Expansive and non-expansive calcium sulfoaluminate-based cements

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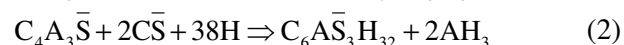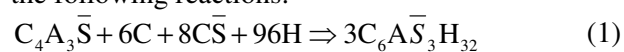
ABSTRACT

Within the curing period 4 hours- 90 days, a dimensionally stable calcium sulfoaluminate (CSA) cement, consisting of 83% CSA clinker and 17% natural gypsum by mass, and an expansive cementitious blend (MIX), composed by 40% CSA clinker, 40% CEM I- class 52.5 R ordinary Portland cement (OPC) and 20% natural gypsum by mass, were submitted to shrinkage and compressive strength tests as well as differential thermal-thermogravimetric analysis (DTA-TG) and mercury intrusion porosimetry (MIP). OPC was also used as a reference term. The early and late mechanical strengths were respectively highest for CSA cement and lowest for MIX cement which, furthermore, showed the minimum shrinkage. These phenomena were attributed to (i) the faster reaction rate of CSA and MIX cements, and (ii) the non-expansive/expansive nature of ettringite respectively formed. Each investigated cement exhibited peculiar features in terms of pore size distribution modalities and threshold pore widths.

Keywords. Calcium sulfoaluminate cements, expansion, dimensional stability, pore size distribution, ettringite.

INTRODUCTION

The interesting engineering properties (Marroccoli et al., 2007) of calcium sulfoaluminate (CSA) – based binders and the environmentally friendly features (Marroccoli et al., 2010) associated with their manufacturing cycle have been widely recognized by the international scientific community and greatly appreciated during the last years (Buzzi et al., 2010; Chen & Juenger, 2011; Gartner & Macphee, 2011; Gastaldi et al., 2011; Juenger et al., 2011; Marchi & Costa, 2011; Winnefeld & Lothenbach, 2010; Valenti et al., 2012). These binders can be used as expansive cements giving shrinkage-compensating and self-stressing effects or dimensionally stable cements with high early hardening and durability (Beretka et al., 1996; Bernardo et al., 2006; Bernardo et al., 2007; Budnikov & Kravchenko, 1968; Cohen & Richards, 1982; Deng & Tang, 1994; Glasser, 2002; Jun-An et al., 1980; Klein & Troxell, 1958; Mehta & Monteiro, 2006; Nakamura et al., 1968; Odler, 2000; Odler & Colan-Subauste, 1999). Their technical behaviour mostly depends on the ability of $C_4A_3\bar{S}$ (ye'elimite, key-component) to generate upon hydration $C_6A\bar{S}_3H_{32}$, ettringite, according to the following reactions:

$$C_4A_3\bar{S} + 6C + 8C\bar{S} + 96H \Rightarrow 3C_6A\bar{S}_3H_{32} \qquad (1)$$

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \Rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \qquad (2)$$

here $C\bar{S}$ refers to both anhydrite incorporated in the CSA clinker and calcium sulfate given by added gypsum or anhydrite.

The first reaction requires the presence of lime which can be produced by the hydration of calcium silicates given by (i) ordinary Portland cements blended with CSA-based binders or (ii) modified Portland cements containing $C_4A_3\bar{S}$ instead of C_3A (tricalcium aluminate); furthermore, calcium hydroxide can be also generated by the hydration of reactive C (calcium oxide) or C_2S (dicalcium silicate) present in CSA clinkers. These can also include C_3A, $C_5S_2\bar{S}$ (ternesite), C_2AS (gehlenite), $C_{12}A_7$ (mayenite), C_4AF (brownmillerite) and other minor constituents.

