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Immobilization of heavy metals by calcium sulfoaluminate cement

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Abstract

Two types of calcium sulfoaluminate cement containing 20% and 30% phosphogypsum, respectively, were investigated for their ability in hazardous waste stabilization. Fourteen series of pastes were prepared, each containing the following soluble salt: $Na_2CrO_4{\cdot}4H_2O$; $Na_2Cr_2O_7{\cdot}2H_2O$; $CrCl_3{\cdot}6H_2O$; $Pb(NO_3)_2$; $Zn(NO_3)_2{\cdot}6H_2O$; $ZnSO_4{\cdot}7H_2O$; and $CdCl_2{\cdot}5H2O$. The level of pollution was 0.069 mol of heavy metal per Kg of cement.

The study has been carried out by means of X-ray diffraction, thermal analysis, scanning electron microscopy, mercury intrusion porosimetry, electrical conductivity, and leaching tests. Very good retention of lead, cadmium, zinc and trivalent chromium is observed. The retention of hexavalent chromium depends upon the nature of the binder: the cement containing 20% gypsum develops the best behaviour. This is explained by the microstructure of the hydrated paste: in the paste containing 30% gypsum, delayed ettringite precipitates and damages the hardened paste.

Keywords: Calcium sulfoaluminate cement; Ettringite; Leaching; Microstructure; Stabilization

1. Introduction

Sulfobelite cements, also called sulfoaluminate-belite cements, contain the phases belite (C_2S), yeelimite or tetracalcium trialuminate sulfate ($C_4A_3\Sigma$), and gypsum ($C\Sigma H_2$) as their main constituents. When CSA cement hydrates, ettringite ($C_6A\Sigma_3H_{32}$) is formed according to the following reactions [1]:

$$C_4A_3\Sigma + 2C\Sigma H_2 + 34H \Rightarrow C_6A\Sigma_3H_{32} + 2AH_3,$$

in absence of calcium hydroxide,

$$C_4A_3\Sigma + 8C\Sigma H_2 + 6CH + 74H \Rightarrow 3C_6A\Sigma_3H_{32},$$

in presence of calcium hydroxide,where:

. $C = CaO$,
. $S = SiO_2$,
. $A = Al_2O_3$,
. $\Sigma = SO_3$,
. $H = H_2O$,

Sulfoaluminate-belite cements have been used to study the formation of oxyanion-substituted ettringites for the purpose of fixation of heavy metals [2–5]. 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. Ca^{2+} ions can be substituted by bivalent ions as

Table 1
Concentration levels of pollutants

Pollutant	Mol/Kg of binder	Quantity of heavy metal added to the binder (g/Kg)
$Na_2CrO_4{\cdot}4H_2O$	0.069	3.6 g of Cr/Kg
$Na_2Cr_2O_7{\cdot}2H_2O$	0.069	3.6 g of Cr/Kg
$CrCl_3{\cdot}6H_2O$	0.069	3.6 g of Cr/Kg
$Pb(NO_3)_2$	0.069	14.3 g of Pb/Kg
$Zn(NO_3)_2{\cdot}6H_2O$	0.069	4.5 g of Zn/Kg
$ZnSO_4{\cdot}7H_2O$	0.069	4.5 g of Zn /Kg
$CdCl_2{\cdot}5H_2O$	0.069	7.75 g of Cd/Kg

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Sample containing sodium dichromate

Sample containing sodium chromate

Fig. 1. Damaged samples. CSA2.

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 $B(OH)_4^-$ [6–10].

The purpose of this study was to evaluate the ability of calcium sulfoaluminate cement (CSA) to immobilize different heavy metal ions: cadmium, chromium, lead, and zinc.

2. Experimental

Two calcium sulfoaluminate cements (CSA) were used:

- CSA1: 80% calcium sulfoaluminate clinker +20% phosphogypsum,
- CSA2: 70% calcium sulfoaluminate clinker +30% phosphogypsum.

