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Experimental study on a mortar. Temperature effects on porosity and permeability. Residual properties or direct measurements under temperature

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Abstract

This study is a part of a large experimental program intended to characterize the effects of increasing temperature upon the hydraulic properties of cement based materials. Initial gas permeability and porosity values of the used material, a normalized mortar with a water/cement ratio of 0.5, clearly show the material homogeneity after a drying phase at 60 °C. The initial permeability is moreover insensitive to confining pressure variation which is evidence of the absence of significant initial micro-cracking in which the flow could occur. Residual properties (at room temperature) were measured after thermal treatments at 150 or 250 °C. These heating phases lead to a clear increase in porosity and permeability being sevenfold its initial value after a 250 °C treatment. This increase in permeability comes from two distinct effects that can be experimentally highlighted: a pore widening observed with the Klinkenberg effect being lower and a micro-crack closure occurring with the increase in confining pressure. Permeability was also measured with gas injection in samples submitted to thermal loading and slightly confined (at 4 MPa). Three levels of temperatures were used: 25, 105 and 200 °C; in a first stage the permeability remained almost constant to finally significantly increased at 200 °C. At 105 °C there is a widening of pores observed with the Klinkenberg effect but not sufficient to vary the permeability. At 200 °C micro-cracks have occurred but their influence upon permeability is lower than for treated material. This is an effect of the confining pressure applied on the material during heating.

Keywords: Permeability; Thermal treatment

1. Introduction

Materials used in the civil engineering area are sometimes submitted to high level of temperature. This is particularly the case for the nuclear industry which has produced radioactive wastes characterized by the important quantity of heat that they can generate over decades. Thus, the structures designed to store these wastes may be subjected to increase in temperature up to 200/250 °C [1]. As cement based materials are most often used for waste conditioning and containers as also as impermeable barriers, it is of particular interest to evaluate the changes in permeability and diffusivity properties of such heated materials. The main objective of this experimental study is to evaluate the effect of high level temperatures upon the gas permeability of a mortar. Two types of permeability tests were performed either at room temperature on previously heated materials (up to 250 °C) or under temperature up to 200 °C. In the second case, a cell was used which has been specially designed for that purpose. In the first part, this paper presents results of experiments carried out on mortars that have been heated up to two temperatures, 150 or 250 °C. The measurements were performed at different values of gas pressure and/or at different levels of confining pressure. Complementary information is provided with classical porosity measures under vacuum conditions.

Very few data are available on permeability measurements of cementitious material under temperature and they

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are mainly concerned with water permeability measures up to a temperature close to 100 °C. In this case, the injected water may lead to further dissolution/precipitation phenomena from which the porous network modifies.

The second part of this paper is devoted to permeability measurements undertaken on mortars that were continuously heated along with gas injection. The gas, pure argon, is chemically inactive thus does not interact with the cement matrix. As a result, micro-structural modifications due to temperature increase will be more easily detected with gas permeability variations.

2. Effects of temperature on cementitious materials

The micro-structural modifications of cement based materials, which occur with temperature increase, are mainly due or influenced by the loss of water. Two major phenomena have to be considered: physical–chemical transformations and thermal strains. Up to a level of 250 °C which is the maximum temperature reached in our study, the main following effects can be underlined [2,3]:

- Between 30 and 120 °C, there is a loss of free water and of a part of adsorbed water. At 120 °C, the non-bounded water is totally lost.
- Between 180 and 300 °C, the first steps of CSH gel desiccation are observed which comes from the loss of bounded water.

