Cement & Concrete Composites 31 (2009) 474–482

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Influence of polyether polyol on the hydration and engineering properties of calcium sulfoaluminate cement

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ARTICLE INFO

Article history:
Received 20 October 2008
Received in revised form 10 April 2009
Accepted 14 April 2009
Available online 24 April 2009

Keywords:
Calcium sulfoaluminate cement
Ettringite
Microstructure
Polyol
Porosity
Shrinkage
Strength

ABSTRACT

The aim of the present paper was to investigate the efficiency of polyether polyol as shrinkage-reducing admixture on pastes and mortars prepared with calcium sulfoaluminate cement (CSA). CSA was prepared by mixing CSA clinker and re-crystallized gypsum in different proportions. Three types of polyether polyol were added at a dosage of 1.5 wt% of CSA when hydrating pure pastes and standard mortars. The engineering properties of mortars (compressive strength, drying shrinkage) and the microstructure of pastes were investigated. The results show that polyol reduces drying shrinkage of CSA-based mortars without affecting the nature of hydrates formed. The effect of polyol mainly depends on its molecular weight.

1. Introduction

The effect of shrinkage-reducing admixtures (SRAs) has been extensively studied in Portland cement concretes, mortars, and pastes [1–11]. SRAs tend to decrease the surface tension of water in concrete pores, thereby lowering the capillary tension within the pore structure and therefore, decreasing shrinkage when water evaporates. Their effect on alkali-activated slag pastes and mortars has also been assessed [12]. Limited information on the pertinence of using SRAs in calcium sulfoaluminate cement (CSA) mortars and pastes is available. Ambroise et al. [13,14] have studied the influence of polyether polyol on the drying and curling of self-leveling screed based on CSA. In such systems, higher water to cement ratios are used than in Portland cement (OPC) and pore diameters are higher than in OPC materials. Therefore, water evaporation is facilitated. The introduction of polyol keeps water inside the structure and increases the formation of ettringite, thus limiting drying shrinkage. When polyol is added to the mixture (0.63% of the cementitious material content), curling is reduced by 23%. Polyol also reduces drying shrinkage by 40%, but does not affect the mass loss of the screed and the pore size distribution of the material.

In the present study, CSA was prepared by mixing CSA clinker (CK) and re-crystallized gypsum (RG) in the following proportions: CK/RG = 100/0; 90/10; 80/20; 70/30; and 60/40. This parametric study has been undertaken because the gypsum dosage depends on the application (high early age strength or shrinkage reduction) as shown in [15]. Three types of polyether polyol were added at a dosage of 1.5 wt% of CSA when hydrating pure pastes and standard mortars. This dosage was fixed following the technical information of the products for use in Portland cement concretes: 1–2 wt% of cement [1–11]. The engineering properties of mortars (compressive strength, drying shrinkage) and the microstructure of pastes were investigated.

2. Experimental work

Calcium sulfoaluminate clinker (CK) was produced in a laboratory kiln by burning at 1350 °C a mixture of re-crystallized gypsum (12.1%), calcium carbonate (26.7%), silico-calcareous fines (25.5%), and bauxite (35.7%). Its chemical composition and that of re-crystallized gypsum are presented in Table 1. Its mineralogy was assessed by X-ray diffraction and gave the following results: yeelimite ($Ca_4Al_6O_{12}SO_4$): 53.5%; larnite (β-Ca_2SiO_4): 21.2%; perovskite ($Ca_3Fe_2TiO_9$): 9.0%; ferrite phase ($Ca_4Al_2Fe_2O_{10}$): 16.3%. Calcium sulfoaluminate cement CSA was prepared by mixing CK and re-crystallized gypsum (RG) in the following proportions: CK/RG = 100/0; 90/10; 80/20; 70/30; and 60/40. RG was a by-product of the manufacture of phosphoric acid by the Prayon PH2 process,

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doi:10.1016/j.cemconcomp.2009.04.009

Table 1
Chemical composition of calcium sulfoaluminate cement (CK) and re-crystallized gypsum (RG) (wt%).

Oxides	CK	RG
SiO_2	7.5	nd
Al_2O_3	30.4	0.2
Fe_2O_3	8.6	nd
CaO	44.2	32.0
Na_2O	<0.1	0.2
TiO_2	1.1	nd
MgO	0.6	0.6
K_2O	0.2	nd
P_2O_5	nd	0.4
SO_3	6.5	45.7
LOI	0.3	20.4

with two hemi-hydrate stages followed by a di-hydrate process producing co-crystallized gypsum with low P_2O_5 content [16]. The pure gypsum content of RG determined by differential and thermogravimetric analyses (DTA–TGA) was 89.4%.

In polymer chemistry, polyols are compounds with multiple hydroxyl functional groups available for organic reactions. A molecule with two hydroxyl groups is a diol, one with three is a triol. Three polyether polyols supplied by Bayer were used in the present study. They belonged to the Acclaim® series. They presented the following properties:

- P1: diol with a molecular weight of 2000 g/mol;
- P2: diol with a molecular weight of 6000 g/mol;
- P3: triol with a molecular weight of 6000 g/mol.

Acclaim® polyols are polyether polyols based on propylene oxide. These high-performance, low-monol polyethers are prepared with Bayer's proprietary IMPACT® technology, using a patented organo-metallic propoxylation catalyst. Acclaim® polyols are normally used in polyurethane and other applications, including cast elastomers, adhesives and sealants, epoxy flexibilizers, defoamers, lubricants, crude oil de-emulsifiers and plasticizers.