Regarding the expansive behaviour, there is a general agreement about the considerable influence exerted by the rate of ettringite formation. As a matter of fact, expansive phenomena, coupled with internal stresses, can occur once the hydrated cement has lost its plasticity and has reached a certain mechanical strength (Beretka et al., 1996; Cohen & Richards, 1982; Mehta & Monteiro, 2006; Odler, 2000; Odler & Colan-Subauste, 1999), in conjunction with a significant ettringite amount produced after setting (due to a large or delayed ettringite generation). Moreover, expansion is enhanced by a relatively high nucleation rate of ettringite, increasing with the increase of the concentration of the ionic species (OH^-, Ca^{++}, SO_4^{--}, $Al(OH)_4^-$) contributing to its formation (Deng & Tang, 1994). Therefore, CSA cements hydrated (i) in a strong alkaline environment, (ii) in the presence of lime or (iii) with a high amount of added calcium sulfate, are expansive; on the contrary, they are dimensionally stable if hydrated together with relatively moderate calcium sulfate additions, at not elevated pH values.

Since 1960's, the cements based on $C_4A_3\bar{S}$ have been mainly used as expansive binders hydrated in the presence of lime (Budnikov & Kravchenko, 1968; Klein & Troxell, 1958; Nakamura et al., 1968): for these cements, the key-reaction is that described by the equation (1).

Later, rapid-hardening and dimensionally stable CSA cements have been developed and manufactured in China (Jun-An et al., 1980), owing to the considerable work carried out by the China Building Materials Academy. According to the reaction (2), they quickly generate, in the presence of nearly stoichiometric amounts of calcium sulfate, non-expansive ettringite and aluminium hydroxide.

In this work, mercury intrusion porosimetry (MIP) was employed in order to characterize two series of paste specimens obtained from the hydration, at various curing times, of (i) a CSA cement consisting of an industrial CSA clinker and added gypsum, to be used as dimensionally stable binder, and (ii) an expansive cement composed by the above mentioned CSA clinker, a commercial CEM I-class 52.5 R (according to EN-197-1 Standard) Portland cement and gypsum; for the sake of comparison, a third series of CEM I-class 52.5 R Portland cement paste specimens was also investigated.

This paper aimed at searching for differences in the porosimetric behaviour between expansive and non-expansive CSA-based binders. The hydration process was also followed by means of differential thermal-thermogravimetric (DTA-TG) analysis. Furthermore, shrinkage measurements and compressive strength tests were performed.

EXPERIMENTAL

Materials

An industrial CSA clinker, a commercial CEM I–class 52.5 R Portland cement and a natural gypsum with about 90% calcium sulfate dihydrate by mass, were used in this research. The

mineralogical composition of CSA clinker, determined by means of the Rietveld method, is indicated in Table 1.

Table 1. Mineralogical composition (mass %) of CSA clinker

phase	$C_4A_3\bar{S}$	C_2S	C_3A	$C\bar{S}$	C_4AF	C_2AS	M	$C_{12}A_7$	$C_5S_2\bar{S}$	*total*
CSA clinker	52.1	23.8	9.4	4.9	4.7	1.6	1.4	1.2	0.9	100.0

The Rietveld results were normalized to 100% of accounted crystalline phases. Three binders were investigated: 1) a CSA cement containing 83% CSA clinker and 17% natural gypsum, by mass; 2) the commercial CEM I–class 52.5 R Portland cement; 3) a cementitious mixture consisting of 40% CSA clinker, 40% CEM I–class 52.5 R Portland cement and 20% natural gypsum, by mass. The three cements were indicated with the symbols CSA, OPC and MIX, respectively. The $C\bar{S}/C_4A_3\bar{S}$ mol ratio available for the CSA cement hydration was 1.7, close to the stoichiometric value required by the reaction (2).

Hydration procedures, shrinkage and compressive strength measurements

Cements were paste hydrated with a water/solid mass ratio equal to 0.5 for curing times comprised between 4 hours and 90 days. The paste samples for MIP and DTA-TG analysis, shaped as cylindrical discs 15 mm high and 30 mm in diameter, were placed in polyethylene bags inside a thermostatic bath at 20°C; at the end of each aging period, they were in part broken and submitted to MIP, in part pulverized for DTA-TG analysis. A treatment with acetone (to stop hydration) and diethyl ether (to remove water), followed by storing in a desiccator over silica gel-soda lime (to ensure protection against H_2O and CO_2), was performed.

For the shrinkage measurements (Unicemento, 1973), the paste samples shaped as small prisms (15x15x78 mm) were water cured at 20°C for 24 hours, then demolded and kept at 20°C in air conditioned at 50% R.H.. The length changes were referred to the initial length taken as that evaluated just after demolding and were determined as average values of 4 measurements with a caliper accurate to ±1 μm.