According several researchers [4,5], desiccation of CSH gel occurs from 105 °C and beyond. This is evidence that the whole phenomenon is not completely understood or described. Moreover, heated mortars and concretes are concerned with strain incompatibilities of their constituents [6]. Aggregates always expand upon heating [2] whereas cement paste expands until 150 °C then shrinks over this level. This shrinkage is attributed to the loss of bounded water [7] and, as a consequence, micro-cracks occur with a possible effect on porosity and permeability. Most of the related effects of temperature upon cementitious material properties derive from residual characteristics measurements (i.e. after thermal treatment). Numerous studies can be found on mechanical properties of concrete [8–11], mortars [12] and pure cement paste [13]. Residual porosity is often measured to evaluate the thermal treatment effect on microstructure [14,15]. The combination of strain incompatibilities and physical–chemical phenomena leads to a deep modification of the porous network which results in an increase in total porosity and a smoother distribution of pore sizes [3,16]. Pores become larger or are created by thermal micro-cracking [2]. As strain incompatibilities concern cement paste and aggregates, it is consistent to observe higher changes in mortar capillary porosity than in pure cement paste [3]. As for porosity, results on permeability are mainly derived from residual permeability measurements. Farage [1] has measured the permeability variations of a cement paste treated up to 300 °C. Despite clear pore structure modifications, the gas permeability did not reveal significant variations in the range of 80–300 °C. Increases in permeability of mortar and concrete are obviously more pronounced as it was shown in [3]. A one order of magnitude variation was found for samples treated at 400 °C compared with those treated at 100 °C which was in good agreement with observed pore structure modifications of the same materials. In fact permeability is known to be more sensitive to micro-cracks aperture and connection than to increases in pore sizes. Therefore micro-cracking is more likely to occur in mortar and concrete than in pure cement past. As mentioned above, results, relative to permeability measures under temperature, were mostly obtained with water injection into concrete up to 100 °C [17]. In this case, dissolution–precipitation phenomena led to a decrease in permeability due to the self-healing of micro-cracks and a pore size reduction.

3. Material and experimental procedures

3.1. Material

The experiments were undertaken on a normalized mortar with a water/cement (W/C) ratio of 0.5 (European Norm EN 191-1). This material has been used for numerous studies performed in our laboratory [18]. Compounds of the mortar are given in Table 1. Beams were cast at the same time (1 m length and 150*150 mm^2 cross section) and preserved from desiccation with plastic sheets until stripping at 48 h. They were then stored at 20 °C in water saturated with lime for 2 years. Cylindrical samples (37 mm in diameter and 70 mm high) were cored from beams and used for permeability and porosity measurements. Even if not under discussion here, the main characteristics of this mortar were an isotropic behaviour, a mean Young modulus and Poisson ratio of, respectively, 32,000 MPa and 0.15.

3.2. Experimental procedures

Two types of gas permeability tests were used for the study. Micro-pulse tests [19] were undertaken on thermally treated specimens (residual property). For a complete description of this test which is a transient method see also Ref. [20]. Measurements carried out under temperature were based on a “quasi permanent” flow rate of gas. This method

Table 1
Compounds of the used mortar with W/C=0.5

Compounds	Mass proportion (kg)	Volume proportion (%)
Normalized sand (Leucate)	1350	58
CPJ-CEM II/B 32,5R cement	450	16
Water	225	26

was developed and validated in numerous cases in our Laboratory [21]. A new cell has been specially designed for this study (Fig. 1). This apparatus allows gas permeability measurements under temperature, up to 200 °C and under confining pressure which was fixed at 4 MPa for the whole set of tests. A complete description of the cell can be found in Ref. [22].

3.3. Residual permeability measures

In a first step, it was necessary, to evaluate a thermal treatment effect, to choose a reference state of the material. It was thus decided to heat the material at a reference temperature of 60 °C until constant weight. This value is considered (in accordance with a number of tests performed in our laboratory) as a reference as it causes evaporation of the free porous water without any notable effect on the CSH gel. A first set of tests was then carried out on the dried (at 60 °C) material to compare the measures with values obtained after heating at 150 or 250 °C. A preliminary study was carried out to determine the necessary heating time for samples to be at constant weight, time which was 10 h whatever the temperature of treatment. The rate of temperature variation was fixed at 1 °C/mn during the increase or decrease phases. After a complete cycle of heating, samples were preserved from re-saturation in water proof plastic bags then prepared to be tested as described below:

- Classical porosity tests under vacuum conditions with ethanol as saturating fluid. This liquid, considered to be neutral with the cement matrix [21], does not perturb porosity measures.
- Gas permeability measurements at room temperature.

