physical constraints, especially de-saturation/re-saturation processes, pore pressure variations and temperature changes will affect the concrete properties. The de-saturation process is linked to relative humidity decreases, and in relation to temperature variations. De-saturation leads to shrinkage strains that often induce micro-cracking. Micro-cracks can increase the concrete permeability and decrease the mechanical properties. This experimental study focuses on the drying process and its consequences. The studied materials are concretes, based on CEM I or CEM V/A-type cements. The influence of temperature and cement composition upon drying shrinkage is shown to be important. Due to this, transport properties depend on cement composition. An increase in temperature of up to 80°C accelerates drying mechanisms by means of thermal activation.

1 INTRODUCTION

The French National Agency for Nuclear Waste Management (Andra) has to design and to study the long-term nuclear waste repository feasibility in deep geological medium. The current concept for intermediate level/long lived nuclear wastes considers facilities at 500m depth, in a clay layer (Callovo-Oxfordian argillite), located in the East of France. The repository is designed as a tunnel network, which leads to concrete vaults where nuclear wastes will be placed. When vaults are filled with wastes, a mixed clay and concrete plug closes the access gallery.

The design has to take into account physical and chemical phenomena due to the waste activity, as well as processes in relation to the geological medium behavior (Andra 2005). Among possible phenomena, the host rock de-saturation/re-saturation processes, in relation to repository building and exploitation, will affect concrete components of the repository. Part of intermediate level waste is exothermic. Thus, a thermal loading has to be taken into account. As a requirement, maximal temperature in intermediate level wastes vaults has to be less than 70°C (Andra 2005). Moreover, in order to describe the long-term (over thousands of years) mechanical evolution of the repository, shrinkage and creep have to be assessed as well as possible. Both mechanical loadings due to *in-situ* stresses and de-

saturation/re-saturation processes are involved in a common ageing process and this must be taken into account.

In relation to these critical industrial issues, the present study investigates the de-saturation process under controlled temperatures and relative humidities, for two concrete materials based on CEM I and CEM V cement types.

2 EXPERIMENTAL APPROACH

2.1 *Concrete formulations*

The studied materials are 'reference concretes' in Andra's program for repository design. Two types of cement are used: (1) a CEM I type, which is made of Portland clinker, and (2) a CEM V/A type, which is constituted of 60% of clinker in mass, 22% of blast-furnace slag, 14% of siliceous filler (i.e. fly ash) and 4% of setting regulator, according to NF EN 196-4 European Standard (Andra & CEBTP 2001, Andra & LERM 2001). Blast furnace slag and fly ash act as pozzolanic additives to CEM V/A cement. The difference between both formulations will be the microstructure of concretes (see section 2.5). Concrete made with a CEM I cement has a water-to-cement ratio (W/C) equal to 0.43 and is called 'CEM I'. Concrete prepared with a CEM V/A cement, with a W/C ratio equal to 0.39, is named 'CEM V'. Table 1 gives both concrete formulations.

Table 1. Concrete formulations.

| Materials | Nature | Quantity [kg/m^3] | |
		CEM I	CEM V
Cement	CEM I 52.5 R	400	-
Cement	CEM V/A 42.5 N	-	450
Sand	Limestone [0-4mm]	858	800
Gravel	Limestone [5-12mm]	945	984
Admixture	Glenium 27	10	11.5
Water	-	171	176.3

2.2 Concrete samples

Samples are made from a single batch for each cement type. Prismatic samples are made in standard moulds with a volume equal to (4×4×16) cm^3. Prior to casting, contact blocks (i.e. studs) are placed in each mould to follow shrinkage evolution.

After un-molding, samples are cured under water at 20°C during six months before use. Therefore, we can consider that hydration process is complete and that concrete microstructure will no longer vary significantly (Baroghel Bouny 1994, Baroghel Bouny et al. 1999). Moreover, concretes are water-saturated at the end of maturation.