The compressive strength test was performed on cement mortar, according to EN-197-2 Standard. The aging times were comprised between 4 hours and 28 days.

Characterization techniques

X-ray diffraction analysis

XRD analysis was performed with a Bruker D4 (Solex detector, Cu kα radiation). The phases used for the Rietveld refinement are indicated in Table 2 together with their AMCSD (American Mineralogist Crystal Structure Database) codes and the pertinent references. A TOPAS software was utilized.

Differential thermal-thermogravimetric analysis

Simultaneous DTA-TG analysis was carried out by means of a Netzsch Tasc 414/3 apparatus operating in the temperature ranges 20°-500°C and 20°-1000°C with a heating rate of 5°C/min and 10°C/min, respectively.

**Table 2. Phases involved in the Rietveld refinement, related crystal systems, AMCSD codes and references**

phase	formula	crystal system	AMCSD code	reference
ye'elimite	$C_4A_3\bar{S}$	cubic	0014178	Saalfeld et al., 1972
larnite	C_2S	monoclinic	0012179	Tsurumi et al., 1994
anhydrite	$C\bar{S}$	orthorhombic	0005117	Hawthorne et al., 1975
tricalcium aluminate	C_3A	cubic	0017746	Steele et al., 1929
mayenite	$C_{12}A_7$	cubic	0009964	Boysen et al., 2007
brownmillerite	C_4AF	orthorhombic	0003442	Redhammet et al., 2004
gehlenite	C_2AS	tetragonal	0007694	Swainson et al., 1992
ternesite	$C_5S_2\bar{S}$	orthorhombic	0014638	Iran et al., 1997
periclase	M	cubic	0000501	Hazen, 1976

Mercury intrusion porosimetry

The porosity measurements were performed using a Thermo Finnigan Pascal 240 Series porosimeter (maximum pressure, 200MPa) equipped with a low-pressure unit (140 Series) able to generate a high vacuum level (10Pa) and operate between 100 and 400kPa. With increasing pressure, mercury gradually penetrates the bulk sample volume. If the pore system is composed by an interconnected network of capillary pores in communication with the outside of the sample, mercury enters at a pressure value corresponding to the smallest pore neck. If the pore system is discontinuous, mercury may penetrate the sample volume provided that its pressure is sufficient to break through pore walls. In any case, the pore width related to the highest rate of mercury intrusion per change in pressure is known as the "critical" or "threshold" pore width (Winslow & Diamond, 1970). A unimodal or multimodal pore size distribution can be obtained, depending on the occurrence of one or more peaks, respectively, in the derivative volume plot.

RESULTS AND DISCUSSION

Figure 1 describes the shrinkage curves for the three cements. Two phenomena are observed: 1) OPC shows a sensitivity to drying-shrinkage higher than that of CSA cement, most likely because calcium silicate hydrate (its main reaction product) has a propensity to release adsorbed water molecules greater than that of ettringite particles; 2) MIX cement displays the
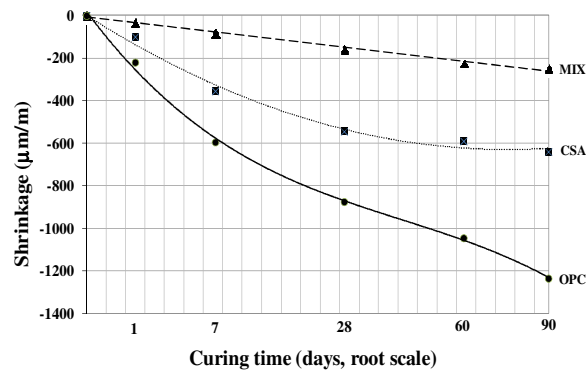
Figure 1. Shrinkage *vs.* curing time for CSA, MIX and OPC cements

lowest shrinkage, owing to the strong shrinkage-compensating effect associated with its expansive nature.