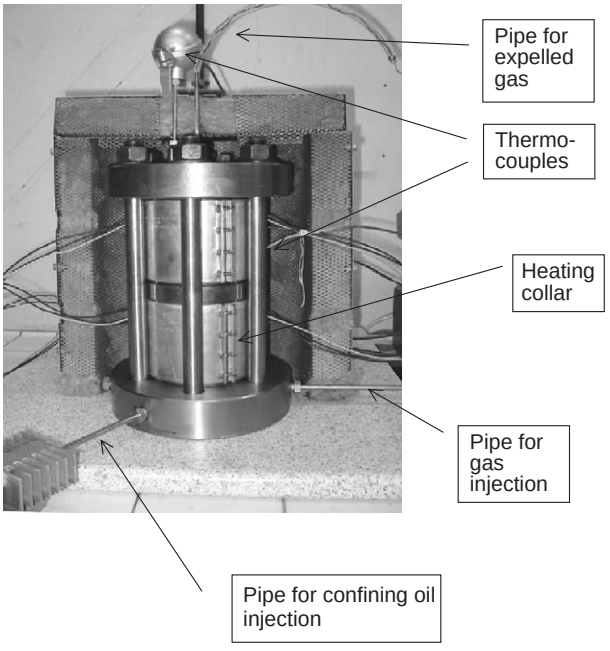

Fig. 1. Picture of the cell specially designed for tests under temperature.

Table 2
Variation of porosity due to thermal treatments

Sample n°	Initial porosity (%)	Porosity after 150 °C	Porosity after 250 °C
1	14	15.3	–
2	14.3	15.7	–
3	13.7	16.3	–
4	14.7	16	–
5	14.2	–	16.8
6	14	–	16.8
7	13.3	–	16.7
8	13.7	–	17.3
Mean value	14	15.8	16.9

3.4. Measurements under temperature

The material, previously dried at 60 °C, was tested at three different temperatures: 25, 105 and finally at 200 °C. It would have been preferable to heat until 250 °C which is the ultimate limit of our experimental apparatus. It was however decided to remain in the range 20–200 °C for safety reasons. Preliminary steps had shown that a waiting time, for 8 h at 105 or 200 °C, was necessary prior to gas permeability measure. The cell was heated with heating collars (Fig. 1) and temperature was regulated with two thermo-couples located between the collars and the cell and inside the cell.

4. Results of residual property measurements

The first step had consisted in measuring the material porosity. The samples used were cylinders 37 mm diameter

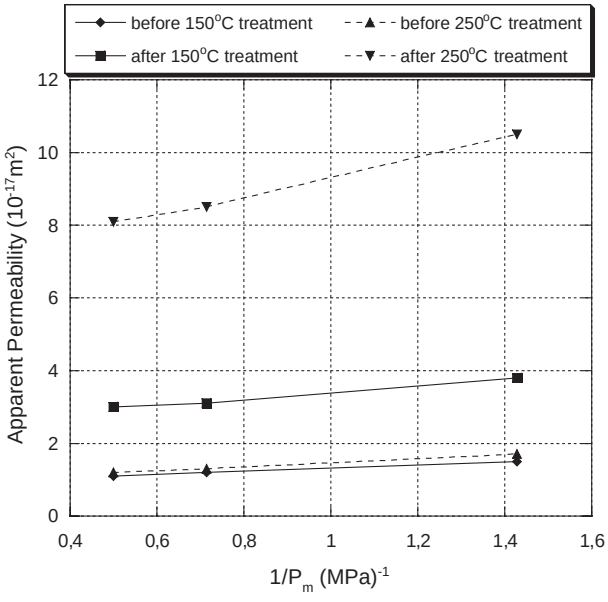

Fig. 2. Effects of the thermal treatment and of the mean gas pressure on the apparent permeability values.

