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The influence of water absorption and porosity on the deterioration of cement paste and concrete exposed to elevated temperatures, as in a fire event

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ABSTRACT

This study investigates why CaO rehydration causes total strength loss of OPC paste compared to only 65% loss of OPC concrete after 800 °C exposure. Subsequent water sorptivity tests revealed paste reacted instantaneously with water, completely disintegrating within minutes. This was attributed to an accelerated rehydration of CaO into $CaOH_2$. This was not observed in concrete. Sorptivity tests using acetone eliminated the disintegration due to CaO reaction with water. Porosity tests indicated a higher porosity and coarser capillary pore size distribution (PSD) in paste compared to paste in concrete. This has an influence on the rate of water absorption. The rate of water absorption determines the CaO rehydration rate and ultimately the growth rate of $CaOH_2$ crystals and type of $CaOH_2$ crystals formed. Different types of $CaOH_2$ crystals cause different levels of deterioration, not always leading to total disintegration. Therefore, the rate of water absorption is the determining factor controlling the extent of deterioration caused by CaO rehydration.

1. Introduction

The behaviour of cement paste and concrete after exposure to elevated temperatures, as in a fire event, has been of interest to many researchers for decades. One of the first studies was conducted by Lea [1] in 1920.

When concrete is subjected to high temperatures, physical and chemical transformations take place resulting in deterioration of its mechanical properties [2]. A common way of investigating those physical and chemical transformations is by dividing the investigation into two steps: (i) the cement paste and (ii) the concrete as a whole, i.e. paste, aggregates and the interface between paste and aggregate.

Investigating (i) the cement paste, Lea and Stradling [3] reported that one product of hydration of ordinary Portland cement (OPC) paste is calcium hydroxide ($CaOH_2$). This compound decomposes at about 400 °C into calcium oxide (CaO) and water. In addition, they proposed that the high loss of water that occurs between 300 and 500 °C is due to the dehydration-dissociation of $CaOH_2$.

Dias et al. [4] reported that although no initial signs of distress were visible on OPC pastes heated to 400 °C or above and cooled to room temperature, all specimens exhibited severe cracking to the point of disintegration after a few days. According to Petzold and Rohrs [5], the reason for this cracking is the expansive, and hence disruptive, rehydration (due to reaction with airborne water vapour) of previously dissociated $CaOH_2$ which is accompanied by a 44% volume increase.

Studies by the authors revealed similar findings [6,7]. The critical temperature of 400 °C for OPC pastes was confirmed. Above this temperature OPC pastes presented total strength loss due to dehydration of $CaOH_2$ and rehydration of CaO. However, dehydration of $CaOH_2$ and rehydration of CaO had no impact in pastes where OPC was partially replaced with ground granulated blast furnace slag (slag), a by-product of the iron blast furnace industry. This is illustrated in Fig. 1. During hydration slag consumes most of the available $CaOH_2$, consequently reducing or even eliminating the negative effects caused by $CaOH_2$ dehydration and subsequent CaO rehydration when cement paste is submitted to elevated temperatures. The compressive strength of OPC and 50% slag pastes after exposure to temperatures up to 800 °C is presented in Fig. 2.

Following the investigation of cement paste, Lea and Stradling [8] assessed the effects of elevated temperatures on (ii), concrete as a whole. Their work stated that specimens of OPC concrete made with Rowley Rag aggregate (volcanic dolerite stone) exposed to 700 °C crumbled to pieces 6 days after the heat treatment.

Khoury [9] stated that, following Lea and Stradling, it was recognised that the $CaOH_2$ problem could be the Achilles' heel of concrete in high temperature applications.

Moreover, other researchers reported strength loss of OPC concrete when submitted to temperatures as high as 1200 °C, but no significant disintegration or crumbling were reported [10–13]. In

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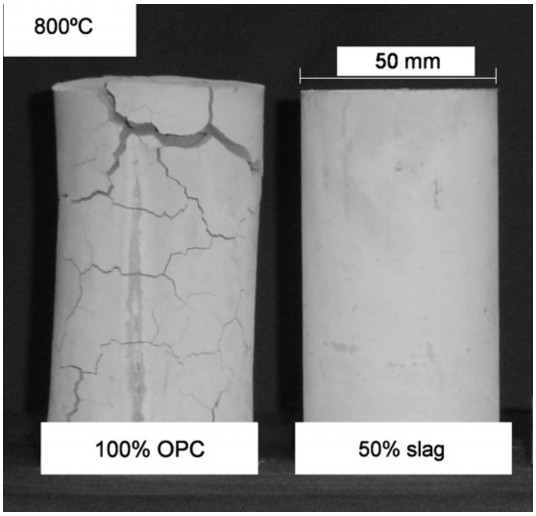

Fig. 1. OPC and 50% slag pastes after exposure to 800 °C.

