



## Effect of the strontium aluminate and hemihydrate contents on the properties of a calcium sulfoaluminate based cement

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**ABSTRACT:** The effect of strontium aluminate ( $\text{SrAl}_2\text{O}_4$ ) on the hydration process of a calcium sulfoaluminate ( $\text{C}_4\text{A}_3\hat{\text{S}}$ ) cement was investigated. Cement pastes were prepared by mixing  $\text{C}_4\text{A}_3\hat{\text{S}}$ , hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,  $\text{C}\hat{\text{S}}\text{H}_{0.5}$ ) and 0, 10 or 20wt% of  $\text{SrAl}_2\text{O}_4$  (SrA). The amount of  $\text{C}\hat{\text{S}}\text{H}_{0.5}$  was 15, 20 or 25wt% based on the  $\text{C}_4\text{A}_3\hat{\text{S}}$  quantity. The cement pastes were hydrated using water to cement ratios (w/c) of 0.4 and 0.5. Samples were cured from 1 to 28 d. The compressive strength and setting time were evaluated and the hydration products were characterized. It was found that the setting time was delayed up to 42 min for the samples containing  $\text{SrAl}_2\text{O}_4$  compared to samples without addition. The samples with 25wt% hemihydrate containing 20wt%  $\text{SrAl}_2\text{O}_4$  developed the highest compressive strength (60 MPa) after 28 d of curing. The main product after hydration was ettringite ( $\text{C}_6\text{A}\hat{\text{S}}_3\text{H}_{32}$ ). The morphology of this phase consisted of thin needle-shaped crystals.

**KEYWORDS:** Strontium aluminate; Ettringite; Sulfoaluminate

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**RESUMEN:** Efecto del contenido de aluminato de estroncio y hemihidrato sobre las propiedades de un cemento de sulfoaluminato de calcio. Se investigó el efecto de la adición de aluminato de estroncio ( $\text{SrAl}_2\text{O}_4$ ) sobre las propiedades de un cemento de sulfoaluminato de calcio ( $\text{C}_4\text{A}_3\hat{\text{S}}$ ). Se prepararon muestras mezclando  $\text{C}_4\text{A}_3\hat{\text{S}}$ , hemihidrato ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,  $\text{C}\hat{\text{S}}\text{H}_{0.5}$ ) y 0, 10 o 20% e.p de  $\text{SrAl}_2\text{O}_4$  (SrA). La cantidad de  $\text{C}\hat{\text{S}}\text{H}_{0.5}$  fue de 15, 20 o 25% e.p. basado en la cantidad de  $\text{C}_4\text{A}_3\hat{\text{S}}$ . Las relaciones agua/cemento utilizadas fueron 0.4 y 0.5. Las muestras fueron curadas hasta 28 d. Se evaluó el tiempo de fraguado y la resistencia a la compresión. Los productos de hidratación se caracterizaron mediante DRX y MEB. El tiempo de fraguado se retardó hasta 42 minutos con la adición del  $\text{SrAl}_2\text{O}_4$  comparado con las muestras sin adiciones. Las muestras con 25% e.p. de yeso y 20% e.p. de  $\text{SrAl}_2\text{O}_4$  desarrollaron la mayor resistencia a la compresión alcanzando 60 MPa a 28 d de curado. Los análisis por MEB y DRX muestran como principal producto de hidratación a la etringita ( $\text{C}_6\text{A}\hat{\text{S}}_3\text{H}_{32}$ ), cuya morfología se observa como cristales aciculares.

**PALABRAS CLAVE:** Aluminato de estroncio; Etringita; Sulfoaluminato

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### 1. INTRODUCTION

The calcium sulfoaluminate ( $\text{C}_4\text{A}_3\hat{\text{S}}$ ) is the key component of calcium sulfoaluminate (CSA) based cements. These binders consist mainly of the phase ye'elemite, also called Klein's salt or tetracalcium trialuminate sulphate ( $\text{C}_4\text{A}_3\hat{\text{S}}$ ) (1). Recently, there has been a renewed interest in CSA cements

because of their potential environmental benefits and performance advantages in special applications, and their rise in popularity has been accompanied with some state of the art reviews (2–4). The term CSA cements is usually reserved for those clinkers containing more than 50wt% of Klein's salt and they may also have minor amounts of phases such as  $\text{C}_2\text{S}$ , CA,  $\text{C}_4\text{AF}$ ,  $\text{C}\hat{\text{S}}$ ,  $\text{C}\hat{\text{S}}\text{H}_2$  (5).

