



Contents lists available at ScienceDirect

## Cement and Concrete Research

journal homepage: [www.elsevier.com/locate/cemconres](http://www.elsevier.com/locate/cemconres)

## Effect of the hydration temperature on the pore structure of cement paste: Experimental investigation and micromechanical modelling

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## ARTICLE INFO

## Keywords:

Pore structure  
Water sorption isotherm  
BET isotherm  
C-S-H  
Porosity  
Homogenization  
Micromechanics

## ABSTRACT

The hydration temperature has a considerable effect on the microstructure of cement paste. The microstructural changes with increasing curing temperature result in a significant decrease of cement mechanical properties. The present work aims at studying these phenomena via micromechanical modelling, based on an experimental characterization of cement microstructure. The pore structure of a class G oil-well cement paste (American Petroleum Institute classification) hydrated at different temperatures, between 7 °C and 90 °C is characterized. Then, the influence of the microstructure variations on the elastic properties of the hardened paste is explored through micromechanical modelling. A previous analysis of the microstructure enabled determining the volume fractions of different phases of a class G cement paste hydrated under different temperatures [1]. A multiscale self-consistent homogenization model is used based on these results to simulate the variations of the mechanical properties with hydration temperature. The results are compared with macro-scale elastic properties obtained from uniaxial compression tests. It is shown that the increasing capillary porosity with elevating hydration temperature, is not sufficient to fully explain this drop of elastic properties. The latter originates mainly from the decrease of the elastic properties of the foam composed of the porous C-S-H intermixed with capillary pores. The pore structure analysis coupled with the micromechanical modelling permitted a back-analysis of the intrinsic porosities of high density and low density C-S-H showing an almost constant LD intrinsic porosity and a significantly decreasing HD intrinsic porosity.

### 1. Introduction

The pore structure is a key element in understanding the properties of cement paste such as the development of strength, creep and shrinkage phenomena and durability of cement based materials. The pore structure of cement paste and its mechanical properties are strongly influenced by the hydration temperature. This is particularly important for understanding the behavior of the cement sheath in oil-well constructions, in which the cement paste is hydrated under different hydration temperatures depending on the depth due to the geothermal gradient [2, 3]. The higher hydration temperature accelerates the initial gain of strength but results in lower mechanical properties of cement at later ages [4, 5]. The decrease of mechanical properties was attributed to the heterogeneous distribution of hydrates that leads to an increase of capillary porosity [6]. Gallucci et al. [7] and more recently Bahafid et al. [1] have demonstrated that this increase of capillary porosity is the result of an increasing density of C-S-H with hydration temperature. Although the effect of the hydration temperature on cement has been the subject of a considerable research, there

remains some non-investigated areas. Especially, a quantitative description of the pore structure of the two C-S-H phases (LD and HD C-S-H) and their variation with temperature are lacking. The purpose of this paper is to gain insight into the structure of C-S-H and to improve the understanding of the effect of hydration temperature on the pore structure, porosity and moisture properties of cement paste. The pore structure of cement is studied by a combination of Mercury porosimetry, Nitrogen sorption, water vapor sorption and scanning electron microscopy. Each of the above methods permits the identification of a pore size range within a cement paste. The puzzled picture of cement pore structure is reconstructed through the assemblage of different porosimetry methods (MIP, NAD, WVS, SEM). Micromechanical modelling together with the experimental characterization of the pore structure permit to provide quantitative and qualitative information on the variation of HD and LD C-S-H characteristics with hydration temperature. The originality of this article is to gather an intensive experimental study of the pore structure of cement paste hydrated under a broad range of temperatures, together with the micromechanical modelling in order to explore the effect of hydration temperature on the

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<https://doi.org/10.1016/j.cemconres.2018.06.014>

Received 26 September 2017; Received in revised form 14 June 2018; Accepted 15 June 2018  
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mechanical properties. It also provides quantitative information about the two C-S-H types (HD and LD C-S-H) at different temperatures. This study is conducted on a class G cement which is designated for oil well constructions. It is a continuation of extensive research for the characterization of the thermo-poro-mechanical and time dependent properties of this cement paste that have been evaluated experimentally and by micromechanical modelling in previous works of co-authors [3, 8–13], and more recently a detailed characterization of its microstructure under the variation of curing temperature [1].

## 2. Materials and methods

The characterization of the pore structure of hardened cement paste under different hydration temperatures is done here by a combination of several experimental methods: Mercury intrusion porosimetry, Nitrogen and water vapor sorption, scanning electron microscopy and uniaxial compression tests. The tested material and the experimental methods are briefly recalled below.