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

- yeelimite ($C_4A_3\Sigma$): 53.5%,
- belite (C_2S): 21.2%,
- ferrite phase (C_4AF): 16.3%, where $F=Fe_2O_3$,
- perovskite (CT): 9%, where $T=TiO_2$.

Phosphogypsum contained 99% pure gypsum.

Four heavy metals were investigated under different water-soluble forms: cadmium, chromium, lead, and zinc. Cadmium was studied under the chloride form: $CdCl_2$.5H2O. Chromium can be found under 3 states, whose valences are +2, +3, and +6. Cr^{3+} and Cr $^{6+}$ are the more frequent states. Cr $^{6+}$ is an acidic form, which forms chromates $(CrO_4)^{2-}$ and dichromates $(Cr_2O_7)^{2-}$. The traditional technique of stabilization of Cr $^{6+}$ is initially to reduce it to Cr^{3+} in acid medium using a reducing agent. The most used reducing agents are ferrous sulphate ($FeSO_4$, $7H_2O$), sodium metabisulfite ($Na_2S_2O_5$), and sodium hydrosulfite ($Na_2S_2O_4$) [11]. In the present research, CSA was directly used to stabilize either sodium chromate ($Na_2CrO_4 \cdot 4H_2O$) or sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$). The fixation of Cr^{3+} was also investigated, using chromium chloride ($CrCl_3 \cdot 6H_2O$).

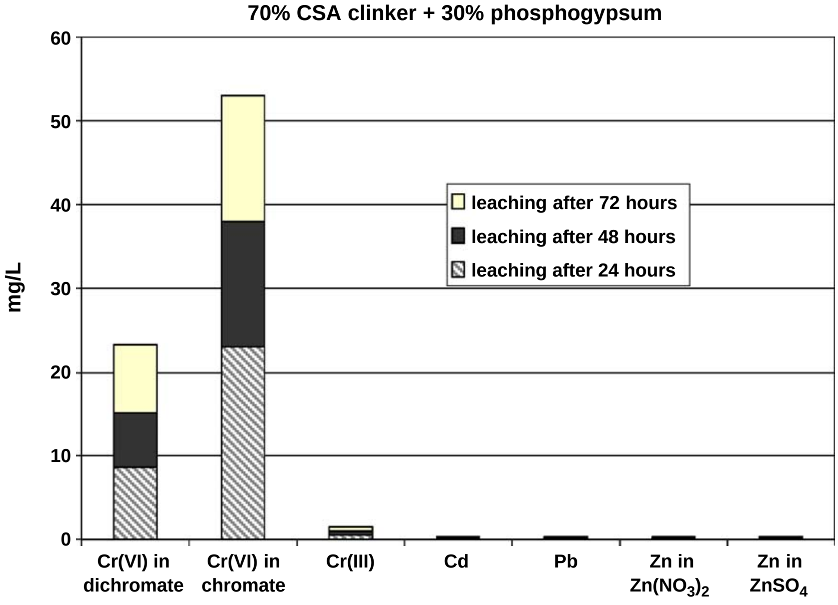

Fig. 2. 28-day heavy metal leach of CSA2 pastes.