2.3 Control of the de-saturation process

Concrete de-saturation is a hydraulic process in which water moves by means of capillary pressure. Capillary pressure is defined as the difference between liquid water and gas pressure:

$$\left|P_{cap}\right| = P_{liq} - P_{gas} \tag{1}$$

Suction is related to decrease in water content, so that, after equilibrium, the smallest pores remain water-saturated.

Kelvin's law relates capillary pressure to current temperature and relative humidity:

$$\left|P_{cap}\right| = \rho_w \frac{RT}{M_w} \ln(rh) \tag{2}$$

where ρ_w is water density (function of temperature) [kg/m^3]; R is the perfect gas constant [J/mol.K]; T is temperature [K]; M_w is water molar mass [kg/mol] and rh is relative humidity. The increase of capillary pressure will be either due to an increase of temperature or to a decrease of relative humidity. These variations lead to physical effects upon concrete.

For a temperature close to 20°C, it is generally admitted that (Baroghel Bouny 1994, Baroghel Bouny et al. 1999, Ma et al. 2007, Yurtdas 2003):

- for relative humidity values from 45% to 100%, the main de-saturation mechanism is liquid water movement due to capillary pressure.

- for lower relative humidity values, diffusion of water vapor is the main phenomenon leading to water transport.

Moreover, an increase in temperature induces so-called 'thermal activation' (Caré 2008, Choinska 2006, Galle et al. 2006, Ishida et al. 2007, Joss & Reinhardt 2002, Noumowe et al. 1996), which accelerates water evaporation and condensation processes. Indeed, properties of liquid and vapor water change with temperature (viscosity decrease for liquid water, and increase for vapor). Hence, transfer properties such as permeability and diffusion are dependent on temperature.

The de-saturation process is studied here at three fixed temperatures (20°C, 50°C and 80°C). Temperature and relative humidity are both controlled using climatic chambers. Fixed relative humidity values are: rh=98%, rh=90%, rh=80%, rh=70% and rh=60%. They have been chosen to approach two saturation degrees for each material (S_w=0.8 and S_w=0.6).

2.4 Measurement procedures: mass, shrinkage and water saturation degree

Three kinds of measurements are carried out to study the de-saturation process as a function of temperature: mass variation, shrinkage and water saturation degree.

Mass evolution over time is measured with an accuracy of +/-0.01g.

Shrinkage is measured under controlled conditions: T=20±5°C and rh=40±5%. Shrinkage measurements use a linear transducer with an accuracy of one micrometer (Garcia Boivin 2001). Drying shrinkage is defined as the difference between total shrinkage and autogenous shrinkage. Autogenous shrinkage is measured on prismatic samples, which are protected from drying by wrapping them in adhesive aluminum (Yurtdas 2003).

At equilibrium at each imposed rh-value, the water saturation degree is calculated with Equation (3):

$$S_w = \frac{m - m_{dry}}{m_{sat} - m_{dry}} \tag{3}$$

where m is mass at the considered rh-value, m_{sat} is saturated mass, obtained after maturation under water during six months, and m_{dry} is dried sample mass, which is estimated using porosity measurements (see section 2.5). Hence, the desorption isotherm of each concrete is estimated as a function of temperature and relative humidity (i.e. as a function of capillary pressure).

2.5 Characterization of initial concrete properties

Characterization of initial concrete properties (porosity and permeability) is made at dried state, in order to avoid any effect of partial water content. This state is obtained after drying in an oven at 60°C until constant mass. This temperature of 60°C is chosen to limit concrete micro-cracking.

Porosity is measured using the mass variation of a sample between the initially water saturated state and the dried state (AFPC-AFREM). Results are an average of 58 samples for each concrete.

Permeability of each concrete is measured with an inert gas (argon) on one dried sample placed in a triaxial cell with a confining pressure P_{conf} = 5 MPa (Skoczylas 2003). Apparent permeabilities are measured as a function of gas injection pressure. The evaluation of Klinkenberg effect (Klinkenberg 1941) allows the calculation of the material intrinsic permeability.