### 2.1. Materials

The cement paste samples were prepared using a class G cement at a water to cement ratio of 0.44 according to the standard API requirements and following the procedure described by Ghabezloo et al. [3]. After mixing, pastes were cured for 4 months at different temperatures, under lime-saturated water in sealed containers to avoid water evaporation and carbonation of specimens. The samples are cured at four different curing temperatures: 7 °C, 20 °C, 60 °C, and 90 °C. After four months of curing, the hydration process has been arrested using a freeze-dryer for experiments that require drying such as Nitrogen sorption and Mercury porosimetry. This technique has been chosen because of its relative rapidity and as it causes less damage to the microstructure compared to oven drying or methanol exchange [14]. It has been shown in a recent study of co-authors [1] that freeze drying is quite comparable to drying at 11% of relative humidity, showing that the freeze drying empties only the gel pores and leaves the interlayer spaces full of water with a monolayer of water covering the surface of the C-S-H. It should be mentioned that the growth of crystals during freeze drying and the applied stresses on the pore walls may potentially result in some damage of the microstructure and affect the porosity and pore size distribution. However, as mentioned before, this potential damage is less important comparing to oven drying or methanol exchange [14].

### 2.2. Methods

#### 2.2.1. Mercury intrusion porosimetry

Mercury porosimetry (MIP) is a common method for studying the porous structure of materials. It owes its popularity to the properties of the injected fluid (Mercury) which has a high surface area making it a non-wetting fluid. However, when increasing the pressure Mercury can enter the pores. The application of the Washburn equation for a cylindrical geometry together with the measurement of the injected Mercury volume up to a certain pressure, enable constructing the cumulative pore volume and the pore size distribution.

$$P_{HG} = \frac{4\gamma \cos(\theta)}{d} \quad (1)$$

where  $\gamma$  is the surface tension of Mercury (0.485 N/m),  $\theta$  the contact angle between Mercury and the pore surface ( $\theta = 130^\circ$ ) [15, 16], and  $d$  is the pore diameter in (m). The porosimeter used in this study is an AutoPore IV 9500 from Micrometrics reaching a maximum pressure of 230 MPa corresponding to a pore size of 6 nm.

#### 2.2.2. Nitrogen sorption

Nitrogen adsorption and desorption (NAD) is a prominent method

for studying the pore structure of materials. It has the advantage to cover the range of radii between 1 nm and 60 nm. The method relies on recoding the quantity of adsorbed or desorbed Nitrogen at different relative pressures, yielding a Nitrogen isotherm. It usually serves for determining the specific surface area of cement pastes. However, if interpreted properly it can provide other useful information about cement pore structure. NAD experiments require pretreatment of tested samples to enable adsorption of the Nitrogen. It is shown that these experiments are very sensitive to drying methods and results vary depending on the amount of moisture removed by each drying method [17, 18]. Juenger et al. [18] have compared oven drying, d-drying and methanol exchange followed by d-drying and shown that the d-drying is the most consistent and reliable drying method. The methanol causes significant variation in the measured parameters and the oven drying does not capture well the variation of the measured parameters. In this study, we used freeze drying which is similar but more gentle than d-drying. Korpa et al. [19] also found that freeze-drying is a good method for drying cement pastes destined to BET experiments.

#### 2.2.3. Water vapor sorption

Water vapor sorption isotherm corresponds to the plot of water content against the relative humidity RH. Its serves for determining the bulk porosity of cement paste and the porosity of the C-S-H phase, the moisture content at different relative humidities and the specific surface area [20, 21]. The water sorption isotherms were collected here through the gravimetric method. The experiments correspond to equilibrating specimens in a sealed desiccator at a given relative humidity. The RH within a desiccator is controlled by saturated salt solution in isothermal conditions ( $T = 20^\circ\text{C}$ ) as described in Table 1. Specimens used for water vapor sorption were wet sawed from cylinders cured under water in sealed conditions to prevent external pre-drying. Thin specimens of 4 to 5 mm of thickness were prepared in order to reach equilibrium quickly following the work of Baroghel-Bouny [20, 21]. The samples are equilibrated at a given relative humidity for at least six months, and then a step by step adsorption curve is collected.

#### 2.2.4. BJH method

The pore size distribution of materials can be obtained from the sorption isotherm through the derivation of the cumulative pore volume with respect to the pore size. Several algorithms exist for the extraction of pores sizes, among which the Barrett-Joyner-Halenda (BJH) method [22, 23] is the most used for determining the pore size distribution. The desorption isotherm is commonly used for those calculations because its thermodynamic equilibrium is nearly complete [23]. Other researchers consider the adsorption isotherm for the characterization of the pore structure [24]. The basic equation used for the extraction of pore sizes is the Kelvin equation. This equation gives the radius of a pore into which capillary condensation occurs at a certain relative pressure:

**Table 1**

Relative humidity controlled by saturated salt solutions at ambient temperature.

Saturated salt solution		
Name	Formula	Relative humidity
Lithium chloride	LiCl	11%
Potassium acetate	CH <sub>3</sub> CO <sub>2</sub> K	20%
Magnesium chloride	MgCl <sub>2</sub>	33%
Potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	44%
Magnesium nitrate	MgN <sub>2</sub> O <sub>6</sub>	55%
Sodium chloride	NaCl	75%
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	81%
Sodium sulfite	Na <sub>2</sub> SO <sub>3</sub>	95.5%

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