Table 3
Apparent and intrinsic permeability variations due to thermal treatment

Permeability	Before and after 150 °C treatment		Before and after 250 °C treatment	
	Before	After	Before	After
K_a (P_m=2 MPa)	1.1 10^{-17} m^2	3.0 10^{-17} m^2	1.2 10^{-17} m^2	8.1 10^{-17} m^2
K_a (P_m=1.4 MPa)	1.2 10^{-17} m^2	3.1 10^{-17} m^2	1.3 10^{-17} m^2	8.5 10^{-17} m^2
K_a (P_m=0.7 MPa)	1.5 10^{-17} m^2	3.8 10^{-17} m^2	1.7 10^{-17} m^2	10.5 10^{-17} m^2
K	0.88 10^{-17} m^2	2.5 10^{-17} m^2	0.92 10^{-17} m^2	6.7 10^{-17} m^2
β	0.49 MPa	0.36 MPa	0.58 MPa	0.39 MPa

Influence on Klinkenberg effect. K_a is apparent permeability and K intrinsic permeability.

and 20 mm length. Eight cylinders were thus cut from several of the cores mentioned before, then dried at 60 °C and tested to obtain a mean 14% porosity value (Table 2). It can be underlined here that it is the connected porosity which was measured. These reference values (see Table 2) show a quite slight scattering which is proof of the mortar homogeneity. From this series of samples, four were then treated at 150 °C and four at 250 °C and tested again. Results in Table 2 indicate a clear increase in porosity as the main values are now 15.8% for samples treated at 150 °C and 16.9% for those treated at 250 °C. This is evidence of the mortar sensitivity to temperature and deep modifications of its porous structure.

Cylinders of 37 mm diameter and 70 mm length were accommodated to measure the gas permeability with a view on the mean gas pressure role (static pressure) and the effects of confining pressure which is also useful to ensure tightness. Tests were carried out by a micro-pulse test technique [20] developed and used in our laboratory. The mean injected gas pressure acts on the Klinkenberg effect [23] in which the constant β (known as Klinkenberg factor) is involved. It allows the effect to be taken into account in calculating the intrinsic permeability K with:

$$K_a = K\left(1 + \frac{\beta}{P_m}\right) \quad (1)$$

where K_a is the apparent permeability and P_m the mean gas pressure in the sample. Much of the interest in measuring β stems from the macroscopic information, relative to the porous structure modification, which is derived from this parameter variation induced by the thermal treatment. Thus, at a given mean pore gas pressure, β is directly linked with the pore size i.e. β increases if the mean pore size decreases. Three levels of static pressure were considered to measure the apparent permeability of the "intact" material (dried at 60 °C) and after both thermal treatments. They were fixed at P_m=2, 1.4 or 0.7 MPa. The influence of P_m changes can be seen in Fig. 2 in which the initial permeability results (intact samples) confirm the material homogeneity. For both samples, the thermal treatment leads to a clear increase, according to the level of heating, of the apparent permeability K_a. The intrinsic permeability K and β values, presented in Table 3, can be deduced from these results and relation (1). As already mentioned, the initial values of K are virtually identical whereas a significant increase in K and a decrease in β occur with temperature of treatment. These observations, in agreement with porosity variations, may be the result of two simultaneous phenomena: a pore widening due to desiccation (or more free space for the flow) and a micro-cracking. The decrease in β is probably linked with the pore widening whereas the K variation is linked with both phenomena. It is thus of interest to apply different confining pressures on the sample as it is well known that if micro-cracks are present, their closure due to hydrostatic pressure will lead to a decrease in permeability. On the other hand, permeability of non-cracked porous medium is quite insensitive to confining pressure variations—see for example Ref. [22]. Increase in confining pressure results in effects plotted in Fig. 3 and tabulated in Table 4. The intact sample is almost insensitive to the confining pressure and the initial value of K_a (measured at 4 MPa