In Table 3 the results of the compressive strength test on the three cements are reported. At very early ages the extremely positive influence of the rapid ettringite formation and its ability to counterbalance both the decreased C_3S hydration rate and the reduced Portland cement concentration are clearly evident for CSA and MIX cements, respectively (Gastaldi et al., 2011). Afterwards, the intensity of these effects tends to decrease because the hydration rate of $C_4A_3\bar{S}$ and Portland cement is strongly reduced and increased, respectively.

Table 3. Compressive strength data (MPa) for CSA, MIX and OPC cements, at various curing times

	4 hours	8 hours	1 day	7 days	28 days
CSA	23.3	27.0	35.8	53.3	61.8
MIX	7.8	18.2	30.0	39.4	54.7
OPC	-	2.0	21.5	49.5	61.0

No effects were recorded by DTA-TG analysis above 300° and 600°C for $C_4A_3\bar{S}$ -based binders and OPC, respectively. Its results for the pastes are illustrated in Fig. 2. The endothermal peaks at 136°±23°C, 270°±6°C and 484°±18°C are related to dehydration of ettringite, aluminium hydroxide and calcium hydroxide, respectively (Taylor, 1997).

For OPC (Figure 2-A), the peak of ettringite (formed by the hydration of C_3A and gypsum) appears at very early ages and quickly reaches a steady state; the effect of calcium hydroxide (derived from the C_3S and C_2S hydration) is barely detected at 4 hours and progressively increases with the increase of curing time.

For CSA cement (Figure 2-B), the peak of ettringite (generated by the $C_4A_3\bar{S}$ hydration) is rising steadily from early to long curing times, while the other hydration product of the reaction (2) (aluminium hydroxide) is clearly visible starting from 1 day of hydration.

For MIX cement (Figure 2-C), the ettringite peak is lower than that shown by CSA, the curing time being the same, due to the reduced $C_4A_3\bar{S}$ concentration; the aluminium hydroxide effect is barely detected within the first 24 hours and subsequently does not appear, owing to the probable reaction of aluminium hydroxide with C_2S to give strätlingite (C_2ASH_8) (Winnefeld & Lothenbach, 2010). No calcium hydroxide arising from Portland cement hydration is observed, most likely because of its combination with other compounds present in the reacting system.

The porosimetric behaviour of the thee cements is described in the Figures 3 and 4 where the cumulative and derivative Hg volume is respectively reported as a function of pore radius for OPC, CSA and MIX cements hydrated at various curing times.