Cements with large amounts of Ye'elimite may have special applications due to their high strength development at early-ages (6). It can be synthesized by calcining stoichiometric proportions of calcium carbonate ( $\text{CaCO}_3$ ), aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) at temperatures ranging from 1250 to 1300 °C for 3 h (7). De la Torre et al. (8) studied the thermal stability of Klein's salt in iron-rich belite sulphoaluminate clinkers. They found that the optimum clinkering temperature, which corresponds to the largest overall amount of  $\text{C}_4\text{A}_3\hat{\text{S}}$ , was 1543 K (1270 °C) but that temperature could be decreased by the addition of boron and sodium to the raw materials. Due to the fact that CSA requires synthesis temperatures 200–300 °C lower than those required for the formation of  $\text{C}_3\text{S}$  in ordinary Portland cement, cements incorporating this phase are also called low-energy cements. Other raw materials used in calcium sulphoaluminate production are: limestone, bauxite, aluminium-rich clay and gypsum (9). Besides gypsum, hemihydrate, fluorgypsum and anhydrite are also used as a source of calcium sulphate (10). This compound generates as main crystalline phases ettringite ( $\text{C}_6\text{A}\hat{\text{S}}_3\text{H}_{32}$ ) and monosulphate when combined with water, lime and/or calcium sulphate (11). The early hydration of the CSA cements is mainly governed by the amount and reactivity of the added calcium sulphate (12, 13). In other investigations the early hydration of CSA in the presence of gypsum was studied with varying amounts of calcium hydroxide (14). Typically about 15–25wt% of gypsum and/or anhydrite are interground with the clinker for optimum setting time, strength development and volume stability (15, 16). The  $\text{C}_4\text{A}_3\hat{\text{S}}$  hydration has been studied by following the rate of ettringite formation and microstructural development. CSA based cements can be employed as shrinkage-resistant, self-stressing and high early strength cements. The process of rapid-hardening is due to the instantaneous formation of non-expansive ettringite which develops relatively large crystals that are able to provide high mechanical strength at early ages (17). In systems with low calcium sulphate additions, the ettringite formation is terminated shortly after setting; thus, expansive ettringite reactions cannot occur. On the contrary, the expansive behaviour of systems with ettringite/gypsum molar ratios of about 1:2 and beyond is related to the ongoing formation of ettringite in systems after setting; such systems exhibit a rigid structure, in which further ettringite formation may cause expansion (18). The expansive effect of ettringite formation from the addition of calcium sulphates and materials rich in phases such as CA,  $\text{C}_4\text{A}_3\hat{\text{S}}$  or  $\text{C}_3\text{A}$ , has been utilized to compensate shrinkage in special

cements (19). The properties of CSA cements are strongly influenced by the addition of other cementive compounds such as strontium aluminate. Strontium aluminate based cements (SrAC) are produced by solid state reaction of SrO or  $\text{SrCO}_3$  and  $\text{Al}_2\text{O}_3$  mixtures at 1500 °C. The main constituent of these cements is the  $\text{SrO} \cdot \text{Al}_2\text{O}_3$ . This phase hydrates slowly giving a hydration product with a formula  $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{--}10\text{H}_2\text{O}$ . This kind of cement has potential applications in the production of high temperature resistant concretes (1). In the family of aluminous cements the potential of strontium aluminate has been sporadically studied without much wide-spread commercial success. Despite the long history and fairly extensive use of calcium aluminate cements, these display certain critical shortcomings in their hydration characteristics and application properties; this led to studies that commenced years ago to evaluate if the alkali-earth oxides like SrO could replace lime in the synthesis of aluminates (20). It is well known that the formation of the calcium aluminate hydrates depends on the temperature at which the reaction occurs. Like CAC, the SrAC also displays hydraulic behaviour in contact with water and converts into distronium aluminate hydrate ( $\text{Sr}_2\text{AH}_n$ ) and  $\text{AH}_3$ . No time or temperature-dependent conversion deleterious phenomena were detected in the preliminary hydration studies. For non-refractory applications, SrAC holds a promising potential for making concretes with seawater resistance as well as for protections against radiation of X-rays and  $\gamma$ -rays (21). In this work, the effect of strontium aluminate and hemihydrate content were investigated in order to improve the properties of a CSA cement.