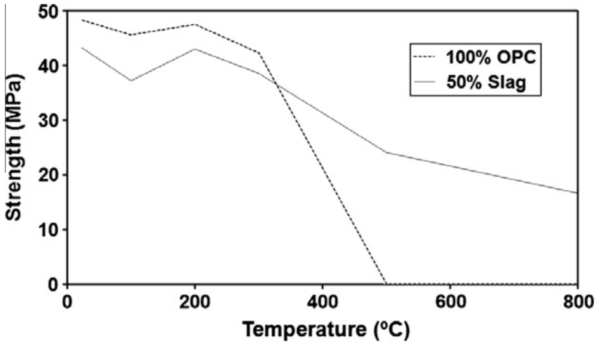

Fig. 2. Compressive strength of OPC and 50% slag pastes at different temperatures.

addition, Khoury [9] affirmed that there was scope for improvement within the temperature range of 300–600 °C. In 2000, Khoury [2] suggested that the deterioration of the mechanical properties of concrete can be reduced by judicious design of concrete mix, with the choice of aggregate possibly being the most important factor. Flint or Thames gravel is said to break up at relatively low temperatures (<350 °C), while granite is expected to exhibit thermal stability up to 600 °C. Basalt aggregate was reported not to undergo phase changes at temperatures up to 800 °C [2,14].

The authors have also performed tests on concrete [15]. The concrete specimens were made with the same OPC cement and slag blends as used in which OPC pastes disintegrated [15]. The coarse aggregate used was basalt, as described above as having high thermal stability. Fig. 3 presents the residual compressive strength for the OPC and 50% slag concretes after exposure to 800 °C followed by either furnace or water cooling. It was found that even though dehydration of $CaOH_2$ and rehydration of CaO occurred as determined by infrared spectroscopy (IR), the OPC concrete did not disintegrate or crumble, even months after the heat treatment.

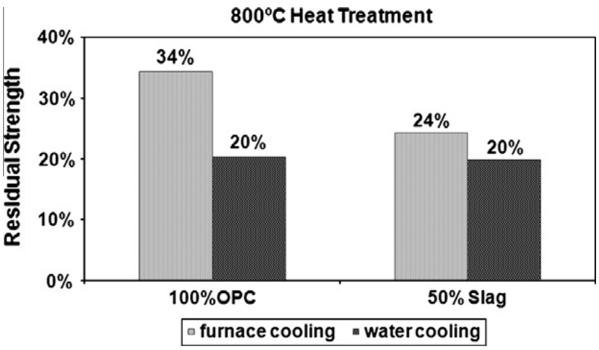

Fig. 3. Residual strength of OPC and OPC/slag concretes after exposure to 800 °C.

The authors have also reported the long-term effects of the CaO rehydration on OPC pastes [7]. It was reported that 1 year after exposure to 800 °C, the OPC paste has been reduced to a powder. This was confirmed to be due to continuous rehydration of CaO via airborne water vapour throughout the year. Based on that, it is thus expected that the OPC cement paste in the concrete would disintegrate, even if over longer time periods, independently of the thermal stability of the aggregate. However, it is clear from the discussion above that after exposure to elevated temperatures, the OPC paste test results does not represent the same deterioration behaviour of the OPC paste present in concrete.

Therefore, the present work aims to identify why the dehydration of $CaOH_2$ and rehydration of CaO is not detrimental for the OPC paste in concrete as it is for an OPC paste specimen (Fig. 1). The study investigates differences in the dehydration/rehydration process of cement paste and concrete and focuses on distinguishing differences in how the water is absorbed by the cement paste and concrete subsequent to heating. Firstly, water sorptivity tests were conducted. Secondly, sorptivity tests using a solvent (acetone) instead of water were performed, which is supposed to cause no damage to the specimens due to reaction of water and CaO. Thirdly, an attempt to determine the porosity of the pastes and concretes using a solvent was made. Afterward, nitrogen adsorption was performed to provide information regarding the pore size distribution of the specimens. Discussion of each technique is presented in the relevant sections.

2. Materials and methods

2.1. Paste

Ordinary Portland cement (OPC) and ground granulated blast furnace slag (GGBFS or "slag") conforming to the requirements of Australian Standard AS 3972 were used as binder materials. The chemical composition and properties of the binders are presented in Table 1. The OPC used in this study has a low C_3A content of <5%. In this investigation OPC was partially replaced (i.e. 50% by weight) with slag. The term water/binder (*w*/*b*) ratio is used instead of the

Table 1
Chemical composition and properties of the binders.

Constituent/property (%)	OPC	Slag
SiO_2	19.90	32.5
Al_2O_3	4.70	13
Fe_2O_3T	3.38	0.22
MgO	1.30	5.47
CaO	63.93	42.1
Na_2O	0.17	0.21
TiO_2	0.245	1.08
K_2O	0.446	0.25
MnO	0.079	0.43
P_2O_5	0.063	bd[a]
SO_3	2.54	4.1
LOI	2.97	0.35
Fineness (m^2/kg)	360	435
Specific gravity	3.15	2.92

[a] Below detection.

water/cement ratio to include both binder types mentioned above. The (*w*/*b*) ratio used was 0.5.

2.2. Concrete

Identical binders to the paste specimens were used. Pakenham Blue Metal (Old Basalt) crushed type was used as coarse aggregate with the following properties: Maximum size = 14 mm; specific gravity = 2.95; and absorption = 1.2%. Lyndhurst washed fine sand was used as the fine aggregate with the following properties: specific gravity = 2.65; absorption = 0.5%. The *w*/*b* ratio used was 0.63. All concrete mixtures contained water reducer WRDA GWA Grace Construction products 4.03 ml/kg of total cementitious materials; Total cementitious content = 300 kg/m^3; and Coarse aggregate = 1100 kg/m^3.