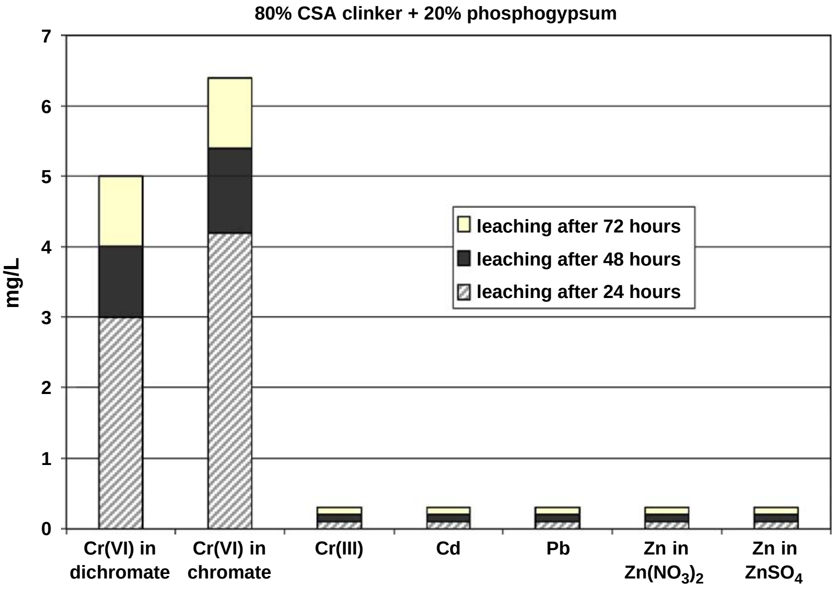

Fig. 3. 28-day heavy metal leach of CSA1 pastes.

Lead is amphoteric and forms soluble, anionic plumbites and plumbates as well as both cations. In this research, the immobilization of lead nitrate [$Pb(NO_3)_2$] was studied. Zinc is also amphoteric and two compounds were investigated: zinc nitrate [$Zn(NO_3)_2.6H_2O$] and zinc sulphate ($ZnSO_4.7H_2O$). Lead and zinc are known as strong retarders of Portland cement.

The water-soluble compounds of heavy metals were mixed in de-ionized water and used as mix-water in preparing the pastes. The water to solids ratio (W/S) was 0.262. 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 ($\phi = 20$ mm, $h = 40$ mm), which were sealed in plastic bags and maintained at 20 °C for 28 or 90 days.

High concentration levels of pollutants were selected to simulate adverse practical situations, as shown in Table 1.

After 28 and 90 days of hydration, the different pastes were crushed to get particles smaller than 4 mm. The crushed pastes were leached in de-ionized water at water to solids ratio of 10 (French standard NF X 31-211). Leachates were collected at 24, 48, and 72 h, and tested for respective

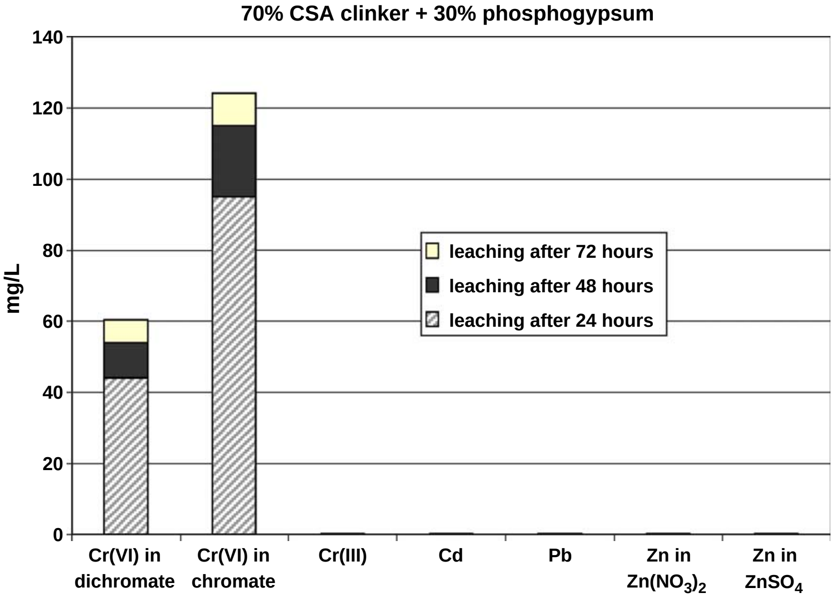

Fig. 4. 90-day heavy metal leach of CSA2 pastes.