## 2. EXPERIMENTAL

Calcium sulphoaluminate ( $\text{C}_4\text{A}_3\hat{\text{S}}$ ) was synthesized at 1350 °C for 4h from a stoichiometric mixture of commercial materials  $\text{CaCO}_3$  (OMYA S.A.),  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (Yesera Monterrey S.A.) and  $\text{Al}(\text{OH})_3$  (Possehl S.A.). The obtained CSA was dry milled in order to obtain a material with a specific surface area within the range of 350–400  $\text{m}^2/\text{kg}$ . The optimum time of milling was determined based on measurements of the specific surface area according to ASTM C-204 (22) (Equivalent to BS EN 196-6: 2010 (23)). Samples were prepared with different compositions by adding 15, 20 or 25wt% of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  to the calcium sulphoaluminate. Some of the samples were mixed with 10 or 20wt% of strontium aluminate ( $\text{SrAl}_2\text{O}_4$ ). Table 1 show the composition and the identification of the samples prepared.

In order to evaluate the properties of the samples, these were hydrated with distilled water using

TABLE 1. Composition of samples prepared

Compound	Weight %								
	s1	s2	s3	s4	s5	s6	s7	s8	s9
C <sub>4</sub> A <sub>3</sub> S̄	85	76.5	68	80	72	64	75	67.5	60
CŜH <sub>0.5</sub>	15	13.5	12	20	18	16	25	22.5	20
SrA	0	10	20	0	10	20	0	10	20

CŜH<sub>0.5</sub>: CaSO<sub>4</sub>·½H<sub>2</sub>O.  
SrA: SrAl<sub>2</sub>O<sub>4</sub>.

w/c ratios of 0.4 and 0.5. Pastes were cast in cubic moulds of 2.54 cm per side. Curing was carried out by immersing the cubes in water at a constant temperature of 20 °C. The setting time of the samples was evaluated according to ASTM-191 (24) (Equivalent to BS EN 196-3: 2005 (25)). The development of compressive strength was evaluated using an automated hydraulic press (Controls 50-C70024) with a capacity of 250 kN and a loading rate of 350 N/s. Four cubes were tested, reporting the average for each time of curing. X-ray diffraction (XRD) was carried out in order to identify the phases present in some representative samples. Samples were taken from the cubes crushed in the compression tests and dried in a vacuum oven for 24 h at 35 °C; these were further ground to a particle size lower than 150 microns using a porcelain mortar. A Phillips PW 3040e diffractometer was employed using CuK $\alpha$  radiation (1.542 Å) and a scanning range of 7–60 degrees 2 $\theta$ . Analyses by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were made to observe the phases formed and the microstructure of the hydration products on fracture surfaces and polished samples mounted in epoxy resin. Analyses were carried out using a Phillips XL 30 SEM; EDS was performed at 2000 magnifications over a 100  $\mu$ m<sup>2</sup> transversal area using 20 kV and a working distance of 10 mm. The samples were analysed using the technique of backscattered electrons for the observation of hydration products. Samples mounted in epoxy resin were abraded with SiC sand paper of 80, 120, 320, 500, 800 and 1200 grit size and then polished with 1 and 0.25 mm diamond pastes. All samples were coated with graphite before analysis.

### 3. RESULTS AND DISCUSSION

Table 2 shows the initial and final setting times of the samples analysed. It was found that the setting time is influenced by the w/c ratio, the amount of hemihydrate and the strontium aluminate incorporated. As for the w/c ratio, an increase from 0.4 to 0.5 increased the setting time up to 42 min compared to samples without aluminate addition.

Similarly, the addition of the strontium aluminate had a retarding effect on the setting time. The addition of 10wt% of strontium aluminate had greater retarding effect than 20wt%. Isothermal calorimetric studies indicated that the heat released during the early stages is higher for the sample with 20wt% SrA (21.2 W/kg) compared to that of the sample with 10wt% SrA (9.1 W/kg). This indicates that the hydration reactions occurred more rapidly in the latter, leading to lower setting times. According to ASTM C 150 (26) (Equivalent to BS EN 197-1:2000 (27)), the initial setting of OPC must not be less than 45 min and the final setting not more than 375 min.