Measurements of the moisture contents of the aggregates were taken the day before and on the day of the concrete mixing. The aggregate weights were adjusted to saturated and surface dry condition.

2.3. Mixing and heat treatment

For the paste, water was first added, followed by the binders. The mixing was conducted in a mechanical mixer of 20 l of capacity, 80 rpm, for 5 min each mixture. For the concrete, the first step was the mixing of aggregates with a third of the water for 30 s. The second step was the addition of the binders and remaining water, followed by 2 min of mixing. The mixture was set to rest for an extra 2 min. The final step consisted of adding the water reducer while mixing for an extra 2 min. For both paste and concrete, the specimens were compacted using a vibration table for better compaction. Specimens were sealed with a plastic sheet and demolded after 24 h and cured for 28 days in lime-saturated water at 23 °C. Specimens were then placed in a controlled temperature room for drying during 30 days, at 23 °C and 50% of relative humidity.

Following drying, the heat exposure was conducted in a muffle furnace. The heat exposure was as follows: constant heating rate of 6.25 °C/min until 750 °C, then 1 h between 750 and 800 °C, and finally 1 h in 800 °C.

Paste and concrete specimens were designated as ‘RT’ for room temperature and ‘800 °C’ for the 800 °C heat exposed specimens.

2.4. Water and solvent sorptivity

Two specimens of each mix (for both paste and concrete) were tested. Sorptivity tests were conducted in accordance with ASTM C 1585-04 Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic Cement Concretes. As ASTM C 1585 has not been designed for heated specimens, the solvent sorptivity test has been used to account for any limitations of ASTM C 1585 in relation to pre-heating specimens and to the effects of disintegration during rehydration after exposure to elevated temperature. The size of pastes and concrete specimens was 100 mm × 50 mm. The specimens were oven dried for 3 days at 50 °C followed by 15 days sealed storage. The 800 °C heat treated specimens were tested immediately after the heat treatment took place. The solvent sorptivity test was performed as per water sorptivity, but ACS reagent grade ($\geqslant$99.5%) acetone was used. The test was conducted inside glass desiccators in order to avoid acetone evaporation.

2.5. Porosity – solvent exchange method

Three specimens of each mix were tested. For the concrete specimens, only the paste was tested (no aggregates). No pre-drying was performed except for the specimens that were exposed to heat tests. The specimens were saturated with acetone in a sealed container until constant mass. The pycnometer test was based in the ASTM D854-05 Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. Acetone density was determined by the pycnometer test.

2.6. Nitrogen adsorption

Nitrogen adsorption and desorption tests were conducted using a Coulter “Omnisorp 360CX” gas sorption analyzer. Outgas was at 3.5×10^{-5} torrs, 40 °C for approximately 30 h. Specific surface areas were calculated by the Brunauer, Emmet and Teller (BET) method over a relative pressure range of 0.05–0.25 on the adsorption/desorption isotherm. Total cumulative pore volume available to nitrogen (1–40 nm pore radius range) and pore size distribution were calculated by the Barrett, Joyner, Hallenda (BJH) method [16] using data from the desorption isotherm.

3. Results and discussion

3.1. Water sorptivity

Sorptivity tests were conducted to determine any difference in the water absorption process of paste and concrete. A difference in water absorption leads to differences in the CaO rehydration process. Sorption is a term used for water ingress into pores under unsaturated conditions due to capillary suction [17]. Sorptivity testing has been previously used as a measure of the ability of concrete to absorb water [17,18]. The specimens in comparison consisted of room temperature ‘RT’ (not exposed to heat) and ‘800 °C’ heat exposed (followed by cooling to room temperature) paste and concrete specimens. For comparison, specimens with partial replacement of OPC with slag (50% by weight) were also tested.

During sorptivity testing, the OPC paste 800 °C released significant heat and cracked immediately upon contact with water. The heat was so intense that the sealing plastic was partially melted. Within a few minutes, the specimen had disintegrated completely (Fig. 4). Similar disintegration is seen when the OPC paste 800 °C is exposed to air moisture for a few days [6], however the excessive heat is not apparent. Therefore, the authors believe that this abrupt disintegration of OPC paste 800 °C in water was due to an accelerated rehydration of CaO. Therefore, the same heat exposure as described in Section 2 was performed on a CaO sample. It was observed that immediately after cooling, and in the presence of water, the CaO reacted instantly, with the temperature reaching ~80 °C within 30 s. Thus, confirming that immersing OPC paste 800 °C in water provided an accelerated exothermic rehydration of CaO.

None of the remaining specimens (OPC concrete and 50% slag paste and concrete) presented the significant deterioration found for the OPC paste 800 °C and therefore, in those specimens, sorptivity tests were possible. The slag specimens (both concrete and paste) presented slightly higher sorptivity values when compared to OPC, this is in accordance with previous work [19]. However, the differences between OPC and 50% slag pastes and concretes were not significant. Therefore, for better visualisation Fig. 5 presents only 50% slag specimens. In Fig. 5, the test time has been transformed to better show sorption differences at earlier times.