In the present study, polyether polyols were added at a dosage of 1.5 wt% of CSA when hydrating pure pastes and standard mortars. Pastes were prepared at water/CSA = 0.25. The composition of standard mortars was as follows: CSA/sand/water = 1/3/0.5. Prismatic samples (40 × 40 × 160 mm) were cast and demoulded after 24 h. Then, they were cured at 20 °C and 50% RH. Compressive strength of mortars was measured at 28 days on prismatic samples having first been subjected to flexural test (40 × 40 × 80 mm). Length variations of mortar samples were continuously recorded.

The microstructure of hydrated pastes was investigated using the following techniques:

- Mercury intrusion porosimetry (MIP) by means of a Micromeritics Autopore III porosimeter under a maximum intrusion pressure of 400 MPa. Total porosity and pore size distribution were assessed. Pores were classified according to the distribution proposed by Brédy [17]:
- micropores: $\phi < 0.1$ μm;
- mesopores: $0.1 < \phi < 0.6$ μm;
- macropores: $\phi > 0.6$ μm.
- Differential and thermogravimetric (DTA–TGA) analyses by means of a Setaram Setsys Evolution instrument: 60 mg of crushed paste was heated from ambient temperature to 1000 °C at a rate of 5 °C/min.
- X-ray diffraction (XRD) using a Siemens D500 apparatus operating between 5° and 70° 2θ, Cu Kα radiation, at a rate of 1°/min. The software used to exploit the results was DIFFRAC Plus Release 2001-EVA v7.
- Scanning Electron Microscopy (SEM) and Environmental Scanning Electron Microscopy (ESEM) by means of a Philips XL30 ESEM-FEG apparatus.

3. Results and discussion

3.1. Compressive strength and specific gravity of mortars

The 28-d compressive strength of mortars is presented in Fig. 1. The best strength was obtained when plain clinker was used as binder (72.8 MPa). Strength close to 50 MPa was obtained with cement containing 20% or 30% gypsum. The presence of polyol decreased the strength of mortar: −14% in average for P1, −66% for P2, and −48% for P3. Higher strength was observed with low molecular weight of polyol (2000 g/mol for P1; 6000 g/mole for P2 and P3). As shown in Fig. 2, the specific gravity of samples containing P2 and P3 was also lower than that of control mortar and mortar containing P1: some air entrainment occurred in these mixtures. The higher air entrainment occurred with P2.

Fig. 1 also shows a decrease of the compressive strength when gypsum was introduced in the mixture: −44% for 10% gypsum, −33% for 20%, −30% for 30%, and −35% for 40%. This may be attributed to another arrangement of the microstructure. Indeed, the compressive strength is not directly connected to the quantity of

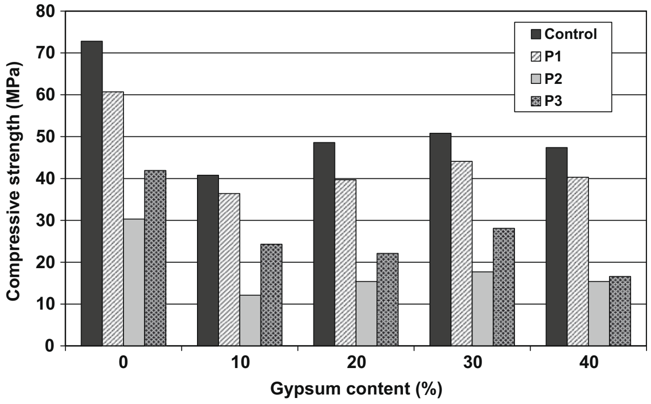


Fig. 1. 28-d Compressive strength of mortars.

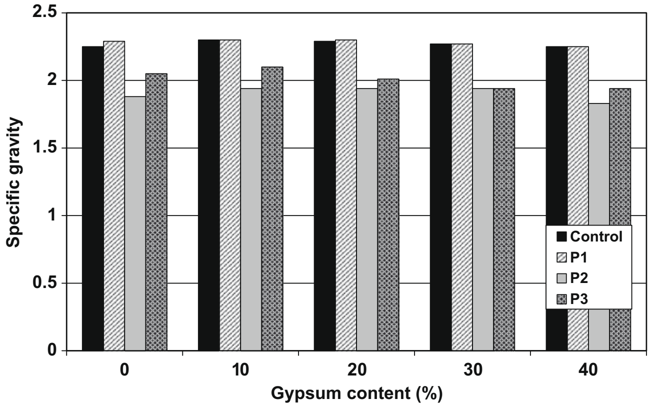


Fig. 2. 28-d Specific gravity of mortars.

Table 2
TGA mass loss of plain CK pastes.