Figure 1 shows the development of compressive strength as a function of curing time of samples with 15wt% hemihydrate and w/c of 0.4 (a)

TABLE 2. Setting times of the samples analysed

Sample	w/c	Setting time (min)	
		Initial	Final
s1	0.4	13	21
	0.5	21	38
s2	0.4	26	43
	0.5	50	92
s3	0.4	14	31
	0.5	30	62
s4	0.4	9	17
	0.5	19	33
s5	0.4	24	39
	0.5	46	84
s6	0.4	14	25
	0.5	27	52
s7	0.4	7	12
	0.5	16	26
s8	0.4	22	36
	0.5	42	78
s9	0.4	13	21
	0.5	20	43

and 0.5 (b), with 0, 10 and 20% of SrAl<sub>2</sub>O<sub>4</sub>. The strength development was greatly influenced by the addition of SrAl<sub>2</sub>O<sub>4</sub>. Samples with 0 and 10wt% additions behaved similarly since there was a decrease in strength after three days of curing followed by a subsequent increase. The maximum strength after 28 d of curing was 30.5 and 39 MPa for w/c=0.4 and of 27.6 and 26.3 MPa for w/c=0.5. The strength decrease at three days of curing was attributed to the delayed ettringite formation which occurs after submerging the samples in water after 1d of curing. This ettringite was formed after the cement paste has hardened and because of the expansive nature of this phase, some cracking were generated. With the addition of 20wt% of SrAl<sub>2</sub>O<sub>4</sub> the reduction in the development of compressive strength at 7 d of curing was negligible. The maximum strengths

reached at 28 d of curing were 53.5 and 31.1 MPa for w/c=0.4 and w/c=0.5, respectively.

Figure 2 shows the development of compressive strength of samples with 20wt% hemihydrate and w/c of 0.4 (a) and 0.5 (b) with the addition of 10 and 20wt% of SrAl<sub>2</sub>O<sub>4</sub>. It was found that there was a favourable effect on the strength development by increasing the amount of hemihydrate. The maximum strength reached after 28 d with the addition of 10wt% of SrAl<sub>2</sub>O<sub>4</sub> were 43.2 and 33.4 MPa using w/c of 0.4 and 0.5, respectively. As in the samples with 15wt% hemihydrate, the addition of 20wt% SrAl<sub>2</sub>O<sub>4</sub> had a great influence on the development of compressive strength as samples reached maximum values of 57 and 36.2 MPa using w/c of 0.4 and 0.5, respectively.

Figure 3 shows the graphs of compressive strength of samples with 25wt% hemihydrate.

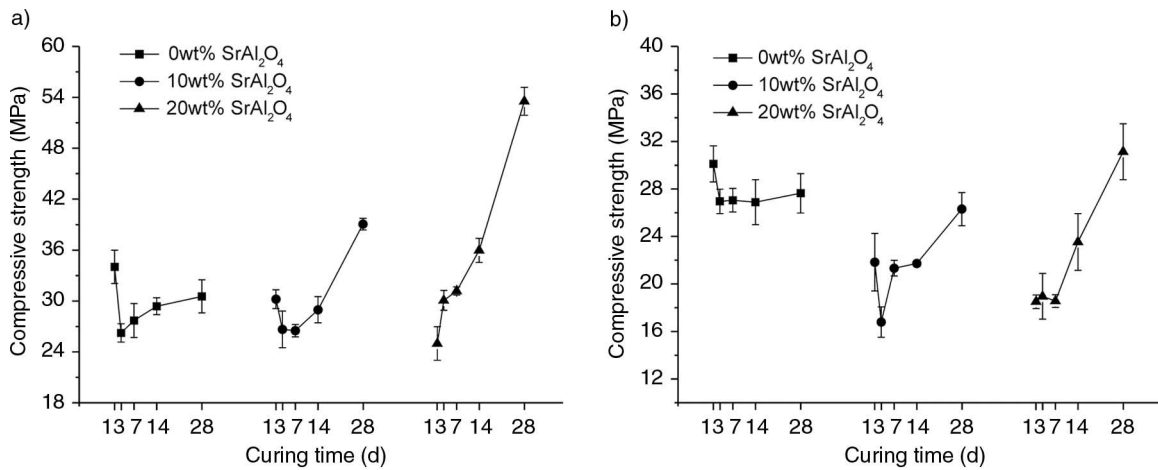


FIGURE 1. Compressive strength of samples with 15wt% hemihydrate using w/c of 0.4 (a) and 0.5 (b).