The specimens are represented by ‘paste and concrete’ and ‘RT’ (not exposed to heat) and ‘800 °C’. When comparing the paste with the concrete it should be taken into account that the concrete specimens consist of approximately 20% paste. Therefore, to enable accurate comparison, the differential mass (ΔMass%) of each spec-

Fig. 4. OPC paste 800 °C. Left, after 800 °C heat treatment. Middle, immediately after water immersion. Right, few minutes after water immersion.

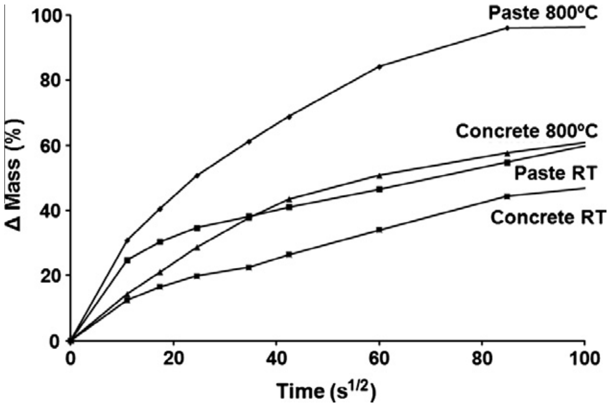

Fig. 5. Water sorptivity test results for the different specimens (50% slag blend).

imen was calculated [20] and is plotted against the time (s$^{1/2}$) in Fig. 5.

It is clear from Fig. 5 that paste 800 °C absorbs water at a significantly faster rate than concrete 800 °C, paste RT and concrete RT. Therefore, this results in more available water for the rehydration of CaO in a shorter period of time. Fig. 5 shows that after 100 s$^{1/2}$ (~3 h) of exposure to water, the paste 800 °C absorbed ~97% of the total amount of water absorbed, while the concrete 800 °C absorbed ~60%. When comparing the pastes RT and 800 °C, it is possible to see that the heat exposure caused the water absorption to increase from 47% to 85% in 60 s$^{1/2}$ (1 h). On the other hand, for the concrete, the increase from RT to 800 °C after 1 h exposure to water was 17%, showing that the effects of the heat treatment on the absorption of concrete were not as severe as for the paste.

3.2. Solvent sorptivity

In the water sorptivity test, the OPC paste 800 °C crumbled and completely disintegrated during the first few minutes of the test, inhibiting completion of the test, and consequently, any determination of its capacity to absorb water. As explained above, the instantaneous disintegration is a result of the accelerated rehydration of CaO caused by the reaction of the dehydrated OPC paste with water. Hence, the need to find a way of determining the absorption of this paste is necessary.

Two issues were of concern when performing the water sorptivity test: the pre-treatment required (drying) and rehydration of CaO leading to damage in the presence of water.

Regarding the pre-treatment required, the fine pore structure of concrete is very sensitive to drying procedures, which might result in microstructural damage [21]. Previous works have used temperatures as high as 105 °C as a pre-treatment prior to porosity test techniques such as sorptivity, MIP or vacuum saturation [22–29]. It is generally considered that, at 105 °C, only free water (evaporable water) is removed from the pore spaces of most materials [23]. However, it has been reported that ettringite crystallinity is readily destroyed, with loss of water, by heating in air ~100–105 °C [30]. In addition, drying may result in structural and physical collapse of other hydrates as monosulfate hydrate (AFm) and C–S–H [30]. The temperature at which the decomposition of C–S–H initiates is not well established but C–S–H is partially dehydrated at 105 °C [23]. Furthermore, it has been reported that even drying temperatures as low as 50 °C may not be appropriate for all concretes [17]. This is because the concretes with low water/cement ratio dry at a much slower rate than those with high water/cement ratio [21]. In addition, drying can introduce microcracks that influence the measured sorptivity.

The other concern relates to the rehydration of CaO in the presence of water. Especially for the 800 °C specimens, on exposure to water, the dried material may also rehydrate [31,32], affecting the accuracy of the sorptivity test measurement.

An alternative to the use of the water as the wetting medium in the sorptivity test is the use of a solvent. The solvent acetone was chosen for the present work because: (i) water is miscible in it, thus it will remove strongly bound pore water; (ii) it has a lower dielectric than water, thus it will be less likely to hydrogen-bond strongly to surfaces; and (iii) it has a lower capacity of formation of covalent bonding to oxides such as CaO, thus will be less likely to significantly react with the highly reactive components in heated cements than water. Acetone has been successfully used to remove free water from cement paste and concrete, i.e. as a drying method prior to mercury intrusion porosimetry (MIP) [33,34]. Therefore, while acetone will remove the capillary water from both the cement paste and concrete, it will penetrate essentially the same pore space as water via capillary attraction, enabling the determination of each specimen's sorption. However, the viscosity and density of acetone and water differ enough to possibly affect some of the results.

Further, the effects of acetone on the microstructure of the cement paste have been the focus of previous works. The main concern being that acetone would impact on an accurate quantitative determination of the $CaOH_2$ content of the hardened cement paste [33]. It is suggested that the length of $CaOH_2$ crystals increased when immersed in acetone [35]. This finding is not expected to significantly impact on the current experiment, especially for the 800 °C specimens, as those have experienced complete $CaOH_2$ dehydration. In addition, Taylor and Turner [36] reported that in the presence of acetone, C_3S paste quickly turned yellow, the colour deepening after a few days to a reddish yellow. This was not observed in the present experiment and may have been an artifact of their experiment. Furthermore, acetone quenching was reported to have preserved the pores better than other drying techniques (freeze drying, oven drying, and vacuum drying) [23,33,37,38].