Temperature range (°C)	Hydrate	Mass loss (%)			
		Control	P1	P2	P3
100–130	AFt	6.61	9.18	7.54	6.70
160–200	AFm + CAH_{10}	2.66	4.71	3.66	3.81
250–280	AH_3	2.64	2.26	2.62	2.71

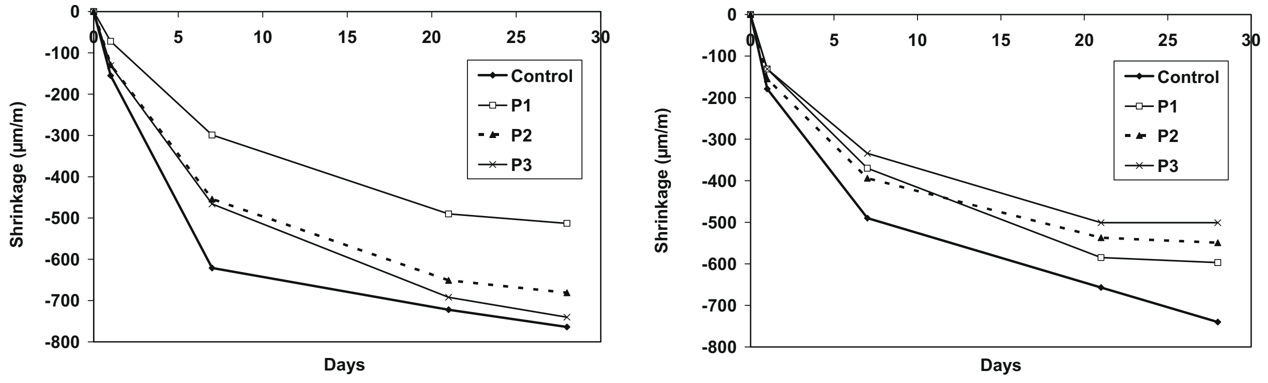
Table 3
TGA mass loss associated to ettringite in mixtures containing gypsum (%).

CK/RG	Control	P1	P2	P3
90/10	12.94	13.19	12.7	12.8
80/20	15.45	16.26	15.90	15.47
70/30	16.15	17.24	16.63	18.28
60/40	17.36	21.43	18.31	19.64

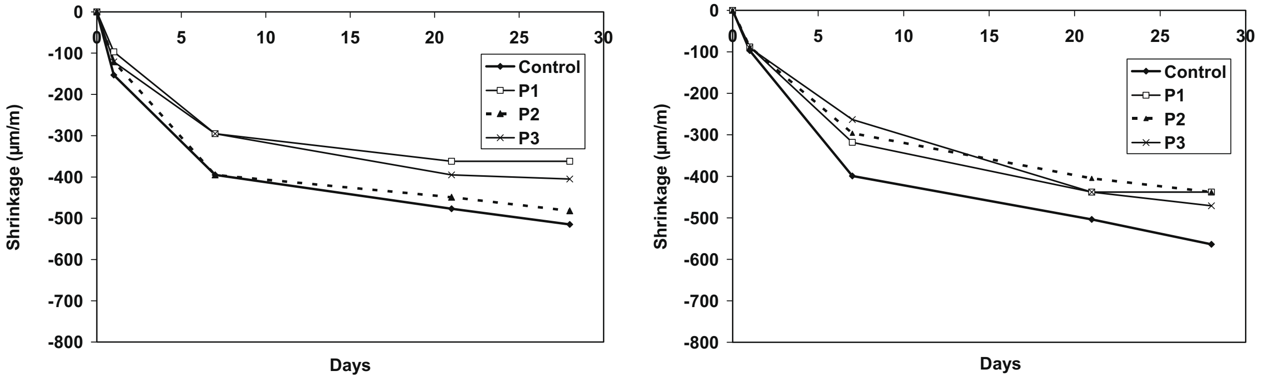
ettringite present in the material, as shown in Tables 2 and 3: it is more important in materials containing gypsum. Monosulfate forms in pure clinker paste while it is absent in pastes containing gypsum.

3.2. Free shrinkage of mortars at 20 °C and 50% RH

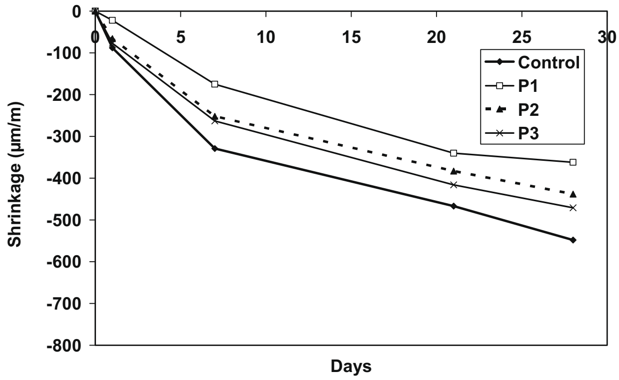
The results obtained on the different mortars are shown in Fig. 3. In control mortars, the lower value of shrinkage was recorded with the binder containing 20% gypsum (−564 μm/m) while the higher was obtained with plain clinker (−764 μm/m).



a) 0% gypsum b) 10% gypsum



c) 20% gypsum d) 30% gypsum



e) 40% gypsum

Fig. 3. Free shrinkage of mortars cured at 20 °C, 50% RH.

The addition of polyol was efficient to reduce drying shrinkage, and especially P1: the average shrinkage reduction was −29%. With P2, it was −17%, and −15% with P3. Here also, lower molecular weight (P1) led to the best performance.