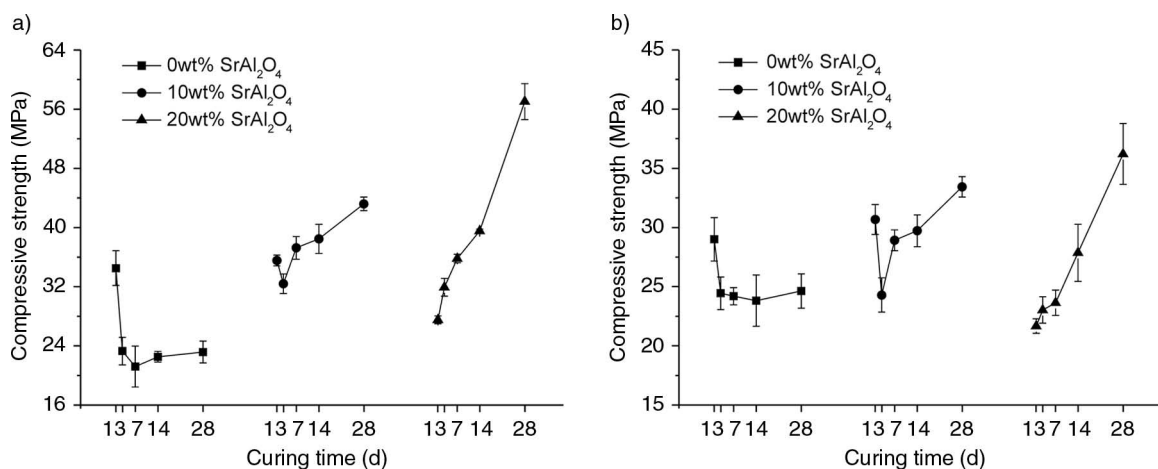


FIGURE 2. Compressive strength of samples with 20wt% hemihydrate using w/c of 0.4 (a) and 0.5 (b).

The evaluation of the compressive strength of the samples with a w/c ratio of 0.4 and without  $\text{SrAl}_2\text{O}_4$  was not possible because of an excessive cracking in the samples. The addition of  $\text{SrAl}_2\text{O}_4$  addition seems to avoid such cracking. A favourable effect on the strength development by was noted after increasing the amount of hemihydrate. The maximum 28 days strengths with the addition of 10wt% of  $\text{SrAl}_2\text{O}_4$  were 45.8 and 36.3 MPa using w/c of 0.4 and 0.5, respectively; whereas for 20wt% of  $\text{SrAl}_2\text{O}_4$  the strength reached maxima of 60.2 and 35.2 MPa using w/c of 0.4 and 0.5, respectively.

Figure 4 shows the XRD patterns corresponding to samples with 15, 20 and 25wt% of hemihydrate

containing 10wt% (a) and 20wt% (b) of  $\text{SrAl}_2\text{O}_4$  after 28 d of curing. The main hydration product was the ettringite phase with its main peak located at 9.09  $2\theta$  degrees. Besides ettringite, monosulphate and a high portion of non-reacted calcium sulphoaluminate were found. No strontium aluminate hydrates could be detected and only a  $\text{Sr}(\text{SO}_4)$  phase was found. As expected, the intensity of ettringite reflections increased with the hemihydrate content while that of calcium sulphoaluminate cement decreased.

Figure 5 shows the microstructure of the samples containing 15(a), 20(b) and 25(c)wt% hemihydrate and 10wt%  $\text{SrAl}_2\text{O}_4$  using a w/c of 0.4 after 28 d of curing. Microanalysis by EDS indicates that large

