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Behaviour of calcium sulfoaluminate cement in presence of high concentrations of chromium salts

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Abstract

This paper deals with the behaviour of calcium sulfoaluminate cement hydrated in presence of high concentration of soluble chromium salts (65 g/kg): chromium nitrate and sodium chromate. Chromium nitrate was chosen to verify the good retention of Cr^{3+} by calcium sulfoaluminate cement. Sodium chromate was employed to assess the ability of calcium sulfoaluminate to immobilize Cr^{6+}.

Leaching tests were carried out on two types of calcium sulfoaluminate cement containing 20% and 30% phosphogypsum, respectively. The microstructure was also investigated at 28 and 90 days.

The results obtained point two main findings:

- the retention of Cr^{3+} is excellent (>99%), regardless of the type of cement,
- the retention of Cr^{6+} depends on the type of cement and, in this case, the U phase is detected and promotes some expansion leading to cracking of the matrix.

Keywords: Calcium sulfoaluminate cement; Ettringite; U phase; Leaching; Stabilization

1. Introduction

In a recent paper, Peysson et al. [1], have shown that calcium sulfoaluminate cement (CSA) could immobilize heavy metals like lead, zinc, cadmium, and chromium. These metals are integrated in the structure of ettringite, which is the main product of hydration of CSA [2]. From a chemical point of view, trivalent ions as Fe^{3+}, Cr^{3+}, and Mn^{3+} [3] can replace Al^{3+} ions in the crystal structure of ettringite [$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$]. Ca^{2+} ions can be substituted by bivalent ions as Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} or Ni^{2+}. Moreover SO_4^{2-} can be replaced by CO_3^{2-}, NO_3^-, SeO_4^{2-}, CrO_4^{2-}, or $B(OH)_4^-$ [4–11].

The work reported in [1] also pointed out that the retention of Cr^{6+} under sodium chromate and sodium dichromate forms was less important than that of Cr^{3+}. This was explained by different microstructures in hydrated cements and the formation of delayed ettringite, leading to higher porosity and cracking. In this study, the quantity of chromium added to CSA was 3.6 g/kg.

In the present research, very high concentration of chromium was used: 65 g/kg. Chromium was introduced as either sodium chromate ($Na_2CrO_4{\cdot}4H_2O$) for Cr^{6+} or chromium nitrate [$Cr(NO_3)_3{\cdot}9H_2O$] for Cr^{3+}. The effect of these salts on the hydration and leaching of CSA was investigated.

2. Experimental

Two calcium sulfoaluminate cements (CSA) were used:

- CSA2080: 80% calcium sulfoaluminate clinker +20% phosphogypsum,

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Table 1
Composition of calcium sulfoaluminate clinker and phosphogypsum

Oxides	Sulfoaluminate cement	
	Phosphogypsum	Clinker
Al_2O_3	0.2	30.4
CaO	32.1	44.2
SiO_2	–	7.5
Fe_2O_3	–	8.6
MgO	0.6	0.6
K_2O	–	0.2
P_2O_5	0.4	–
TiO_2	–	1.1
SO_3	45.7	6.5
SrO	–	0.2
LOI	20.4	0.3

- CSA3070: 70% calcium sulfoaluminate clinker +30% phosphogypsum.

The composition of calcium sulfoaluminate clinker, assessed by X-ray diffraction and chemical analysis (Table 1), was as follows:

- yeelimite ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$): 66.4%,
- belite ($2CaO{\cdot}SiO_2$): 15.6%,
- mayenite ($12CaO{\cdot}7Al_2O_3$): 7.1%,
- perovskite ($3CaO{\cdot}Fe_2O_3{\cdot}TiO_2$): 9.9%.

The composition of phosphogypsum is also given in Table 1. Gypsum was the sole phase detected by X-ray diffraction (XRD). Its content was estimated at 96.7%.

Chromium was introduced as either sodium chromate ($Na_2CrO_4{\cdot}4H_2O$) for Cr^{6+} or chromium nitrate [$Cr(NO_3)_3{\cdot}9H_2O$] for Cr^{3+}. These water-soluble compounds were mixed in de-ionized water and used as mix-water in preparing the pastes. The water to CSA ratio (W/CSA) was 0.40. Sulfoaluminate clinker and phosphogypsum were mixed for 1 min, then polluted water was added and mixing was continued for 3 min. The pastes were cast in mini-cylinders (ϕ M=20 mm, h=40 mm), which were sealed in plastic bags and maintained at 20 °C for 28 or 90 days. The composition of pastes is shown in Table 2. The concentration of chromium was very high (65 g/kg of CSA), compared to that selected by Peysson et al.: 3.6 g/kg of CSA). The ratios of chromium salts to CSA were 50% for chromium nitrate and 29.25% for sodium chromate, respectively. This was done to verify if:

1) the retention of Cr^{3+} remains important regardless of the concentration (chromium nitrate),
2) the U phase reported by Dosch and Zur Strassen [12], Li et al. [13–15] can precipitate in CSA cement. The U phase is a sodium-substituted AF_m phase and its approximate composition was established to be as $4CaO{\cdot}0.9Al_2O_3;1.1SO_3{\cdot}0.5Na_2O{\cdot}16H_2O$. It belongs to the group of hexagonal or pseudo-hexagonal layered structures like AF_m, but differs from the latter in the fact that it contains sodium between the layers and possesses a higher interlayer distance. High concentrations in alumina and sulfate are necessary for the U phase formation, which is the case in CSA. This phase was observed in Portland cement-based systems containing high alkali concentration [13,14,16–19].

After 28 and 90 days of hydration, the different pastes were crushed to get particles smaller than 9.5 mm. The crushed pastes were leached in de-ionized water at water to solids ratio of 16 (Brazilian standard NBR 10005). Leachates were collected at 24 h, and tested for chromium release by means of ICP-MS (Inductively Coupled Plasma-Mass Spectrometry).

At the same ages (28 and 90 days), the leached and uncontaminated pastes were milled to get particles smaller than 100 µm. These powders were subjected to X-ray diffraction (XRD) analysis using Cu-K_α radiation, differential thermal analysis (DTA), and X-ray energy dispersive spectrometry (EDS).

3. Results and discussion

3.1. Leaching tests

Table 3 shows that the efficiency of CSA towards Cr^{3+} immobilization is very important (>99%), regardless of the age (28 or 90 days) and the composition of CSA (CSA2080 or CSA3070). This table also points out that the stabilization of Cr^{6+} depends upon the binder used:

– it is greater than 83% for CSA2080,
– it is in the range of 66 to 69% for CS3070.

The leachate was analyzed by ICP-MS at 28 and 90 days. The results are presented in Fig. 1. It is clearly shown that Cr^{3+} was immobilized in the cementitious matrix, regardless of the composition (CSA2080 or CSA 3070): no Cr peak present. It is also pointed out that the release of Cr^{6+} is more important in CSA3070 than in CSA2080: higher Cr peak.

Table 2
Composition of pastes (%)

Material	CSA2080		CSA3070	
	$Cr(NO_3)_3{\cdot}9H_2O$	$Na_2CrO_4{\cdot}4H_2O$	$Cr(NO_3)_3{\cdot}9H_2O$	$Na_2CrO_4{\cdot}4H_2O$
CSA clinker	80	80	70	70
Phosphogypsum	20	20	30	30
Chromium salt	50	29.25	50	29.25
Water	40	40	40	40

Table 3
Efficiency of CSA towards chromium retention (%)

Type of CSA	Age (days)	Cr concentration: 65 g/kg		Cr concentration: 3.6 g/kg [1]	
		Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}
CSA2080	28	99.21	83.23	99.9	97.5
	90	99.84	87.69	99.9	98.2
CSA3070	28	99.99	66.51	99.9	85.6
	90	99.99	68.82	99.9	65.4

When these results are compared to those obtained by Peysson et al. [1], it can be concluded that chromium concentration does not play an important role in Cr^{3+} retention by CSA, over the range of concentrations used in the study. The efficiency of CSA towards Cr^{3+} immobilization is higher than 99%, regardless of the chromium concentration: 3.6 g/kg or 65 g/kg. When chromium concentration increases from 3.6 g/kg to 65 g/kg, Cr^{6+} retention varies from:

- 97.5% to 83% at 28 days for CSA2080,
- 85.6% to 66.5% at 28 days for CSA3070.

In this case, the influence of chromium concentration is more marked, but the release of Cr^{6+} is not proportional to the quantity of Cr^{6+} initially introduced in CSA. It also appears that we may have exceeded the capacity of CSA 3070 to bind Cr^{6+}.