3.3. Results obtained on pastes hydrated at W/C = 0.25

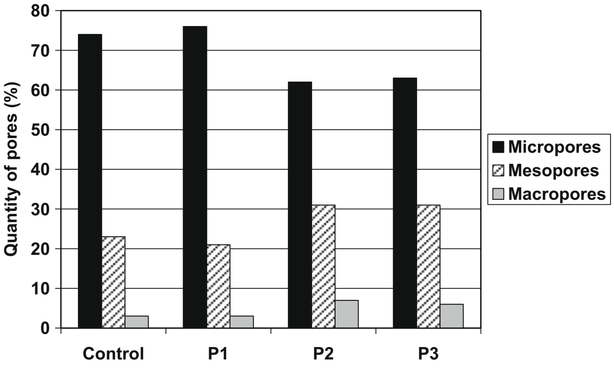
When sulfoaluminate clinker hydrates in presence of gypsum ($CaSO_4{\cdot}2H_2O$), non expansive ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and gibbsite $Al(OH)_3$ are formed according to the following reaction [18]:

$$\begin{aligned} &\underset{610}{4CaO \cdot 3Al_2O_3 \cdot SO_3} + 2[\underset{172}{CaSO_4 \cdot 2H_2O}] + 34\underset{18}{H_2O} \\ &\Rightarrow \underset{1254}{3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O} + 4\underset{78}{Al(OH)_3}, \qquad (1) \end{aligned}$$

in which each number under the compound formula indicates its molecular weight. According to this reaction, the full formation of ettringite and gibbsite requires an elevated water amount (stoichiometric water/solid mass ratio equal to 0.78). In the present study, the water/cement ratio was 0.25, which means an incomplete hydration and may explain some of the results which will be presented hereafter.

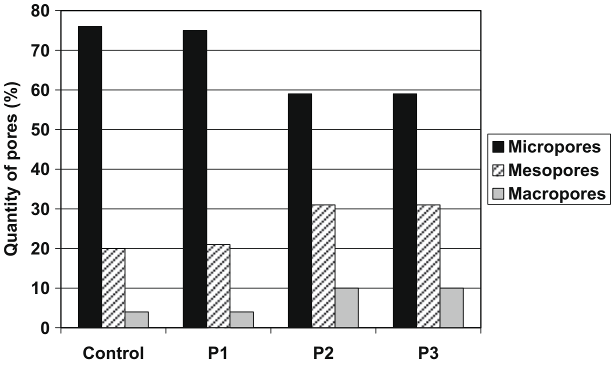
3.3.1. Porosity

The pore size distribution of the different pastes after 28 days of hydration is presented in Fig. 4. Polyol P1 did not significantly modify the pore size distribution of the material. P2 and P3, which led to higher air entrainment in mortars, presented the same effects: they reduced the quantity of micropores (−18%, in average), and increased those of mesopores (+39%) and macropores (+122%).



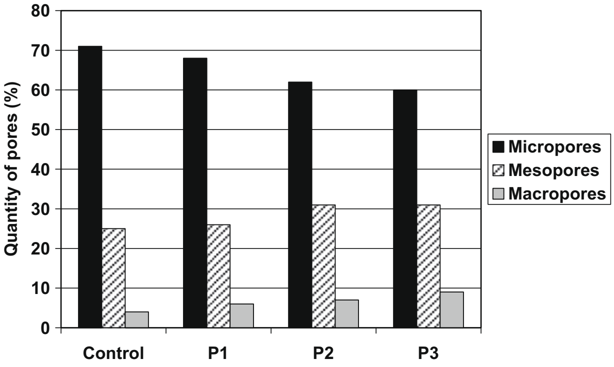
a) 0% gypsum

b) 10% gypsum



c) 20% gypsum

d) 30% gypsum



e) 40% gypsum

Fig. 4. Porous distribution of pastes at 28 days of age.

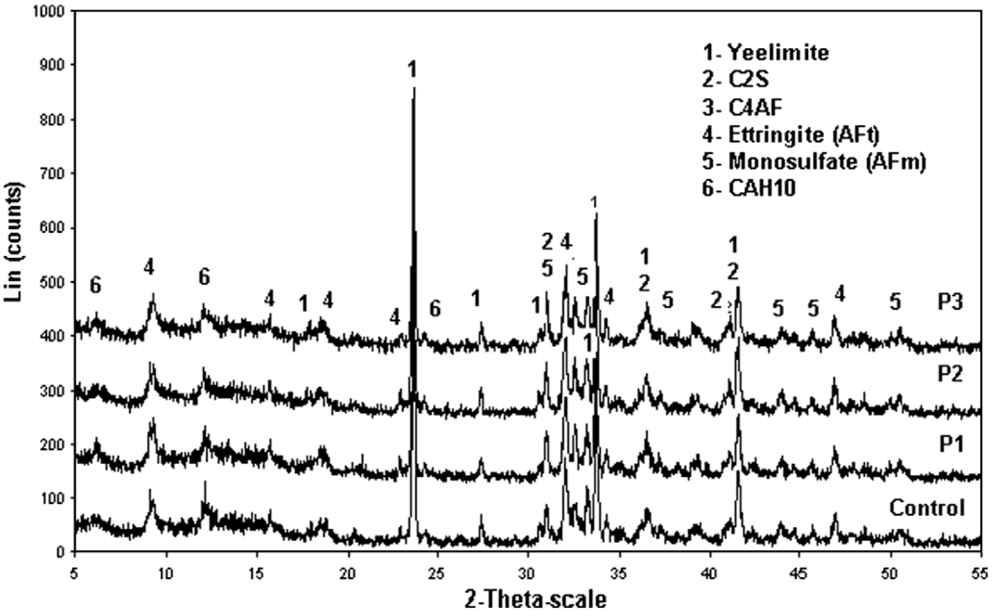


Fig. 5. XRD patterns of plain CK pastes hydrated for 28 days.