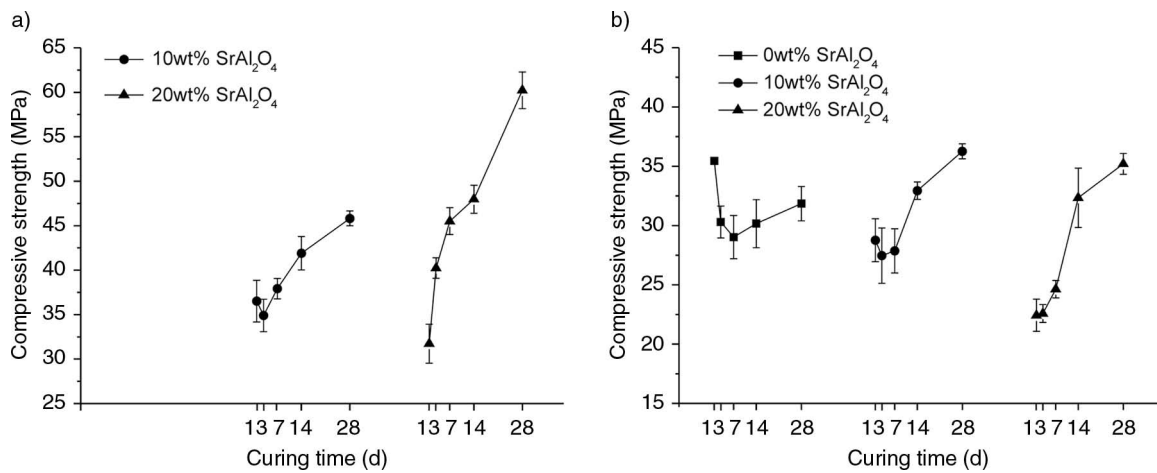


FIGURE 3. Compressive strength of samples with 25wt% hemihydrate using w/c of 0.4 (a) y 0.5 (b).

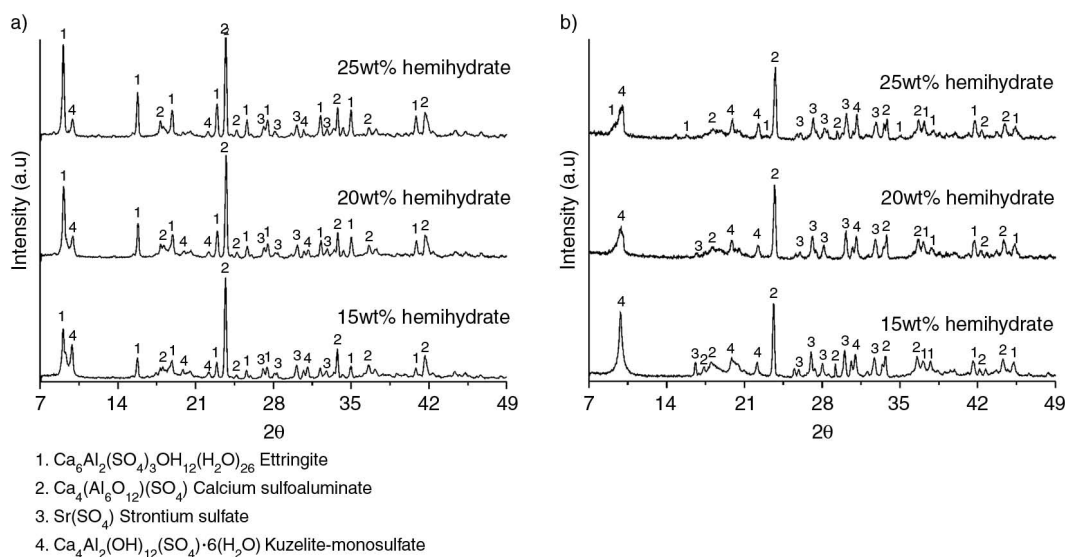


FIGURE 4. XRD patterns of samples with 15, 20 and 25wt% of hemihydrate containing 10% (a) and 20wt% (b) of  $\text{SrAl}_2\text{O}_4$  after 28 d of curing using 0.4 w/c.