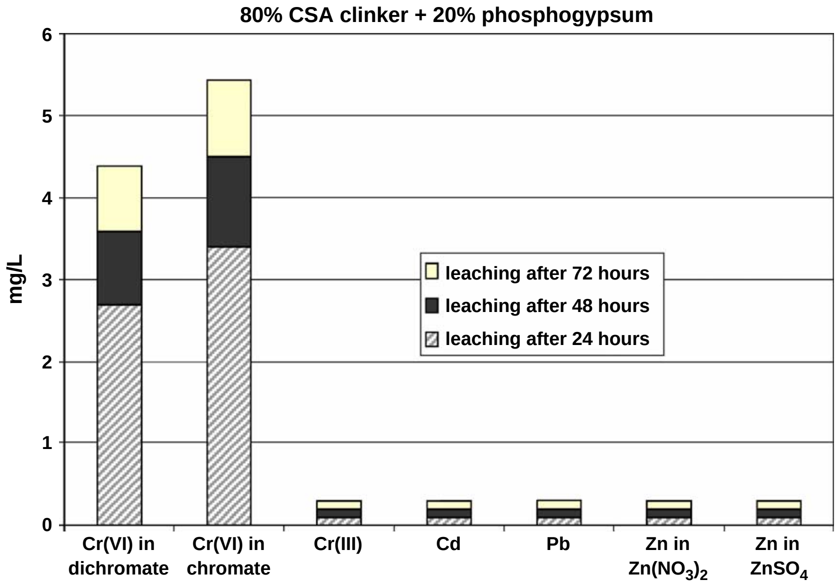

Fig. 5. 90-day heavy metal leach of CSA1 pastes.

heavy metal by means of ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry).

At the same ages (28 and 90 days), the hydration of pastes was stopped using acetone. Then, the samples were maintained under vacuum to avoid their carbonation, before being crushed to get particles smaller than 100 μm. These powders were subjected to X-ray diffraction (XRD) analysis using Cu-K_α radiation and thermal analysis (DTA-TGA, Setys Evolution from SETARAM). Scanning electron microscopy (SEM) was also performed on pieces of mini-cylinders, as well as mercury intrusion porosimetry, using a Micromeritics Autopore III porosimeter.

A specific study of interactions between chromium and calcium sulfoaluminate cement (CSA) was conducted by means of electric conductivity and ions analysis (ICP-OES). Electric conductivity was carried out on suspensions prepared at water to solids ratio of 4 [12]. Each series of tests was repeated three times to check reproducibility. The electric conductivity of suspensions was measured over a period of 15 h, using a multiplexor conductometer developed by Vernet [13]. Nine cells were simultaneously investigated, each of them containing 70 mL of de-ionized water polluted by the chromium compound and 17.5 g of CSA. The ratio between the chromium compound and CSA was 0.024 mol/Kg. At different times (varying from