Moreover, the stiffness of each concrete is estimated by measuring the drained bulk modulus K_b of two dried samples preliminary placed inside a triaxial cell (Rougelot 2009), with P_{conf} varying between 30 and 250 MPa. In the theory of poromechanics, developed in (Coussy 2004), the drained bulk modulus K_b relates volumetric strain variation to confining pressure variations (ΔP_{conf}) (equation (4)) when there is no variation in interstitial pressure (pore pressure is usually set at atmospheric pressure, i.e. in drained conditions).

$$\Delta \varepsilon_v = \frac{\Delta P_{conf}}{K_b} \qquad (4)$$

where $\Delta \varepsilon_v$ is volumetric strain variation.

Finally, porosity distribution is measured by mercury intrusion porosimetry (MIP) using concrete samples of less than 1cm^3 at dried state (Fig. 1).
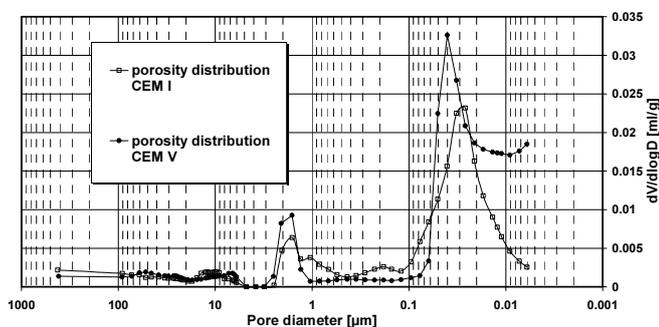

Figure 1. Porosity distribution of concretes measured by mercury intrusion porosimetry (MIP).

Preliminary characterization of concretes is presented in Table 2.

Table 2. Porosity, gas permeability and drained bulk modulus of concretes at dried state.

	CEM I	CEM V
Porosity [%]	8	12
Intrinsic permeability [m^2]	5.10^{-18}	2.10^{-18}
Drained bulk modulus K_b GPa]	30	20

Comparison between both concretes shows that the CEM I concrete is less porous and more permeable than the CEM V one. This is due to the pozzolanic additions in CEM V cement which induce a thinner porosity, but with a higher total porosity (Perlot et al. 2006, Lobet 2003, Kourounis et al. 2007).

Results of drained bulk modulus K_b show that CEM I concrete presents a more deformable matrix than CEM V concrete, which is link to the higher porosity for CEM I concrete.

3 EXPERIMENTAL RESULTS

All results are averages of measurements carried out on three prismatic samples at each temperature and for each concrete.

3.1 Desorption isotherms

Figures 2 and 3 present desorption isotherms as a function of temperature, respectively for CEM I and CEM V concretes.
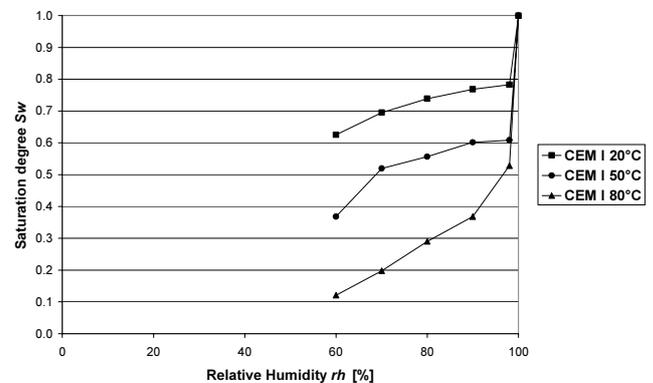