According to the scientific literature (Cook & Hover, 1999; Hearn & Hotorn, 1992; Winslow & Diamond, 1970), for Portland cement pastes both total porosity and threshold pore width decrease with the increase of curing time. At early ages, the differential curves show a sharply defined initial peak, indicating a unimodal pore size distribution centered on the lowest width of pore necks connecting a continuous system. Then, at smaller pore sizes, there is the presence of a second peak corresponding to the pressure required to break through the blockages formed by the hydration products isolating the interior pore space. At the same time, the cumulative pore volume is strongly reduced.
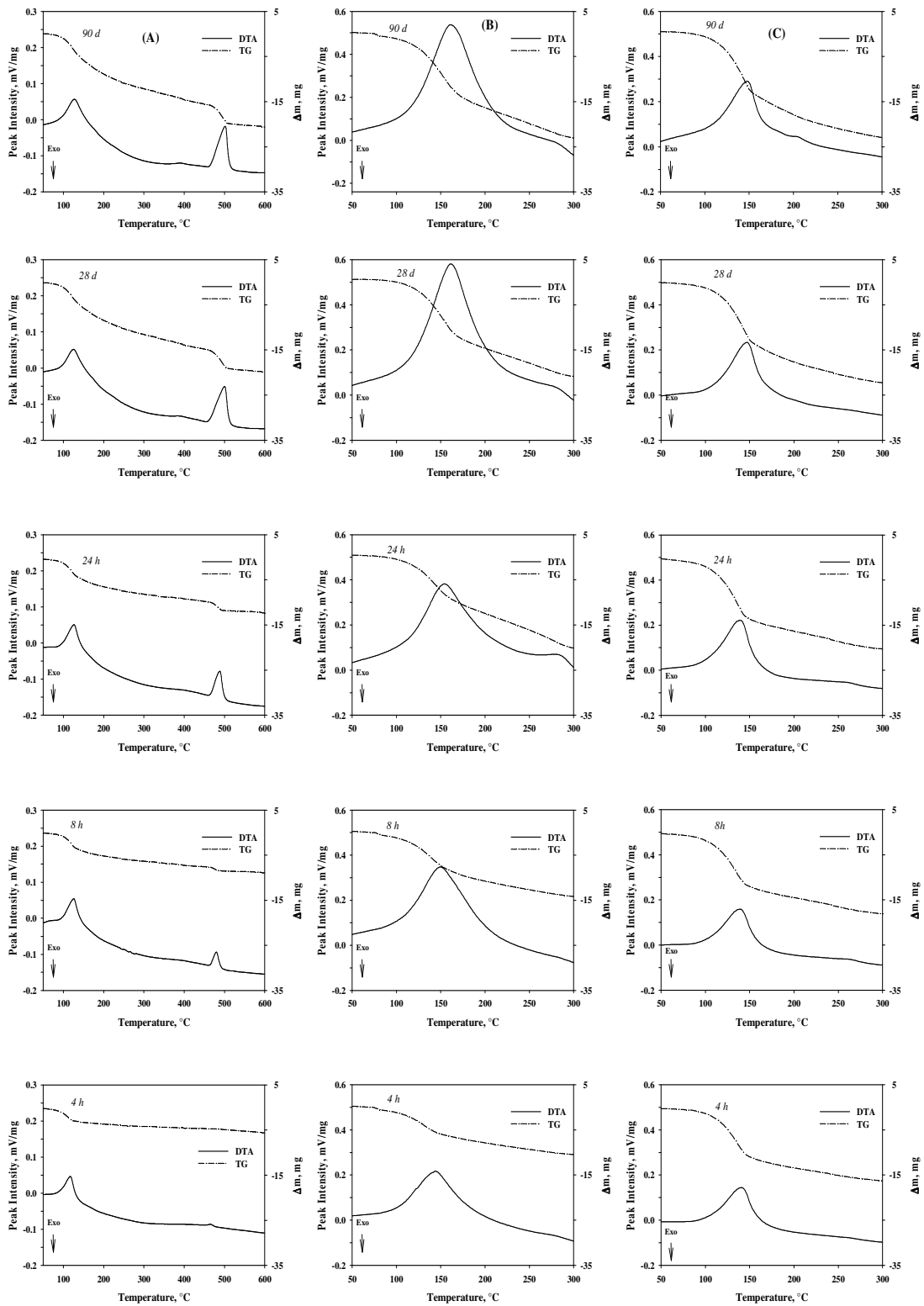
Figure 2. DTA-TG thermograms for paste hydrated OPC (A), CSA (B) and MIX (C) cements at various curing times