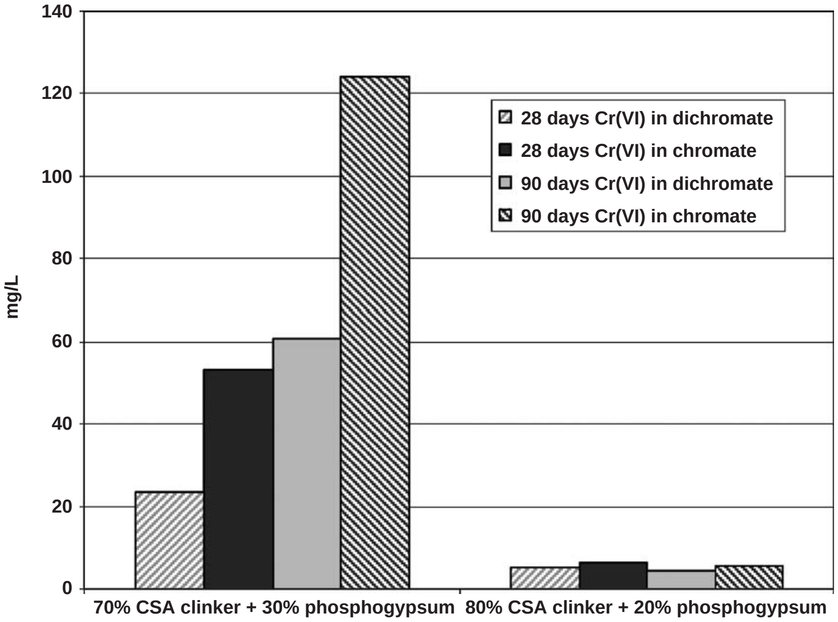

Fig. 6. Total Cr(VI) leached in the two kinds of binder.

2 to 15 h), the suspension was filtered. The liquid was analyzed by means of ICP-OES.

3. Results and discussion

3.1. Leaching tests

3.1.1. Results obtained at 28 days

After 28 days of hydration, the samples cast with CSA2 presented some damage in presence of chromate or dichromate ions (Fig. 1).

As shown in Figs. 2 and 3, the behaviour of pastes containing lead, cadmium, and zinc was about the same, regardless of the composition of the binder. The quantity of heavy metal present in the leachate was low (0.1 mg/L) and remained constant during the successive leaching operations. For trivalent chromium, the quantity of leached chromium was slightly higher than that recorded for lead, cadmium, and zinc: 0.5 mg/L for CSA2 and 0.1 mg/L for CSA1, respectively. This quantity remained constant during the different leaching tests.

For sodium chromate or dichromate, the first leaching led to the highest quantity of chromium in the leachate. Higher leached quantities of heavy metal were recorded, especially when using CSA2. For sodium dichromate, the total quantity of Cr^{6+} leached from CSA2 paste was 4.7