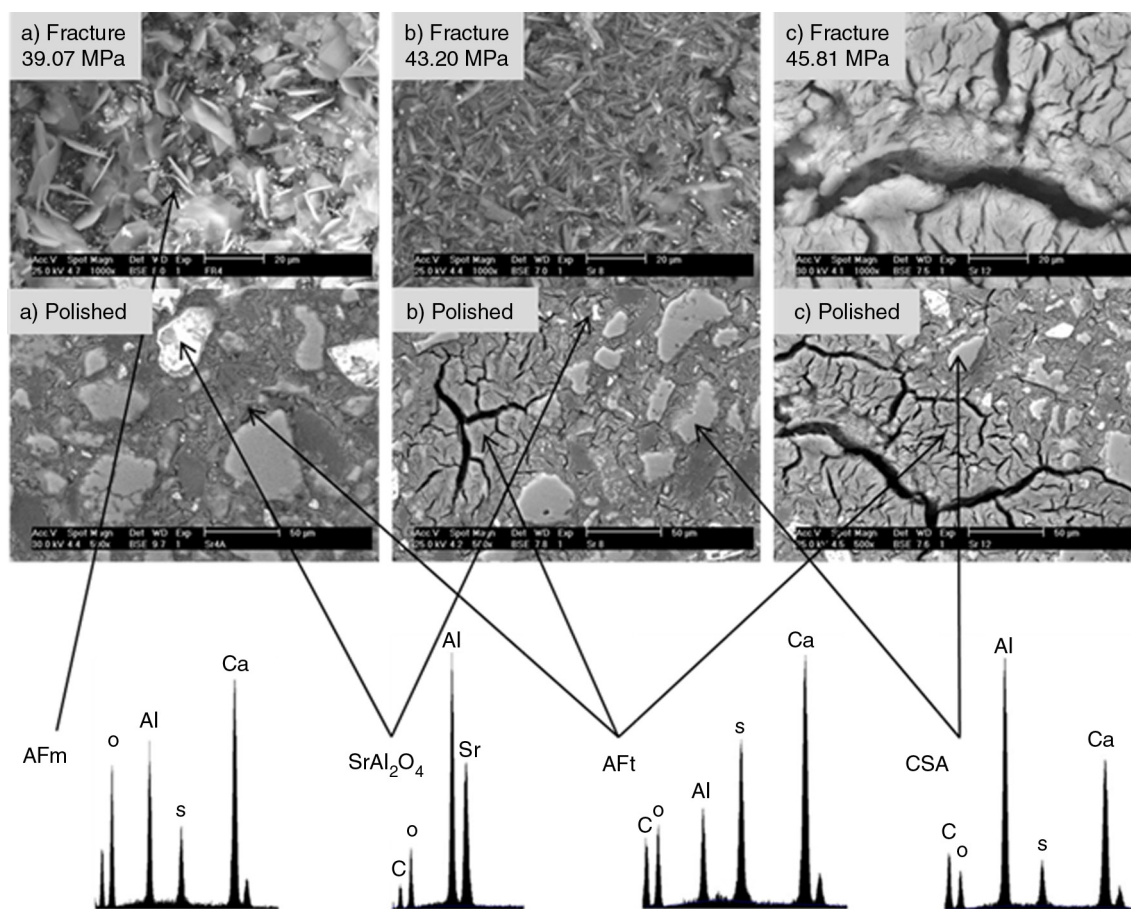


FIGURE 5. Micrographs of samples containing 15(a), 20(b) and 25(c)wt% of hemihydrate and 10wt% of  $\text{SrAl}_2\text{O}_4$  after 28 d of curing.

light-coloured particles correspond to a calcium sulphoaluminate phase and the matrix is mainly composed of ettringite, which is the main hydration product as indicated by DRX. It was observed that calcium sulphoaluminate was not completely reacted and that the formation of ettringite caused some cracking in the specimens, as can be noted in the fracture surfaces that showed the needle-like morphology of the latter. Figure 5(a) shows hexagonal plate-shaped particles which are attributed to monosulphate phase (28, 29). Figure 5(b) shows needle-shaped crystals having a maximum length of 10  $\mu\text{m}$  and were homogeneously distributed throughout the analysed area. In Figure 5(c) it was observed how ettringite crystals have grown enough to impinge and form a cracked structure.

Figure 6 shows the microstructure of the samples containing 15(a), 20(b) and 25(c)wt% of hemihydrate using a w/c of 0.4 and containing 20wt% of  $\text{SrAl}_2\text{O}_4$  after 28 days of curing. Micrographs show a partially reacted calcium sulphoaluminate particles surrounded by a matrix formed mostly by strontium aluminate. In these samples ettringite is observed as smaller but coarser needle-shaped crystals; it appears

that the presence of  $\text{SrAl}_2\text{O}_4$  inhibits the growth of ettringite crystals, avoiding an excessive cracking of the samples.