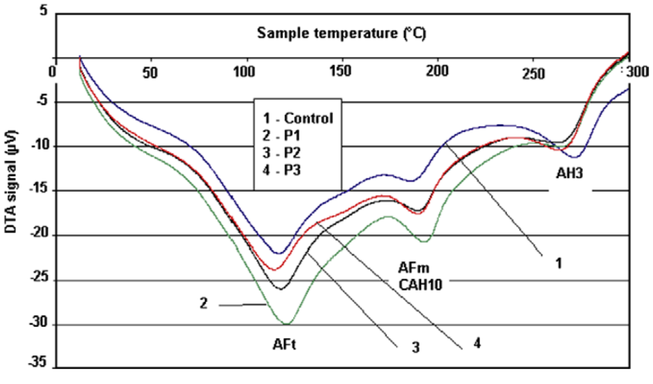


Fig. 6. DTA curves of plain CK pastes hydrated for 28 days.

3.3.2. Microstructure of plain calcium sulfoaluminate clinker paste

XRD analysis (Fig. 5) pointed out the presence of ettringite (Aft), monosulfate (AFm), and CAH_{10} ($CaO{\cdot}Al_2O_3{\cdot}10H_2O$). Aft and AFm were yielded by the hydration of yeelimite. This is not in agreement with the literature. According to Odler [18], in pure water, yeelimite only yields monosulfate and aluminium hydroxide (gibbsite) as products of hydration:

$$4CaO \cdot 3Al_2O_3 \cdot SO_3 + 18H_2O \Rightarrow 4CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2Al(OH)_3, \quad (2)$$

The presence of ettringite and gibbsite (AH_3) was confirmed by DTA analysis (Fig. 6). The presence of CAH_{10} is explained by traces of calcium aluminate (CA) or mayenite ($C_{12}A_7$) in calcium sulfoaluminate clinker, which had not been detected in XRD analysis due to their low content (<2.5%).

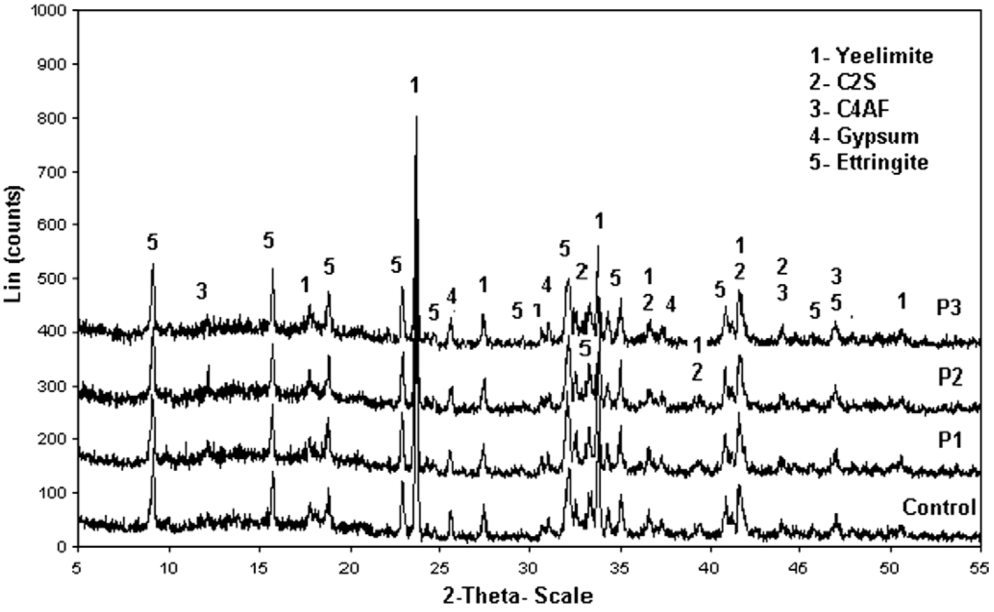


Fig. 7. XRD patterns of paste containing 10% gypsum hydrated for 28 days.

Table 2 shows the mass loss associated to these phases, measured by TGA. The presence of polyol increased the formation of ettringite: the mass loss associated to AFt increased by 39% for P1, 14% for P2, and 1.4% for P3. The same phenomenon appeared for AFm. The quantity of gibbsite remained quite constant.

3.3.3. Microstructure of calcium sulfoaluminate cement pastes

In mixtures containing gypsum (from 10% to 40%), the only hydrate identified by XRD was ettringite (Figs. 7–10). Due to the low water/cement ratio, hydration was incomplete at 28 days and gypsum was still present in all mixtures.

DTA pointed out the presence of ettringite and gibbsite, according to Eq. (1). Table 3 presents the mass loss associated to the decomposition of ettringite for all mixtures. Polyol P1 increased the formation of ettringite, but its effect was less marked than in plain clinker. The higher the gypsum content the higher the effect of P1: +2% ettringite for 10% gypsum, +5% for 20%, +7% for 30%, and +23% for 40%. P2 and P3 had no effect for gypsum contents of 10% and 20%. The effect of P3 was more effective than that of P2 on other mixtures.

SEM and ESEM investigations were carried out on pastes containing 20% gypsum hydrated for 28 days. In the control paste (without polyol), ettringite was found in pores, as shown in Fig. 11a. Different crystal morphologies were present (Fig. 11b): thin needles mixed with longer and thicker crystals.