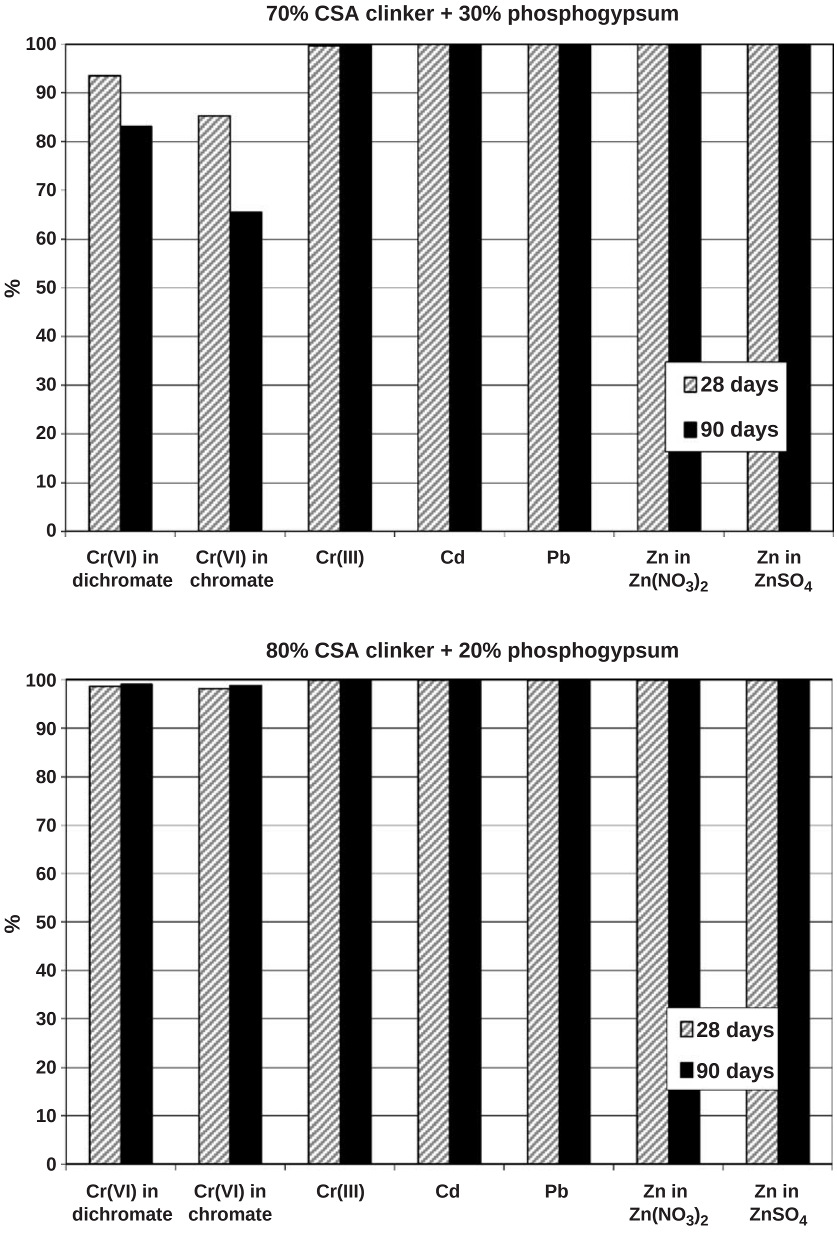

Fig. 7. Degree of metal stabilization as percentage of total concentration in pastes during leaching tests.