#### 4. CONCLUSIONS

The addition of strontium aluminate has a retarding effect on the setting of the samples leading to obtain a crack-free cement with high strength. The setting time increased 42 min compared to samples without aluminate in samples with 15wt% hemihydrate and 10wt% of  $\text{SrAl}_2\text{O}_4$ . The water to cement ratio strongly influences the development of mechanical properties, those hydrated using a w/c of 0.4 develop higher strengths. Also, the addition of  $\text{SrAl}_2\text{O}_4$  has a favourable effect on the development of compressive strength; the maximum values reached with 10 and 20wt% of  $\text{SrAl}_2\text{O}_4$  were 29.1 and 60.2, respectively. Ettringite was the main hydration product having a hexagonal needle-shaped morphology growing on cement grains. Monosulphate phase was also found as hexagonal plate-shaped crystals. These cements are very promising materials for the construction industry.

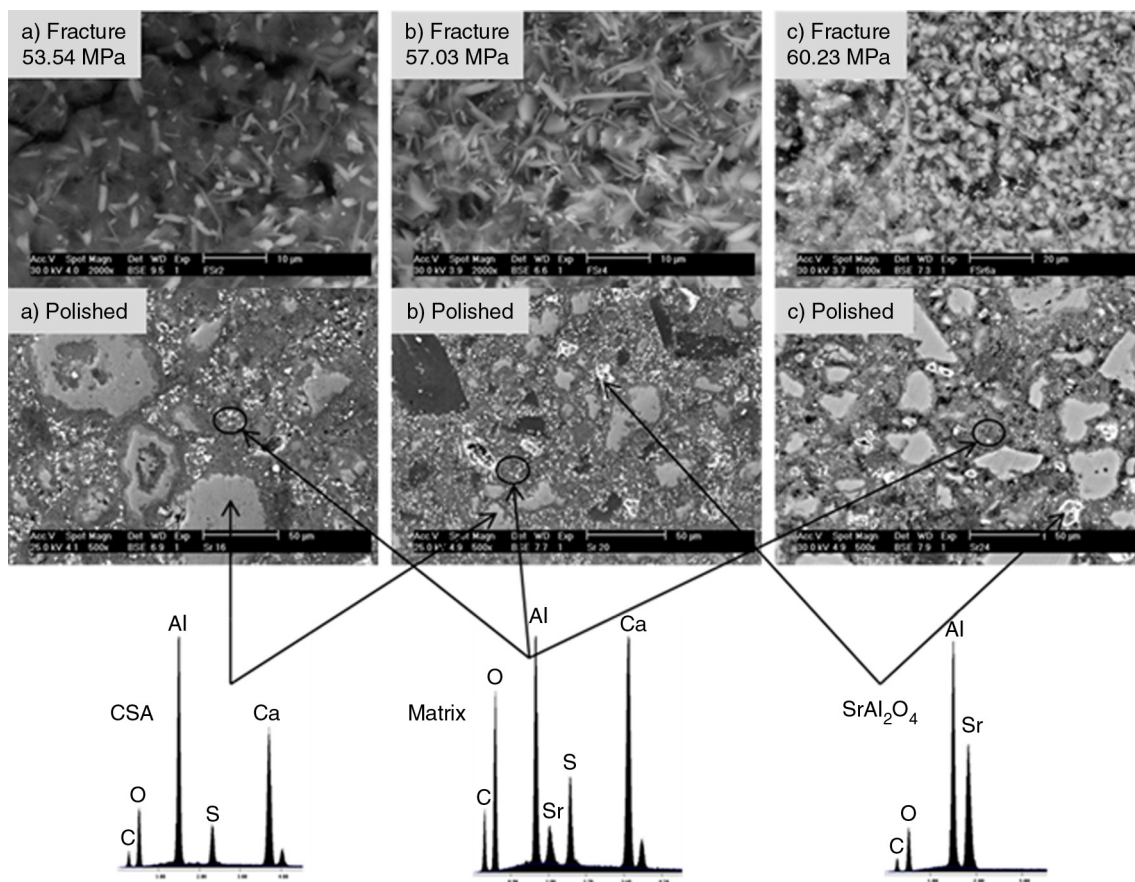


FIGURE 6. Micrographs of samples containing 15(a), 20(b) and 25(c)w% of hemihydrate and 20wt% of  $\text{SrAl}_2\text{O}_4$  after 28 d of curing.

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