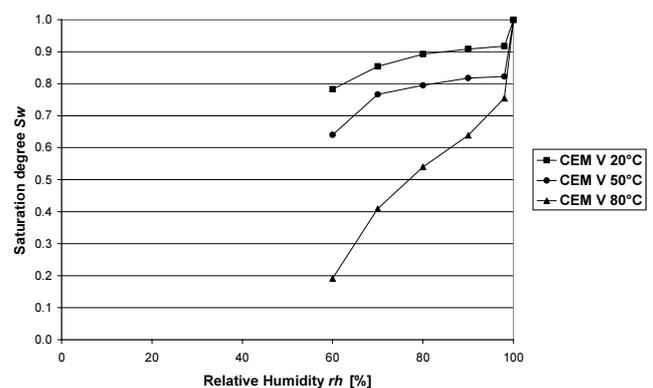Figure 2. Desorption isotherms of CEM I concrete as a function of temperature.

Figure 3. Desorption isotherms of CEM V concrete as a function of temperature.

3.1.1 *Influence of temperature*

For *rh*>90%, water transport is mainly due to permeation of liquid water. The increase of temperature leads to a decrease of viscosity, which increase the permeability.

Once *rh*<90%, two complementary phenomena are predominant. Transport by diffusion is accelerated with temperature because of a local increase in vapor pressure and thermal agitation of water molecules induces an increase in transfer properties.

The evolution of water saturation degree with relative humidity at 20°C and 50°C are similar. However, we can notice that the behavior at 80°C is very different. The de-saturation increases faster for a temperature of 80°C than for the two other temperatures. Such evolution at 80°C suggests that there is a possible dehydration of CSH.

Similar trend with temperature is also described by S. Poyet, who identified the desorption isotherm of a CEM I concrete by means of saturated salt solutions (Poyet 2009).

Influence of concrete composition

Considering desorption isotherms at identical temperature shows that CEM I concrete presents lower water saturation degrees whatever the *rh*-value is. For instance, at 20°C, the target value S_w=0.8 is obtained for CEM I concrete at *rh*=98% and, for CEM V concrete, at *rh*=60%.

Indeed, the bigger microstructure gives a higher permeability value for CEM I concrete which leads to a higher mass loss than in CEM V. Moreover, the porosity (and water content) of CSH is more important in CEM V concrete than in CEM I, that is why, once the drying front reaches the CSH porosity scale, mass loss kinetics slow down for CEM I concrete and increase for CEM V concrete (which has more CSH-pore water).

3.2 *Drying shrinkage*

Shrinkage is a macroscopic consequence of local compression of the cement matrix due to an increase of the capillary pressure. Figure 4 and 5 show the drying shrinkage at equilibrium as a function of capillary pressure and temperature, respectively for CEM I and CEM V concretes.
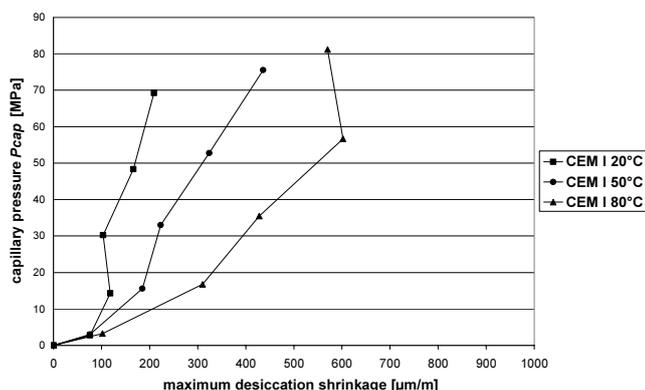
Figure 4. Drying shrinkage of CEM I concrete as a function of capillary pressure and temperature.
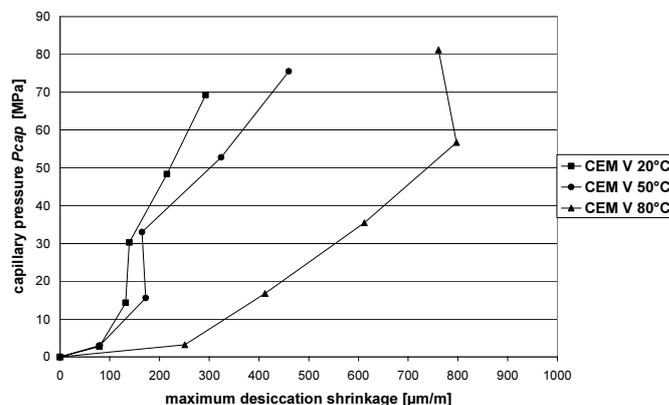
Figure 5. Drying shrinkage of CEM V concrete as a function of capillary pressure and temperature.