Thus, the sorptivity test was repeated using acetone. Fig. 6 presents the acetone sorptivity results for all OPC specimens, as completion of OPC paste 800 °C sorptivity test was now possible without the reaction of CaO with water that lead to complete disintegration. The 50% slag specimens presented similar acetone

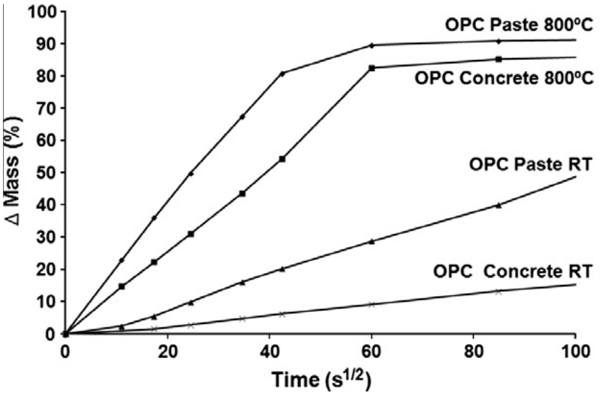

Fig. 6. Acetone sorptivity test results for the different OPC specimens.

sorptivity results as OPC, and for better visualisation, only OPC specimens are presented in Fig. 6. It is possible to see that concrete RT (room temperature) absorbs acetone slowly, approximately 9% in 60 $s^{1/2}$ (first hour). In a faster rate than concrete RT, paste RT absorbed ~29% in the same period of 60 $s^{1/2}$. Interestingly, a slower rate of acetone sorption was observed for the paste and concrete RT in comparison to the rate of water sorption as seen in Fig. 5. This may be a result of the acetone reaction with $CaOH_2$ as described by others [33,35]. In addition, the slower rate may be also a result of the lower surface tension of acetone compared to water; the very small pores present in concrete RT (see BET section) may be less accessible to acetone than water.

For the concrete 800 °C, a different scenario was found. While the acetone absorption of this specimen was quite fast, 82% in 60 $s^{1/2}$ (first hour – Fig. 6), the water absorption was slower 50% in the same period (Fig. 5). This suggests that although the OPC concrete 800 °C capacity to absorb a liquid is significant, when the liquid is water this absorption is slower when compared to acetone. The slower rate is also related to the greater viscosity and density of water compared to acetone.

The OPC paste 800 °C absorbed ~89% of the total amount of acetone absorbed in 60 $s^{1/2}$ (first hour). This shows the higher capacity of this specimen to absorb a liquid when compared to the remaining specimens.

Fig. 7 presents the acetone absorption for the OPC and 50% slag paste 800 °C. It can be seen that OPC and 50% slag paste 800 °C specimens presented similar acetone absorption. Therefore, the 50% slag water absorption results would provide an indication of the OPC paste 800 °C rate of water absorption (Fig. 8 – dashed line). For the 50% slag paste 800 °C, water and acetone were absorbed in a very similar way, approximately 85% of water and 93% of acetone absorption after 60 $s^{1/2}$ (first hour). Since OPC paste 800 °C acetone absorption is about 92% over 60 $s^{1/2}$, and is essentially the same as that observed for the slag specimen (93%), water absorption would be expected to be similar. Considering the 50% slag paste 800 °C rate of water absorption of 84% in the first hour, it is reasonable to expect that the OPC paste 800 °C rate would also be of similar value for the same period. This is represented in Fig. 8 (dashed line) and is expected to be the minimum amount absorbed during the first 100 $s^{1/2}$ (~3 h). In addition, as described in the previous section, OPC paste 800 °C disintegrated within minutes of being in the presence of water. The reason for this fast disintegration was attributed to the rehydration of CaO. Therefore, indicating that in the OPC paste 800 °C this reaction is almost instantaneous.

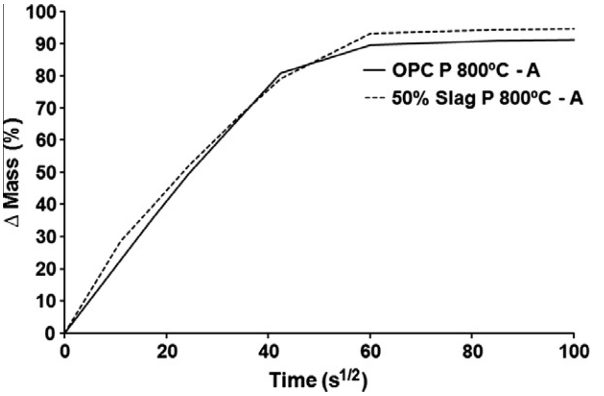

Fig. 7. Comparison between OPC and 50% slag pastes 800 °C (acetone sorption).