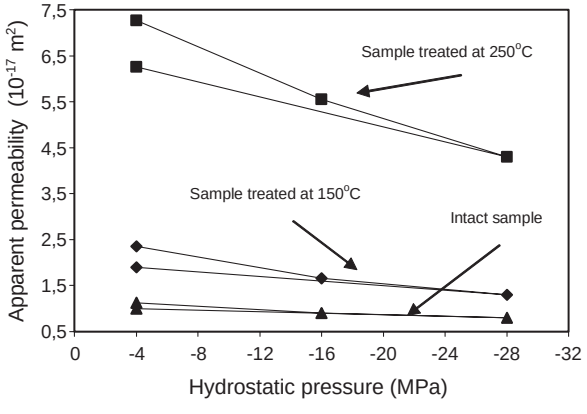

Fig. 3. Variation of the apparent permeability due to hydrostatic loading and unloading. Intact or treated samples.

Table 4
Variation of the apparent permeability due to the confining pressure

Confining pressure (MPa)	Apparent permeability		
	Intact sample (m^2)	Sample heated at 150 °C (m^2)	Sample heated at 250 °C (m^2)
4	1.1 10^{-17}	2.4 10^{-17}	7.3 10^{-17}
16	0.9 10^{-17}	1.7 10^{-17}	5.5 10^{-17}
28	0.8 10^{-17}	1.3 10^{-17}	4.3 10^{-17}
4 (after unloading)	1.0 10^{-17}	1.9 10^{-17}	6.3 10^{-17}

Static pressure P_m is 2 MPa.

hydrostatic loading) is restored after a complete cycle. However these effects are more pronounced as the temperature treatment has been increased. This is due to the closure of micro-cracks induced by thermal treatment. Moreover, after a loading–unloading cycle, it can be observed an irreversible closure of cracks accentuated with the level of temperature.

As a partial conclusion, it can be assessed that two phenomena are present: widening of pore (see the β decrease) and micro-cracking (effect of confining pressure). Both lead to a clear increase in porosity and permeability.

5. Results of measurements under temperature

The confining pressure was maintained at a constant 4 MPa level since three temperatures were successively applied (25, 105 and 200 °C). The injected gas pressure (P_{inj}) was either 1 or 1.5 MPa to calculate the intrinsic permeability (i.e. correction with the Klinkenberg effect). As the downstream side of the sample is freely drained, at atmospheric pressure P_o, the mean pressure P_m is $P_m = 0.5 \times (P_{inj} + P_o)$. The results are presented in Fig. 4 and in Table 5 in which it is of interest to firstly observe that the permeability remains almost constant up to 105 °C. Permeability can be here either apparent or intrinsic. There is however a slight decrease of β which drops from 0.51 to 0.35. That can be interpreted through the desiccation phenomenon and the evaporation of free water leading to a pore widening however not sufficient to notably modify the permeability. Hence, a very clear increase in permeability takes place at 200 °C. This is attributed to micro-cracks which occur at this temperature level and become connected. Moreover, the Klinkenberg coefficient is now 0.13 MPa that is evidence of a significant widening of pores. Comparisons with the measures of residual properties show that the intrinsic permeability measured at 200 °C is lower than those obtained after thermal treatments at 150 or 250 °C. This is proof that the micro-cracking phenomenon is slighter in the case of direct measurement under temperature. This can be easily explained by an effect of confining pressure (4 MPa during the heating) that lessens micro-crack development. That was also reported in Wong [24].