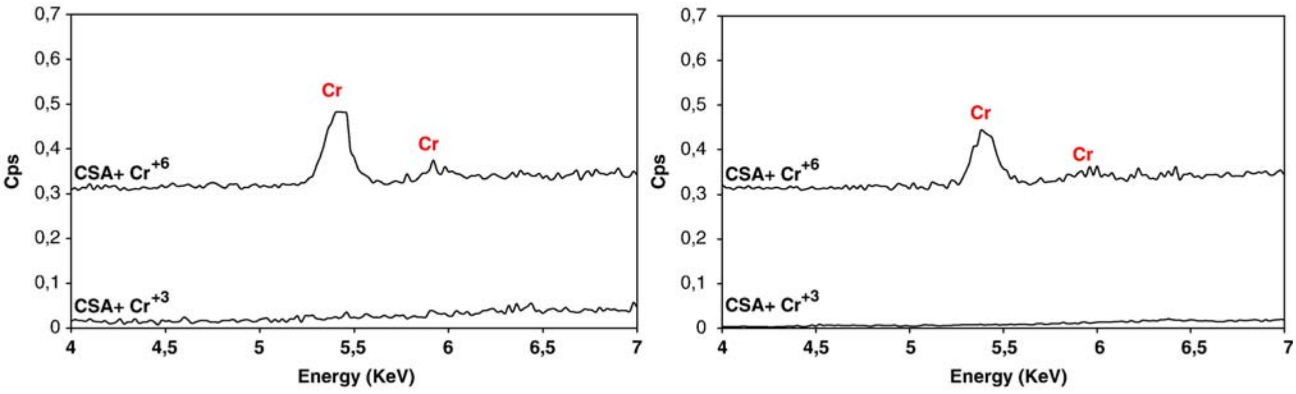
The behaviour of the two cements was different during leaching. As shown in Fig. 2, CSA2080 grains remained undamaged after leaching, while CSA3070 grains were cracked. Fig. 3 presents the evolution of pH during leaching tests, carried out at 20 °C. The concentration of chromium was very high (65 g/kg of CSA). Due to higher basicity of sodium chromate, pH was higher when Cr^{6+} was leached. When pastes containing chromium nitrate (Cr^{3+}) were leached, the behaviour of both cements was quite similar. It was slightly different for Cr^{6+}:

- after 1.5 h, the same value ($pH = 10.9$) was obtained for both cements,
- after 4.5 h, for CSA2080, pH value increased to 11.1 while it remained constant in CSA3070,
- at the end of the test, pH value reached 11.2 for CSA2080, while it dropped to 10.8 in CSA3070.

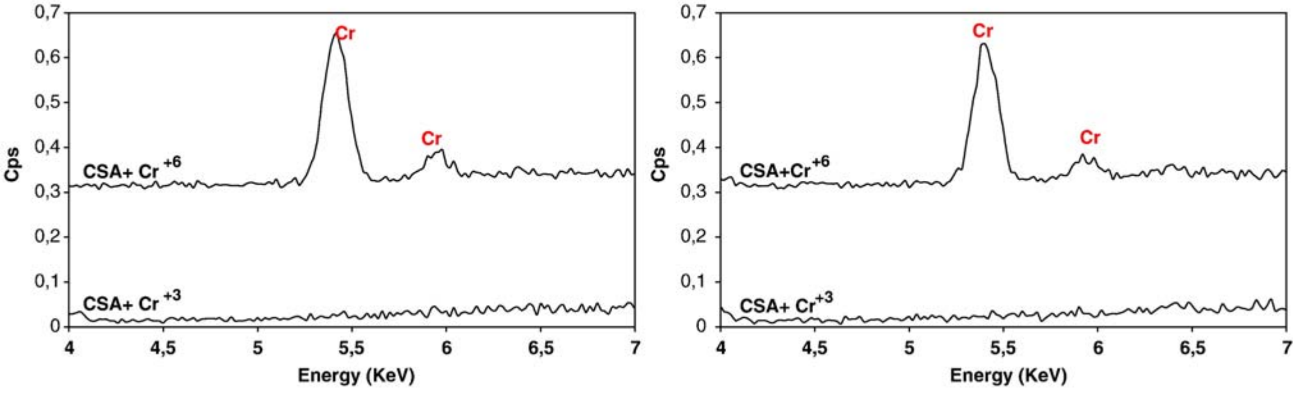
Such behaviour shows lower availability of ions in the CSA3070 solution. A new phase certainly precipitated.

3.2. Microstructure of pastes

Uncontaminated and polluted CSA pastes were subjected to X-ray diffraction analysis after 90 days of hydration. The results are presented in Figs. 4–7.