The presence of polyol (especially P2 and P3) increased the porosity of the matrix, as already observed in MIP analysis. Ettringite also precipitated in the pores. Hollow ettringite was observed,

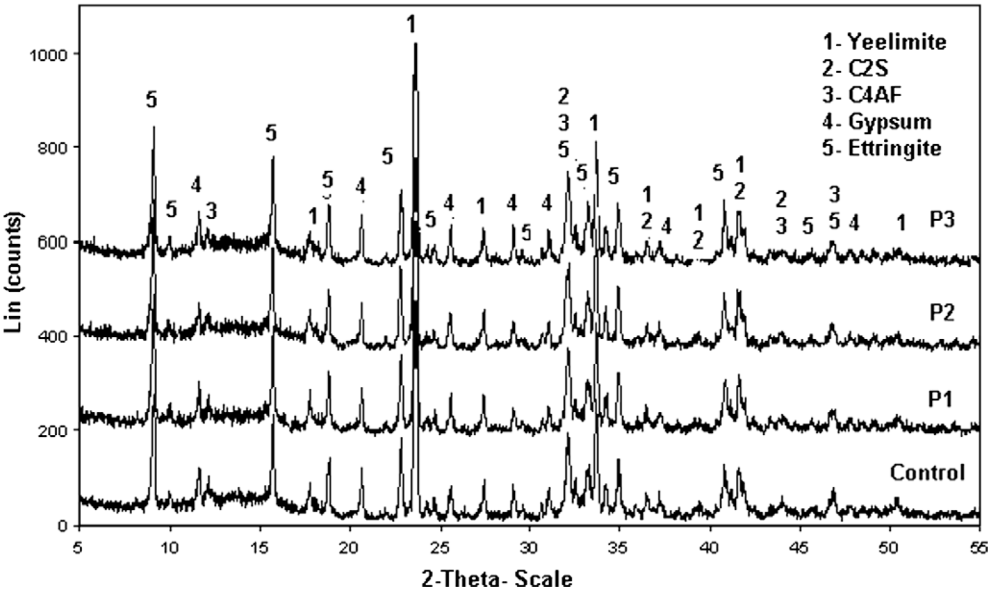


Fig. 8. XRD patterns of paste containing 20% gypsum hydrated for 28 days.

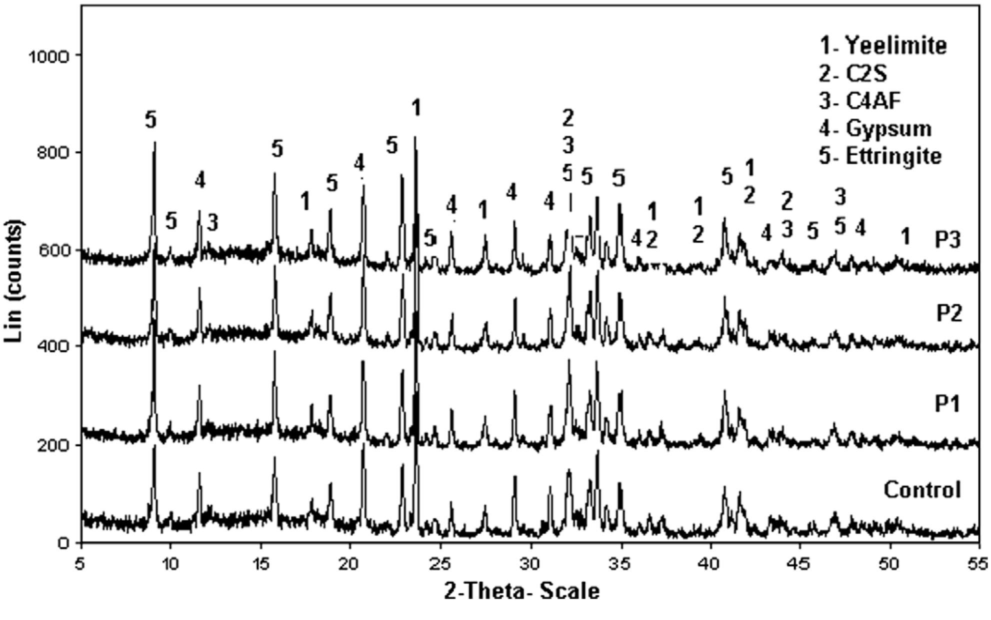


Fig. 9. XRD patterns of paste containing 30% gypsum hydrated for 28 days.