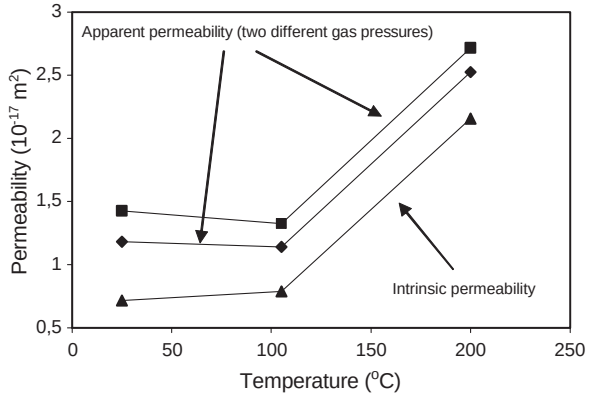

Fig. 4. Variations of apparent and intrinsic permeability with temperature. Measures carried out under thermal loading.

Table 5
Variation of apparent or intrinsic permeability and of Klinkenberg factor in the range 25–200 °C

Temperature (°C)	K_a (P_{inj}=1.0 MPa) (m^2)	K_a (P_{inj}=1.5 MPa) (m^2)	K (m^2)	β (MPa)
25	$1.4\ 10^{-17}$	$1.2\ 10^{-17}$	$0.7\ 10^{-17}$	0.51
105	$1.3\ 10^{-17}$	$1.1\ 10^{-17}$	$0.8\ 10^{-17}$	0.35
200	$2.7\ 10^{-17}$	$2.5\ 10^{-17}$	$2.1\ 10^{-17}$	0.13

P_{inj} is the injection pressure.

6. Conclusion

Gas permeability measures are of interest to investigate structural modifications of cement based material as the chosen gas (Argon U) is chemically inert with cement matrix which is not the case for water. In the present study these measurements were used to evaluate the heating effects upon a mortar which can affect either residual properties (porosity and permeability) or permeability under temperature. Large micro-structural modifications were induced as desiccation phenomena and thermal strains of constituents occur with temperature increase. As they lead to micro-cracking and widening of pores, a very clear increase either in apparent or in intrinsic permeability was measured after thermal heating at 150 or 250 °C. This increase was confirmed with porosity measures. The growth of pore sizes in relation with temperature was observed by a continuous decrease of the Klinkenberg coefficient whereas a significant micro-cracking was detected for samples treated at 250 °C. This was highlighted by a hydrostatic loading which led to a sensible decrease in permeability (i.e. closure of cracks). This closure is partly irreversible as the permeability remains lower than the initial value after the sample is unloaded.

A cell, specially designed for this study, allowed the gas permeability to be measured under temperature. Three measures were performed at 25, 105 and 200 °C on an initially dried material. The intrinsic permeability remained almost constant up to 105 °C then increased at higher levels. At 200 °C the gas permeability was threefold the initial value since the residual value, measured after a treatment at 250 °C, was sevenfold the initial value. The difference may come from an effect of confining pressure which was applied during the direct measurements and therefore lessened the micro-cracking development. Nevertheless there was a decrease in the Klinkenberg effect which occurred as the temperature was increased. This is evidence that structural modifications are preponderant relatively to thermal agitation of gas molecules that would lead to an increase of that effect. The continuous decrease in the Klinkenberg coefficient indicates a significant widening of pores induced by evaporation and loss of bounded water.

References

[1] M.C.R. Farage, J. Sercombe, C. Gallé, Rehydration and microstructure of cement paste after heating at temperatures up to 300 °C, Cement and Concrete Research 33 (2003) 1047–1056.

[2] A. Noumowé. Effet des hautes températures (20–600 °C) sur les bétons, cas particulier du béton à hautes performances, Thèse de doctorat (PhD Thesis in French), INSA Lyon, 1995.

[3] M. Tsimbrovska. Dégradation des bétons à hautes performances soumis à des temperatures élevées, évolution de la perméabilité en liaison avec la microstructure, Thèse de doctorat (PhD Thesis in French), Université Grenoble 1, 1998.

[4] T.Z. Harmathy, Thermal properties of concrete at elevated temperatures, ASTM Journal of Materials 5 (1970) 47–74.