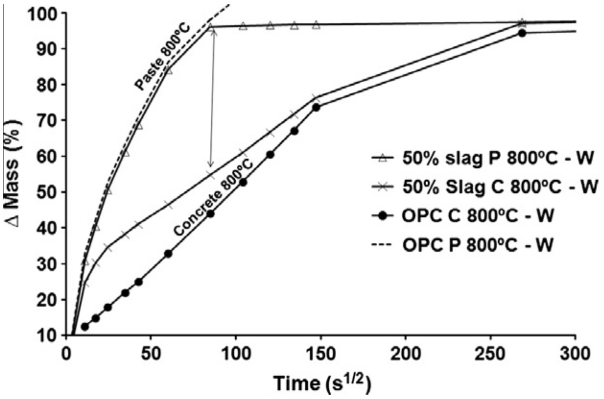

Fig. 8. Water absorption of OPC and 50% slag blends 800 °C. Dashed line indicates expected absorption for the OPC paste 800 °C.

This is an important finding as it shows that the OPC paste 800 °C rate of water absorption (expected to be ~85% in 1 h and >90% after 3 h) occurs in a much faster way compared to OPC concrete 800 °C (approximately 32% in 1 h and 53% after 3 h). This is represented in Fig. 8 by the arrow, with the top indicating paste 800 °C and the bottom, concrete 800 °C.

Differences in rate of water absorption lead to differences in growth rates of $CaOH_2$ – fast growth of crystals favours crystal growth at selected faces of the crystal, the crystals are acicular while slow growth yields equant crystals [39]. Faster water absorption provides more water for CaO rehydration, and consequently can lead to faster growth of $CaOH_2$. Acicular and fast crystal growth are more conducive for causing damage to a porous matrix than slow and equant crystal growth, which may or may not cause any damage [39]. Ramachandran et al. [40,41] analysed the hydration of CaO pressed compacts exposed to either a limited quantity of liquid water or to water vapour. The compacts are reported to have a void content of 46% by volume and a CaO content of 54%. For the liquid water the compact remained strong and undamaged. In contrast, for the compact exposed to water vapour, a volume increase was observed resulting in disintegration. Chatterji [39] concluded that not all crystal growth leads to disintegration of the constraining body.

Thus, the differences in the rate of water absorption observed for the OPC paste and concrete 800 °C lead to differences in the growth rate of $CaOH_2$ crystals during rehydration of CaO. The different $CaOH_2$ crystals formed will lead to different deteriorations. This may explain why OPC paste disintegrates after exposure to 800 °C followed by air moisture and/or water (CaO rehydration), and why, on the other hand, the OPC concrete does not disintegrate, even though CaO rehydration has been confirmed to take place.

In conclusion, the dehydration of $CaOH_2$ and rehydration of CaO might cause damage to OPC paste and concrete after exposure to temperatures above 400 °C followed by exposure to air moisture. However, the extent of the deterioration is not only related to the occurrence of rehydration, but most importantly, is related to how the rehydration occurs, i.e. the rate of water absorption.

3.3. Porosity – solvent exchange method

The fast rate of acetone absorption of both paste and concrete 800 °C, in which ancillary reactions are expected to be minimal, indicates differences in the porosity of those specimens when compared to the RT specimens. As reported previously [24,42], the porosity of concrete allows movement and retention of water and other substances.

An accurate measurement of porosity and pore size distribution of hardened cement paste is extremely difficult to obtain [37,43]. While determining porosity, there are evidences that the fragile microstructure of the cement matrix can be damaged by two causes: by the drying procedure itself and/or, by the measurement technique employed for the pore structure determination [37,38,44].

Based on that, the present work used the solvent exchange method to minimize the effects of both pre drying and the technique itself. No drying is required using the solvent exchange method. Parrot [45] used methanol as a drying treatment prior to nitrogen adsorption and concluded that the pore structure had not been excessively disturbed and that subsequent desorption and adsorption of methanol rather than nitrogen might be used to study pore structure. In 1984, Parrot [46] concluded that solvent exchange can provide a simple physical measure of diffusion in cementitious pastes, that can reflect the effects of pore structure alterations arising from previous drying. Robler and Odler [34] used an acetone-ether extraction to determine the porosity of the cement paste. Having free water removed by acetone-ether and bound water by loss on ignition, it was concluded that an accurate measurement of porosity was obtained [34]. Day and Marsh [43] concluded the alcohol exchange process, followed by removal of the alcohol, may be a preferred drying method if accurate pore size distributions are to be obtained.

The acetone used in the present work, as described in the previous section, is expected to have a low detrimental impact on the microstructure of the specimen. Saturating the specimen with acetone enabled estimation of porosity. It is assumed that total penetration of the acetone into the pores occurred. The total mass of acetone absorbed by each specimen was recorded after constant mass was attained. As the acetone's density at the test temperature is known, the volume of acetone in the specimen can then be determined. In a similar way, the volume of the specimen can be determined by the known mass and bulk density. The porosity is then determined by the following equation:

$$P\,(\%) = Va/Vs \tag{1}$$

where *P (%)* refers to the porosity of the specimen in percentage, *Va* the volume of acetone inside the specimen and *Vs* the volume of the specimen. For comparison, a pycnometer of known volume was weighed, filled with a known mass of finely ground specimen and acetone until saturation, followed by weighing. With the mass and density of acetone and total volume known, the volume of the sample and its particle density can be calculated. Finally, with the known bulk density (ρ_{bulk}) and particle density ($\rho_{particle}$) the porosity *P (%)* can be determined by the following equation:

$$P\,(\%) = \rho_{bulk}/\rho_{particle} \tag{2}$$

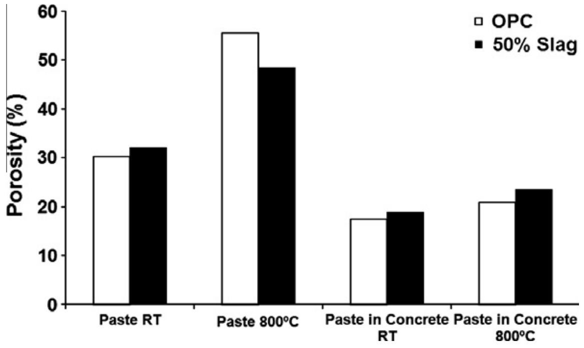

Fig. 9. Porosities determined by the solvent exchange method using acetone, for both OPC and 50% slag specimens.

Both the solvent exchange method and the pycnometer method provided very similar results and those are presented in Fig. 9. For the concrete specimens the porosity results are related to the paste in concrete only, not considering aggregates and ITZ porosities. For the room temperature specimens, as expected, paste is more porous compared to the paste in concrete [26]. In addition, partial replacement of OPC with slag tends to slightly increase the porosity of concrete RT and 800 °C and paste RT. This is in accordance with previous work [33]. For the paste 800 °C, a different scenario was found, with the OPC paste presenting higher porosity than 50% slag paste, possibly due to the higher deterioration that occurred due to $CaOH_2$ dehydration. The higher porosity of OPC paste 800 °C is in accordance with same trend found for the compressive strength, in which higher porosity lead to a higher deterioration of mechanical properties. This is in accordance with previous works [11,22,34].

3.4. Nitrogen adsorption

As described by Day and Marsh [43], when only one porosity measurement technique is used during an examination, interpretation of results is restricted because the method is based on a number of underlying assumptions. As an example, differences in viscosity, density and surface tension for acetone and water mean that slightly different pores will be accessed by these two solvents. While the authors believe the differences will have minimal effect on the bulk results, it is useful to have another means to prove the specimen pore space. Therefore, nitrogen adsorption technique was performed to complement the porosity characterisation obtained by the acetone exchange methods described in the previous section. It must be noted that nitrogen absorption/desorption isotherms only prove a specific range of pore sizes, and thus is also limited in its ability as a stand-alone technique in characterising the porosity of paste and concrete.

Adsorption measurements using various adsorbates (N_2, H_2O, Kr, etc.) generate values of specific surface areas and cumulative pore volumes [31]. The cement paste has by volume a relatively large porosity, which can be defined in terms of void volume, capillary pores and gel pores. The voids are formed on mixing when air is entrapped into the mixture and the resulting voids can vary in size from approximately 1 to 500 μm. Capillary pores have an average radius greater than 50 Å and are originally water filled. When interconnected these pores dominate water transport [47]. Gel pores have a radius less than 50 Å [47]. The water present in gel pore is more strongly bound water and can be removed only by drying [31] or by solvent exchange.

In the case of heat exposed specimens, structural changes which may result from dehydration processes are predominantly effectual in a pore radius range below 40 Å [48]. The occurrence of structural changes in this range might be investigated by N_2 adsorption [48].

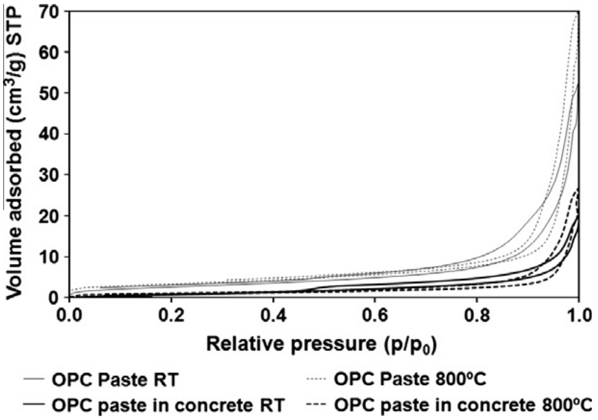

Fig. 10. Nitrogen adsorption isotherms for OPC paste and concrete, RT and 800 °C.

Fig. 10 presents the adsorption isotherms for OPC paste and concrete, RT and 800 °C. In general, the results are in accordance with the porosity results presented in Fig. 9. OPC paste RT has a N_2 adsorption volume of ~52 cm^3/g while paste in concrete RT has an adsorption volume of ~20 cm^3/g. A higher adsorption is found for the OPC paste 800 °C at the same p/p_0 compared to the paste RT. The OPC paste 800 °C has an adsorption volume of ~70 cm^3/g while OPC paste in concrete 800 °C has ~26 cm^3/g. This supports the findings described in the previous section, as the OPC paste 800 °C presented higher total adsorption, and therefore greater porosity, when compared to the OPC paste in concrete 800 °C.