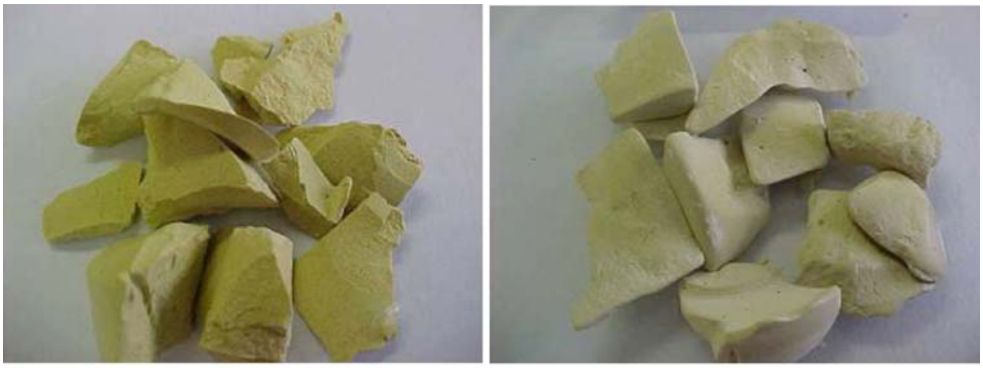


CSA2080 28 days CSA2080 90 days



CSA3070 28 days CSA3070 90 days

Fig. 1. EDS analysis of leachates at 28 and 90 days.



CSA2080 before leaching CSA2080 after leaching

CSA2080 before leaching CSA2080 after leaching

Fig. 2. Behaviour of pastes containing sodium chromate during leaching at 28 days.

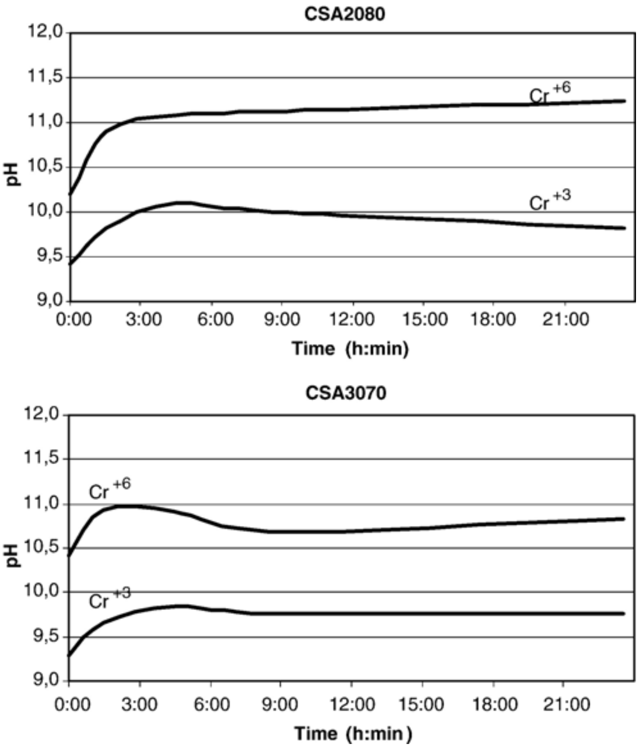


Fig. 3. Evolution of pH during leaching tests at 90 days.

Regardless of the type of CSA, the main crystalline product of hydration in the uncontaminated samples was ettringite. Unreacted yeelimite and gypsum remained in the pastes.

In pastes polluted by chromium nitrate, the quantity of ettringite was lower, yeelimite was almost entirely hydrated, and more gypsum was left unreacted. It seems that the presence of chromium nitrate at high concentration inhibited the dissolution of gypsum, but not that of yeelimite. As SO_4^{2-} can be replaced by CO_3^{2-}, NO_3^-, SeO_4^{2-}, CrO_4^{2-}, or $B(OH)_4^-$ in the structure of ettringite [4–11], there was a competition between

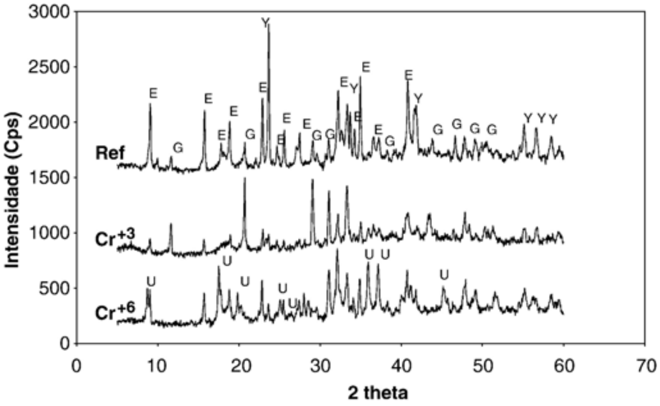


Fig. 4. X-ray analyses of CSA2080 pastes at 90 days.