3.2.1 *Influence of temperature*

Shrinkage deformations, expressed as a function of capillary pressure, show amplitude increase with temperature, especially between 50°C and 80°C. This suggests that, in addition to capillary pressure variations, others mechanisms have to be considered.

Capillary pressure acts as an internal stress applied to concrete microstructure. Therefore, this may lead to a shrinkage amplified by the creep of the CSH. Indeed, it is believed that sheets of CSH slide over one another, so as to relax internal stresses due to capillary pressure variations. Hence, creep of CSH is activated by temperature.

Shrinkage, measured as a macroscopic deformation, is then a sum of microscopic processes involving microstructure, hydrates creep, capillary pressure. These processes are strongly temperature/water saturation dependant.

3.2.2 *Influence of composition*

Shrinkage evolution is also influenced by cement type. CEM I concrete, which reaches the lowest saturation degrees compared to CEM V at a given relative humidity, shows less shrinkage. The proportion of saturated porosity in CEM V based material (i.e. submitted to capillary pressure) is higher than that of CEM I.

Due to higher stiffness (see section 2.5.), and less amount of water at a given relative humidity, the CEM I cement matrix shrinks less than CEM V under capillary pressure.

3.3 *Mass variation versus shrinkage*

Considering relative mass variation *vs* shrinkage, it is possible to see three successive phases.

At first a 'sleeping phase' corresponds to water loss near the sample surface, and to an early micro-cracking, which counterbalances shrinkage.

The second phase relates linearly mass variation to shrinkage, with the increase of capillary pressure.

The third phase, which presents an evolution of mass loss without any shrinkage evolution, is attrib-

uted either to micro-cracking around aggregates, or to a non-linear behavior of the cement matrix.

Figure 6 and 7 present drying shrinkage *vs* mass variation as a function of temperature, for CEM I and CEM V concretes respectively.
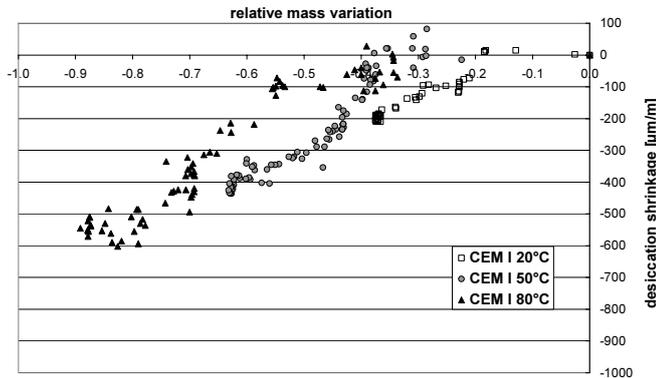

Figure 6. Drying shrinkage versus mass variation of CEM I concrete as a function of capillary pressure and temperature.
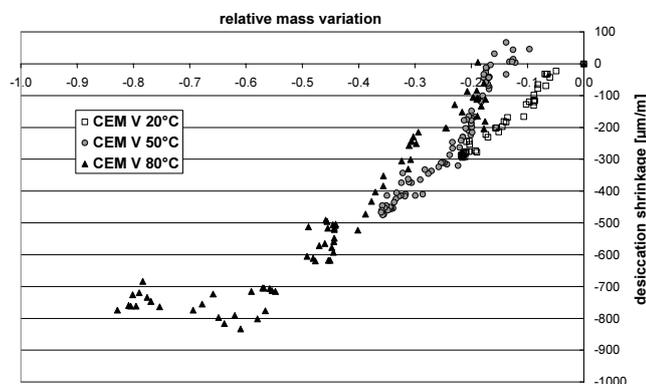

Figure 7. Drying shrinkage versus mass variation of CEM V concrete as a function of capillary pressure and temperature.