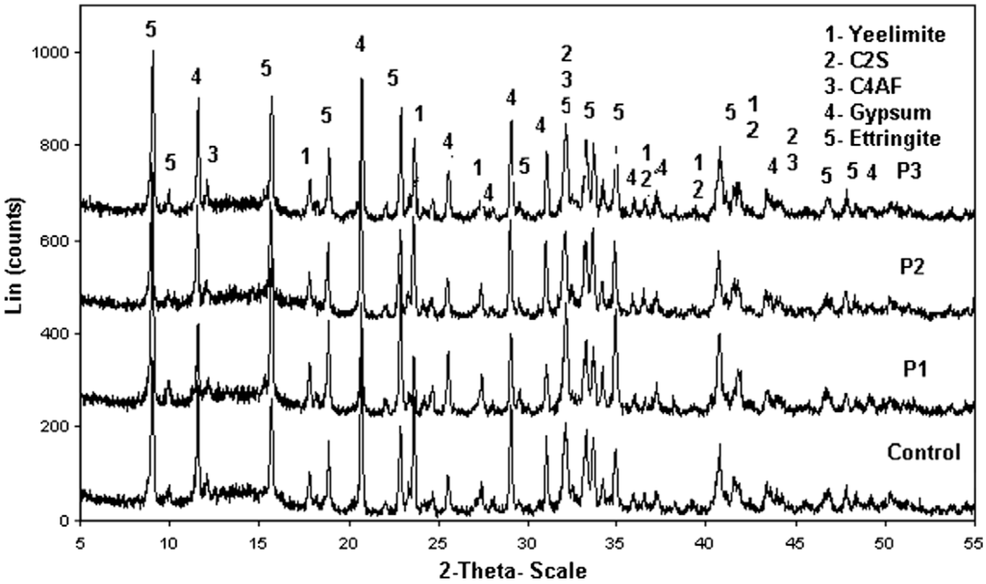
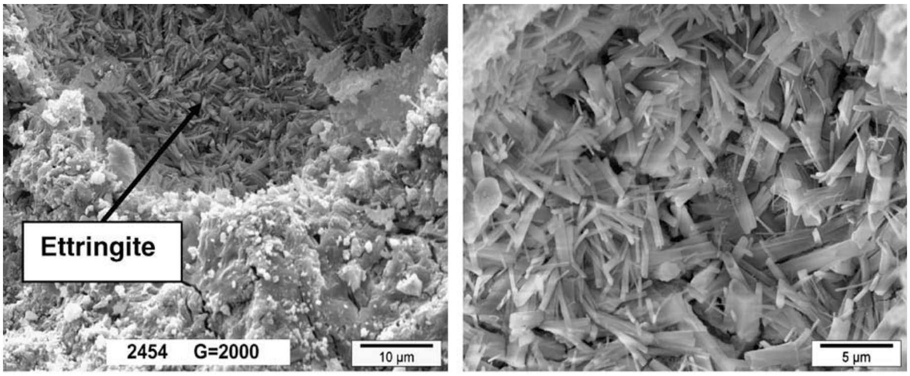


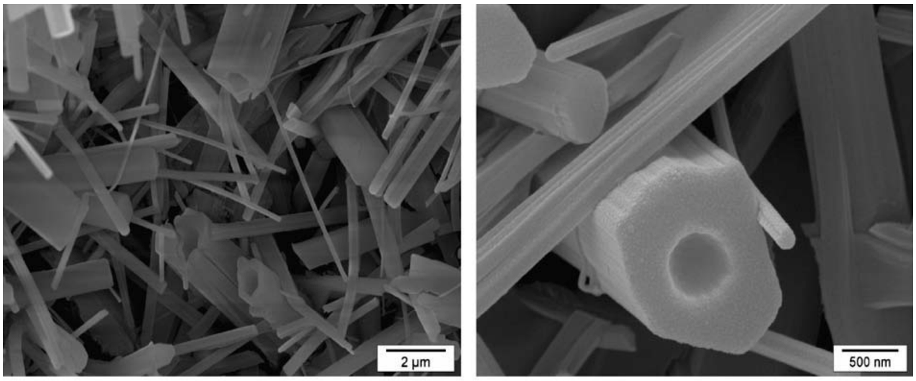
Fig. 10. XRD patterns of paste containing 40% gypsum hydrated for 28 days.



a) Magnification: x2,000

b) Magnification: x4,000

Fig. 11. SEM micrographs of control paste containing 20% gypsum.

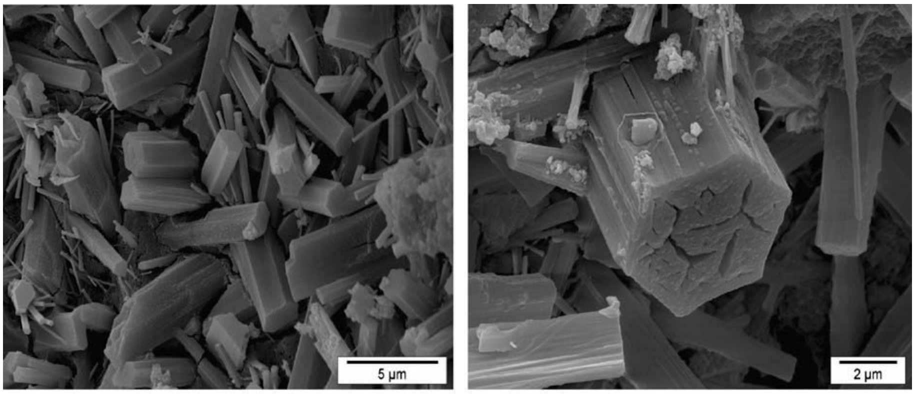


a) Magnification: x8,000

b) Magnification: x32,000

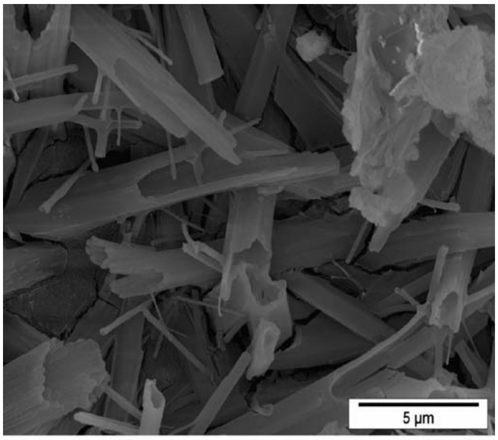
Fig. 12. SEM micrographs of paste containing 20% gypsum and P1.

as well as thin and prismatic hexagonal crystals. In sample containing P1, many hollow crystals were present (Fig. 12a and b). Such crystals were exceptional in sample containing P2 (Fig. 13a and b). They were also found in sample containing P3 (Fig. 14). The presence of P3 affected their crystallization because crystals appeared with damaged lateral sides, indicating that their crystallization was not achieved. In order to verify that the preparation of samples for SEM analysis (gold metallization under low vacuum:



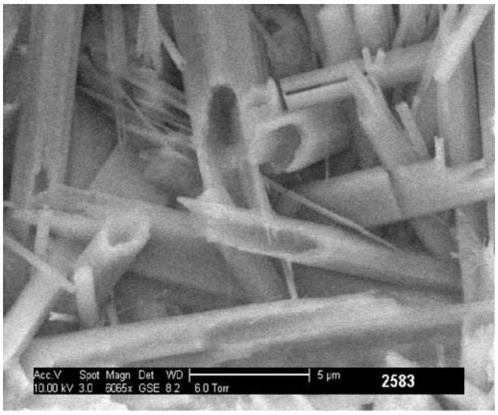
a) Magnification: x5,000 b) Magnification: x8,000

Fig. 13. SEM micrographs of paste containing 20% gypsum and P2.



Magnification: x6,000

Fig. 14. SEM micrograph of paste containing 20% gypsum and P3.



Magnification: x6,000

Fig. 15. SEM micrograph of paste containing 20% gypsum and P3.

10^{-5} Torr) did not damage ettringite [19], ESEM observations were also performed at a vacuum of 2 Torr which did not affect the morphology of ettringite. The same type of ettringite was found using either SEM (Fig. 14) or ESEM (Fig. 15). Thus, it can be concluded that P3 affected ettringite crystallization.

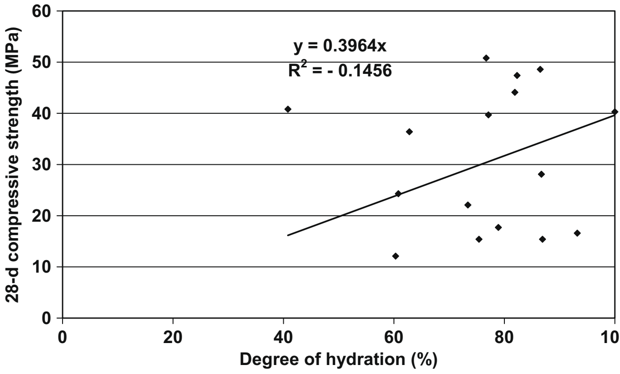


Fig. 16. Correlation between the compressive strength and the degree of hydration.

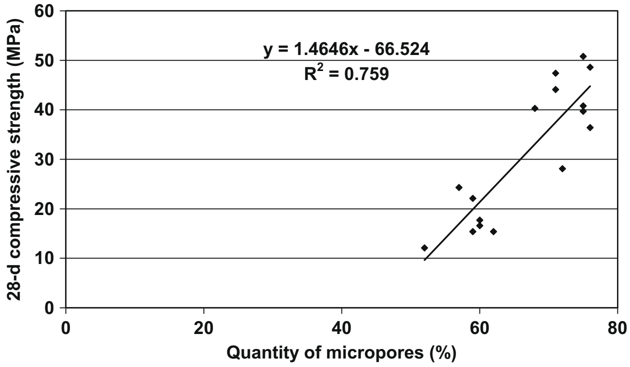


Fig. 17. Correlation between the compressive strength and the quantity of micropores.

3.4. Correlation study

The degree of hydration (e.g. quantity of ettringite formed) has been determined from the mass loss observed in TGA (Tables 2 and 3). Fig. 16 shows that there is no direct relationship between the compressive strength and the degree of hydration ($R^2 = -0.1456$). Fig. 17 indicates a better correlation between the compressive strength and the quantity of micropores ($R^2 = 0.759$). Fig. 18 points out that there is no direct relationship between the final value of drying shrinkage and the degree of hydration ($R^2 = -1.5187$).

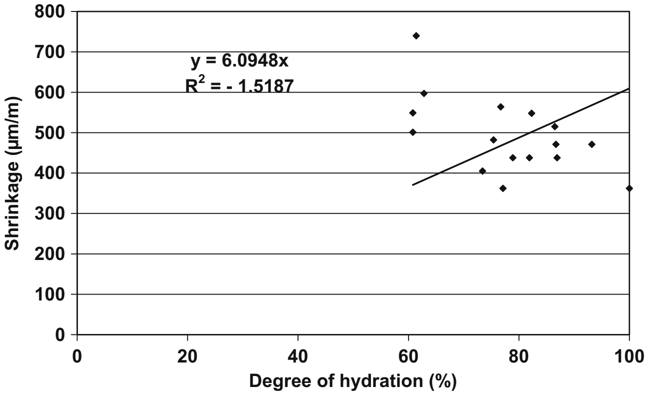


Fig. 18. Correlation between shrinkage and the degree of hydration.

4. Conclusions

On the basis of this study, the following conclusions can be drawn:

(1) Polyether polyol acts as shrinkage-reducing admixture (SRA) of CSA-based mortars: at 20 °C and 50% RH, drying shrinkage is reduced by 15–29% at 28 days of age.

(2) The efficiency of polyether polyol depends on its molecular weight. Low molecular weight (2000 g/mol) leads to the higher reduction of shrinkage, does not affect the porous distribution, and limits the strength loss. Increased air content in mortars containing polyol with high molecular weight is partially responsible of high strength loss.

(3) The presence of polyether increases the quantity of ettringite in hydrated pastes and modifies the morphology of ettringite, leading to the formation of hollow crystals.

Other studies are under investigation, and especially intend to assess if SRA decreases the surface tension of water in concrete pores, as in Portland cement-based materials.

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