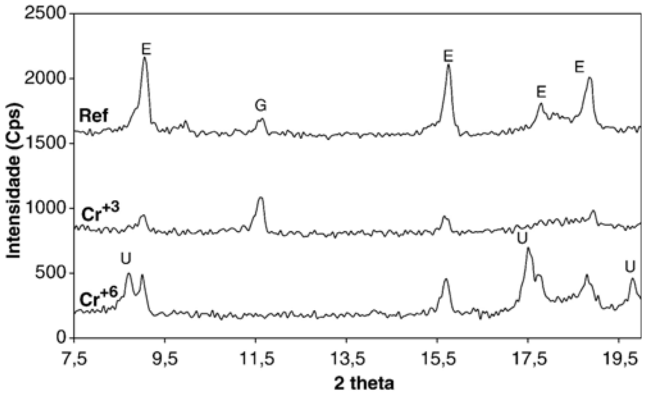


Fig. 5. XRD spectra of CSA2080 pastes at 90 days. Zoom between 2θ = 7.5° and 2θ = 20°.

SO_4^{2-} and NO_3^- which led to the formation of nitrate substituted ettringite.

In pastes polluted by sodium chromate, small quantity of ettringite was identified, gypsum was entirely consumed, and yeelimite remained in small quantify. A new phase was identified by its first peak (2θ = 8.7°): the U phase, as shown in Figs. 4–7. In these pastes, ettringite evolved towards the U phase due to the high alkalinity of the pore solution and the availability of sulfates coming from yeelimite and gypsum. Studies conducted by Ogawa and Roy [20] have shown that the presence of sodium accelerated the reactivity of yeelimite and the dissolution of calcium sulphate. This phenomenon explains the consumption of both gypsum and yeelimite. As reported in [14], the secondary formation of the U phase is associated to an expansion and this may explain the presence of cracks in the CSA3070 sample after leaching.

4. Conclusions

The following conclusions can be drawn:

1) The efficiency of CSA towards Cr^{3+} immobilization is very important (>99%), regardless of the age (28 or 90 days) and the composition of CSA (CSA2080 or CSA3070).

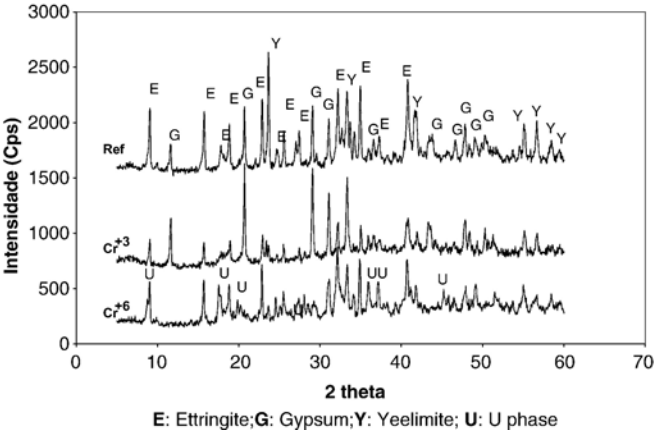


Fig. 6. X-ray analyses of CSA3070 pastes at 90 days.

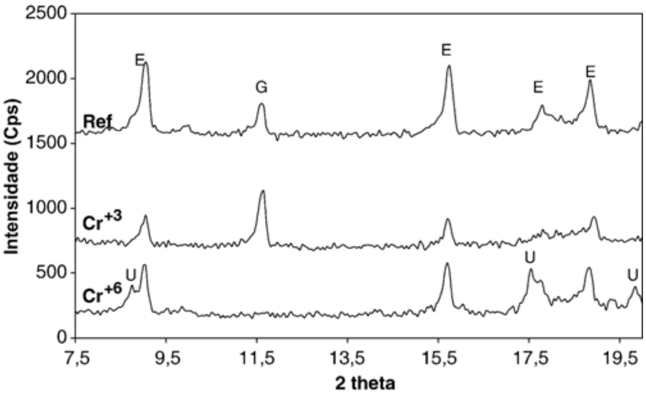


Fig. 7. XRD spectra of CSA3070 pastes at 90 days. Zoom between 2θ = 7.5° and 2θ = 20°.

2) The presence of chromium nitrate at high concentration inhibits the dissolution of gypsum, but not that of yeelimite.
3) The stabilization of Cr^{6+} depends upon the binder used: it is greater than 83% for CSA2080, and in the range of 66 to 69% for CS3070.
4) In pastes polluted by sodium chromate, the U phase is identified. Ettringite evolves towards the U phase due to the high alkalinity of the pore solution and the availability of sulfates coming from yeelimite and gypsum.
5) The secondary formation of the U phase is associated to an expansion.

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