3.3.1 *Influence of temperature*

Results show the strong influence of temperature on the extent of the initial 'sleeping phase'. Shrinkage is greater with temperature increase (at 20°C: it is near 0.18% for CEM I concrete and 0.05% for CEM V, at 50°C the maximal value of the 'sleeping phase' shrinkage is about 0.37% for CEM I and 0.16% for CEM V material, and at 80°C it is nearly 0.4% for CEM I material and 0.19% for CEM V). This is due to thermal activation, which accelerates evaporation-diffusion processes: thermal activation induces an increase in water amount near sample surface, which can better evaporate (Choinska 2006).

The second linear phase confirms the influence of capillary pressure upon drying shrinkage. The increase of capillary pressure with temperature leads to more shrinkage deformations.

Finally, the third phase is only observed on the evolution of drying shrinkage at 80°C: it is equal to 500μm/m for CEM I concrete and to 700μm/m for CEM V. This phase present an increase in mass loss does not lead to continued shrinkage. Hence, we can confirm that variation of capillary pressure is not the main and single shrinkage mechanism. The creep thermal activation of CSH, which explains the difference in amplitude of shrinkage deformations with temperature, might be the additional mechanism responsible for this observation.

3.3.2 *Influence of composition*

Considering the same temperature, it is possible to compare concretes in terms of shrinkage, and hence, in terms of induced micro-cracking.

At first, it can be noticed that the second phase is in good agreement with previous results, namely that CEM I concrete has a higher mass loss and a lower shrinkage than CEM V at the same capillary pressure.

The initial 'sleeping phase' means that there is micro-cracking on the concrete surface. The CEM I has the higher 'sleeping phase', whatever the temperature is. Therefore, this concrete develops more micro-cracking on his surface than CEM V.

Micro-cracking around aggregates occurs during the third phase. This phase is more pronounced for CEM V material. Hence, this concrete is more micro-cracked around aggregates than CEM I.

4 CONCLUSIONS

Our results show that concrete drying is strongly dependent on temperature. Mass loss (water desorption process) and related shrinkage increase with temperature with a significant difference between 50°C and 80°C, compared to the difference between 20°C and 50°C.

The temperature increase leads to higher water vapor pressure, then the concrete water saturation degree is lower than at ambient temperature at a given relative humidity. Shrinkage deformations increase with temperature. Hence, the risk of micro-cracking increases with temperature (thermal deformation and drying). Results show that hydraulic behavior not only depends on capillary pressure but also, potentially, on a thermal activation of long-term creep of CSH.

Behavior of studied concretes subjected to drying is also influenced by cement type. Concrete made with a CEM V/A cement (blended cement: clinker/BFS/Fly ashes), presents a microstructure thinner than the porosity of a CEM I (pure clinker cement type) concrete. As a consequence, despite a higher total porosity, CEM V concrete is less permeable and less diffusive than CEM I concrete. Due to significant difference of the total pore volume and pore size distribution, CEM I material presents a lower water saturation degree during drying. CEM V concrete drying shrinkage is more important than CEM I concrete. This difference is due to a higher amount of water at given relative humidity drying and a less deformable matrix of the CEM V based

material, as shown by drained bulk modulus measurements.

As a conclusion, cement type as well as boundary conditions clearly show their influence on drying process and the physical consequences on concrete. Thus, in order to assess the mechanical long term behavior of concrete structures, these processes have to be taken into account.

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