In this investigation, the change of regime for OPC cement occurs after 2 days of hydration.
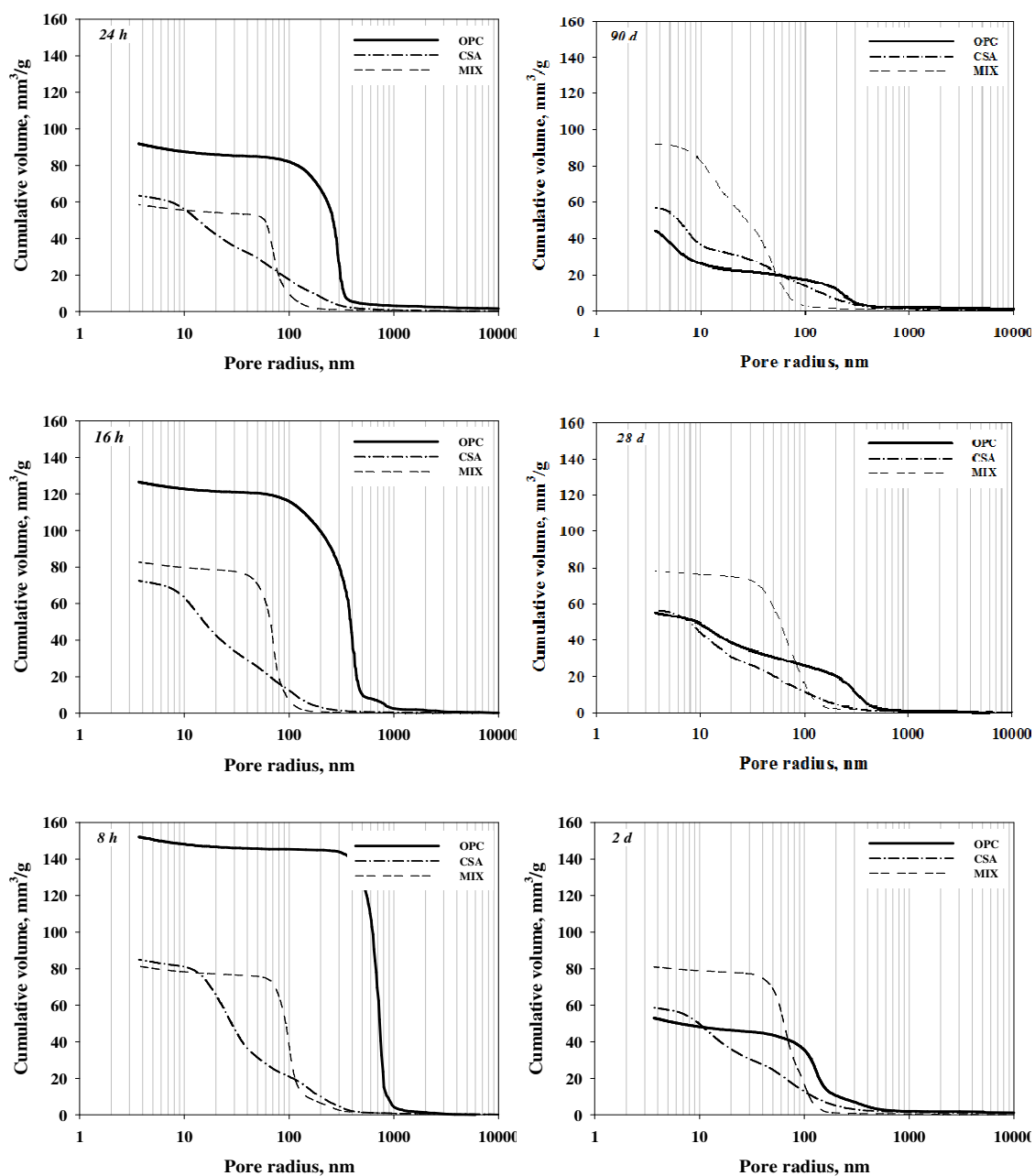
Figure 3. Cumulative Hg volume *vs*. pore radius for OPC, CSA and MIX cement pastes cured at various ages

For CSA cement, due to the rapid formation of hydration products, a multimodal pore size distribution is quickly established with prevailing low porosity regions; then, a behaviour similar to that of OPC cement is shown at longer ages.