Fig. 11A and B presents the BJH desorption cumulative pore size distribution for the different OPC specimens. In Fig. 11A, a comparison between paste RT and 800 °C is made in order to determine the effects of the heat exposure on the pore size distribution of the cement paste. For both RT and 800 °C the peaks near 5 nm relates to the gel pores [47] which are of a size that is not conducive to unsaturated flow by capillary attraction. As discussed above, the water present in the gel pores is more strongly bound water and can be removed only by drying and the prior removal of water from larger pores [31]. After exposure to 800 °C, it can be seen that the gel pores and pores of ~10 nm diameter have drastically decreased. This is evidenced by the increase in larger capillary pores and, presumably, probably formation of microcracks, which when interconnected dominate the water transport [47]. Thus, this change in pore size, and change in the volume of pores of different sizes (i.e. gel and capillary), facilitates rapid absorption of water in the heated sample.

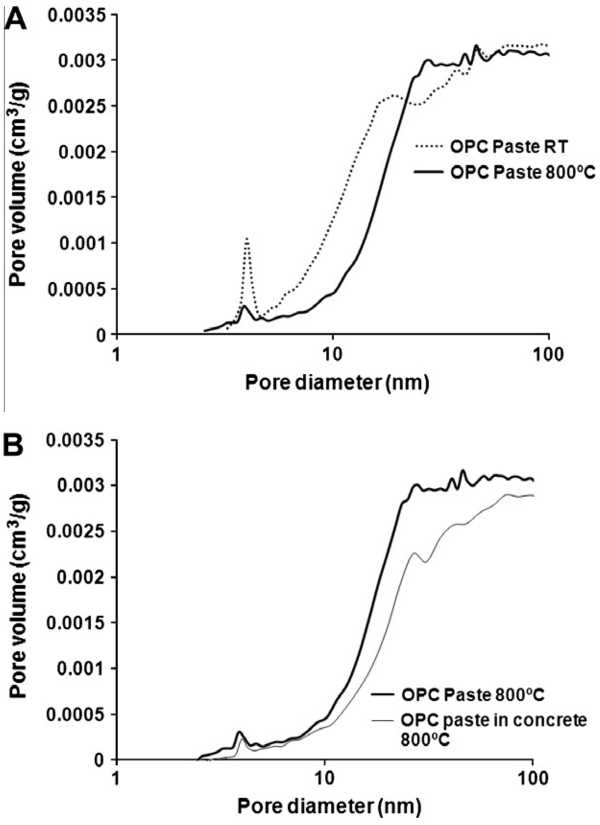

Fig. 11. BJH desorption pore size distributions. 'A' OPC paste RT and 800 °C. 'B' OPC paste and paste in concrete 800 °C.

In Fig. 11B, OPC paste is compared to paste in concrete 800 °C so that the differences between the pore size distributions of those specimens can be assessed. Regarding the gel pores, the heat treatment seems to result in similar loss of gel pore volume, as a result of dehydration of bound water. However, regarding the capillary pores, the OPC paste 800 °C presents a greater volume of the coarser pore size distribution. As discussed above, the capillary pores dominate the water transport, therefore leading to greater absorption of water by the paste 800 °C when compared to the paste in concrete 800 °C. This is in accordance with the sorptivity tests discussed in the previous sections, confirming that OPC paste 800 °C absorbs water at a faster rate when compared to OPC paste in concrete 800 °C. This results in different CaO rehydration process between those specimens.

4. Conclusions

The present work investigated why, after exposure to 800 °C, rehydration of CaO causes total strength loss in OPC paste, leading to complete disintegration of the paste yet only 65% strength loss in OPC concrete.

Water sorptivity tests have shown that OPC paste 800 °C specimens reacted instantaneously with water, releasing heat and disintegrating, inhibiting test completion. This was found to be due to an accelerated rehydration of CaO in the presence of water; an expansive, exothermic and instantaneous reaction.

Acetone sorptivity tests provided an indication of the OPC paste 800 °C rate of water absorption. It was thus concluded that OPC paste 800 °C absorbed water faster than OPC concrete.

The rate of water absorption determines the growth rate of $CaOH_2$ crystals and ultimately the type of $CaOH_2$ crystals formed. Therefore, the faster rate of water absorption observed for OPC paste 800 °C compared to OPC concrete 800 °C, lead to different $CaOH_2$ crystal formation in each specimen. Different crystal forms cause different levels of deterioration, not always leading to the total disintegration of the constraining body.

This increased water absorption explains why OPC paste disintegrates after exposure to 800 °C followed by air moisture and/or water (CaO rehydration), and why, on the other hand, the OPC concrete 800 °C does not disintegrate, even though CaO rehydration has been confirmed to have taken place.

Therefore, the extent of cement paste deterioration is not only related to the occurrence of CaO rehydration, but most importantly it is related to the rate of water absorption. The rate of water absorption is the determining factor controlling the extent of deterioration caused by CaO rehydration.

The solvent exchange method using acetone provided a good indication of the porosity of the specimens. In addition, it eliminated the negative effects of the pre-drying required by other porosity testing techniques such as mercury intrusion porosimetry

(MIP). The porosity was significantly higher for the paste 800 °C compared to the paste in concrete 800 °C.

Nitrogen adsorption tests confirmed the porosities results obtained with acetone exchange method. A greater volume of the coarser pore size distribution, capillary pores (radius greater than 50 Å), known for dominating the water transport, was found in the OPC paste 800 °C in comparison to the paste in concrete 800 °C. This supports the finding that paste 800 °C absorbs water faster than the paste in concrete 800 °C.

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