[5] R. Lachaud, Le comportement du ciment à la chaleur : étude de l'évolution d'une alite hydrate dans la gamme de température 20–400 °C, Matériaux et Constructions 1 (1968) 365–378.

[6] S.D. Venecanin, Thermal incompatibility of concrete components and thermal properties of carbonate rocks, ACI Materials Journal 87 (1990) 602–607.

[7] C.R. Cruz, M. Gillen, Thermal expansion of Portland cement paste, mortar and concrete at high temperatures, Fire and Materials 4 (1980) 66–70.

[8] X. Luo, W. Sun, Y.N. Chan, Effect of heating and cooling regimes on residual strength and microstructure of normal strength and high-performance concrete, Cement and Concrete Research 30 (2000) 379–383.

[9] Y.N. Chan, G.F. Peng, M. Anson, Residual strength and pore structure of high-strength concrete and normal strength concrete after exposure to high temperatures, Cement and Concrete Composites 21 (1999) 23–27.

[10] C.S. Poon, S. Azhar, M. Anson, Y.L. Wong, Comparison of the strength and durability performance of normal- and high-strength pozzolanic concretes at elevated temperatures, Cement and Concrete Research 31 (2001) 1291–1300.

[11] G.T.G. Mohamedbhai, Effect of exposure time and rates of heating and cooling on residual strength of heated concrete, Magazine of Concrete Research 38 (1986) 151–158.

[12] M.S. Culfik, T. Ozturan, Effect of elevated temperatures on the residual mechanical properties of high-performance mortar, Cement and Concrete Research 32 (2002) 809–816.

[13] R. Sarshar, G.A. Khoury, Material and environmental factors influencing the compressive strength of unsealed cement paste and concrete at high temperatures, Magazine of Concrete Research 45 (1993) 51–61.

[14] V. Vydra, F. Vodak, O. Kapickova, S. Hoskova, Effect of temperature on porosity of concrete for nuclear-safety structures, Cement and Concrete Research 31 (2001) 1023–1026.

[15] F.S. Rostasy, R. Weib, G. Wiedemann, Changes of pore structure of cement mortars due to temperature, Cement and Concrete Research 10 (1980) 157–164.

[16] J. Piasta, Z. Sawicz, L. Rudzinski, Changes in the structure of hardened cement paste due to high temperature, Matériaux et Constructions 100 (1984) 291–296.

[17] H.W. Reinhard, M. Jooss, Permeability and self-healing of cracked concrete as a function of temperature and crack width, Cement and Concrete Research 33 (2003) 981–985.

[18] I. Yurtdas. Couplage comportement mécanique et dessication des matériaux à matrice cimentaire : étude expérimentale sur mortiers, Thèse de Doctorat (PhD Thesis in French), Université Lille 1, 2003.

[19] F. Skoczylas, O. Coussy, Z. Lafhaj, Sur la fiabilité des mesures des perméabilités hétérogènes par injection de gaz. Micro-pulse tests, Revue Française de Génie Civil 7 (2003) 451–469.

[20] E. Dana, F. Skoczylas, Gas relative permeability and pore structure of sandstones, International Journal of Rock Mechanics and Mining Sciences 36 (1999) 613–625.

[21] H. Loosveldt-Claudot, Z. Lafhaj, F. Skoczylas, Experimental study of gas and liquid permeability of a mortar, Cement and Concrete Research 32 (2002) 1357–1363.

[22] M. Lion. Influence de la température sur le comportement poromécanique ou hydraulique d'une roche carbonate et d'un mortier. Etudes expérimentales, Thèse de Doctorat (PhD Thesis in French), Université Lille 1, 2004.

[23] L.J. Klinkenberg, The permeability of porous media to liquids and gases, API Drilling and Production Practices, 1941, pp. 200–213.

[24] R.H.C. Wong, K.T. Chau, P. Wang, Microcracking and grain size effect in Yuen long marbles, International Journal of Rock Mechanics and Mining Sciences 33 (1996) 479–485.