For MIX cement, owing to the fast generation of expansive ettringite, a peculiar unimodal pore size distribution is observed together with cumulative pore volumes higher and lower (up to 1 day of hydration) than those of CSA cement and OPC, respectively; the critical pore
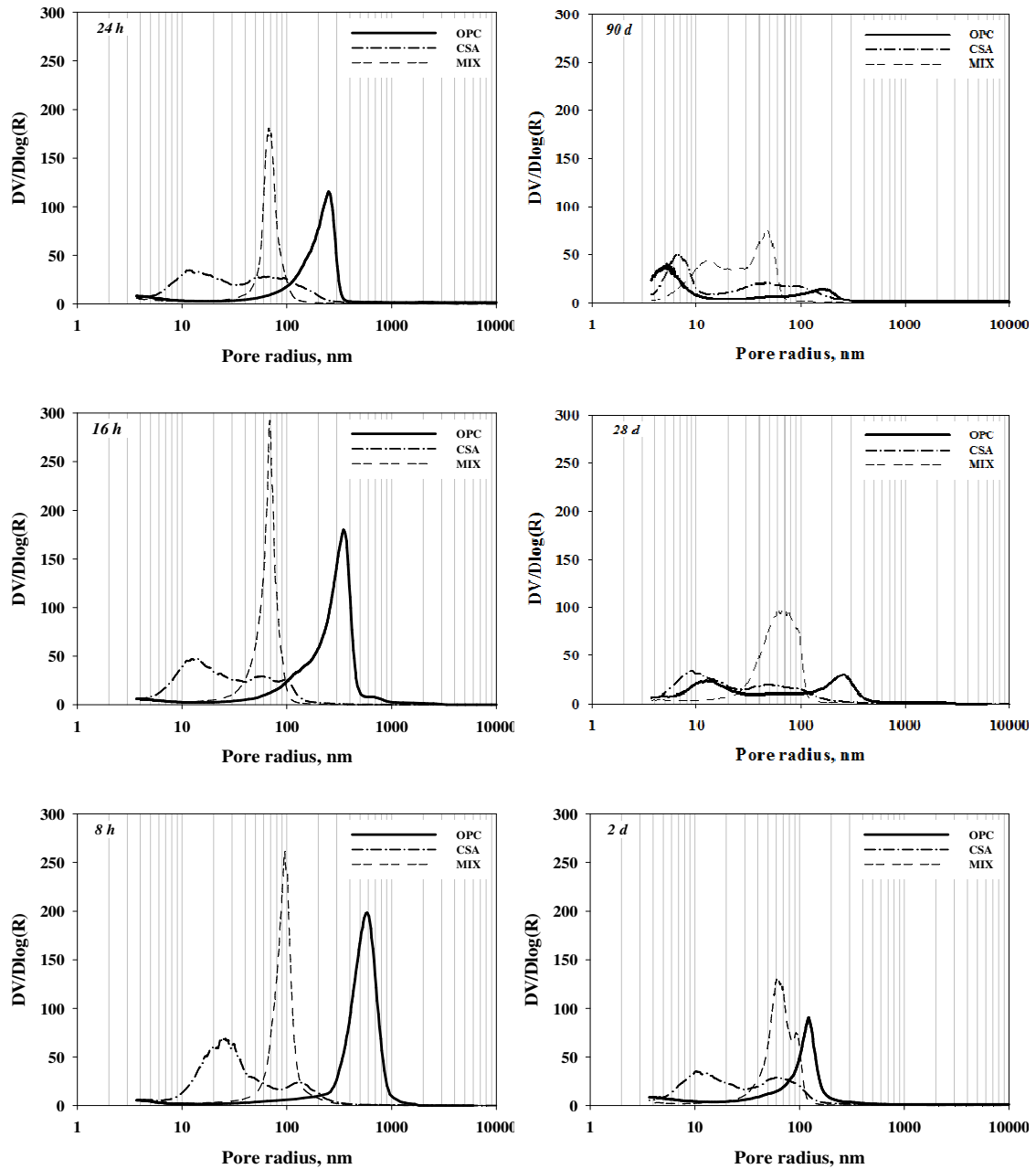
Figure 4. Derivative Hg volume *vs*. pore radius for OPC, CSA and MIX cement pastes cured at various ages

radii are, during all the investigated curing period, much larger than those of CSA cement and some multimodality appears in the pore size distribution at longer ages.

CONCLUSIONS

From DTA-TG results it can be argued that, compared to a CEM I – 52.5 R Portland cement (OPC), a non-expansive CSA cement, containing CSA clinker and gypsum, and an expansive ternary cementitious blend (MIX), composed by CSA clinker, OPC and gypsum,

have a higher initial reaction rate, being the amount of (non expansive) ettringite generated by the higher than that of (expansive) ettringite originated by the latter. This explains why, compared to OPC whose main hydration product is a calcium silicate hydrate very prone to the release of absorbed water molecules, CSA cement gives greater mechanical strength and lower shrinkage, whereas MIX cement shows higher early (up to 1 day) hardening and even more reduced shrinkage.

The porosimetric behaviour of MIX and CSA cements is respectively related to the expansive or non-expansive nature of the produced ettringite. The pore size distribution of the former is unimodal (as for early cured OPC) with critical pore sizes larger than those of the latter, characterized by a multimodal distribution.

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