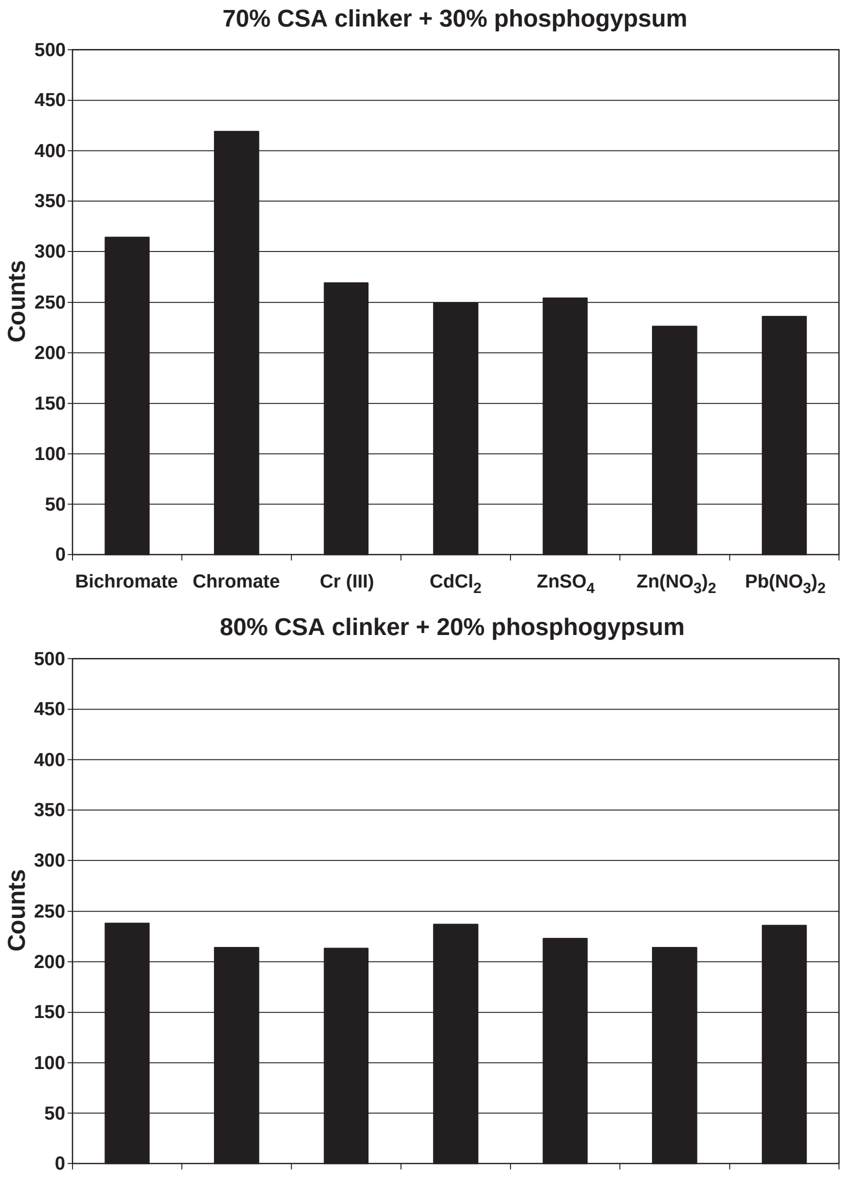

Fig. 8. Intensity of main diffraction peak of ettringite at 28 days of age.

times higher than that collected from CSA1 paste. For sodium chromate, the leaching of CSA2 paste led to a quantity of 8.3 times higher than that collected from CSA1 paste.

Table 2
Mass loss of the different pastes in the range 100–150 °C (%)

Pollutant	CSA1		CSA2	
	28 days	90 days	28 days	90 days
$Na_2Cr_2O_7 \cdot 2H_2O$	16.0	17.6	20.9	23.7
$Na_2CrO_4 \cdot 4H_2O$	15.6	16.1	23.0	23.6
$CrCl_3 \cdot 6H_2O$	16.5	16.9	16.3	17.4
$CdCl_2 \cdot 5H_2O$	16.7	17.0	18.2	18.3
$Pb(NO_3)_2$	15.2	15.7	16.8	17.4
$Zn(NO_3)_2 \cdot 6H_2O$	16.0	16.1	18.0	18.9
$ZnSO_4 \cdot 7H_2O$	16.2	16.7	17.0	18.8

3.1.2. Results obtained at 90 days

The results obtained after 90 days are presented in Figs. 4 and 5. For Cr^{3+}, Cd, Pb, and Zn, the quantities leached were low (0.1 mg/L), regardless of the cement used. In the

Table 3
Theoretical quantity of ettringite (%)

Pollutant	CSA1		CSA2	
	28 days	90 days	28 days	90 days
$Na_2Cr_2O_7 \cdot 2H_2O$	34.9	38.3	45.5	51.6
$Na_2CrO_4 \cdot 4H_2O$	33.9	35.1	50.2	51.5
$CrCl_3 \cdot 6H_2O$	36.0	36.9	35.5	37.8
$CdCl_2 \cdot 5H_2O$	36.3	37.0	39.6	39.8
$Pb(NO_3)_2$	33.0	34.1	36.5	37.8
$Zn(NO_3)_2 \cdot 6H_2O$	34.8	35.0	39.2	41.1
$ZnSO_4 \cdot 7H_2O$	35.3	36.4	37.0	41.0

Table 4
Porosity of pastes at 28 days of age

Cement	Pollutant	Total porosity (%)	Pore size distribution (%)		
			Micropores <0.1 µm	Mesopores 0.1 to 0.6 µm	Macropores >0.6 µm
CSA1	Na_2CrO_4·$4H_2O$	24.0	74.2	19.4	6.4
	$Na_2Cr_2O_7$·$2H_2O$	23.3	73.7	20.2	6.1
	$CrCl_3$·$6H_2O$	20.6	72.9	21.2	5.9
	$Pb(NO_3)_2$	20.4	74.8	17.7	7.5
	$Zn(NO_3)_2$·$6H_2O$	24.9	71.5	21.5	7.0
	$ZnSO_4$.$7H_2O$	24.0	74.2	19.4	6.4
	$CdCl_2$·5H2O	23.3	73.7	20.2	6.1
CSA2	Na_2CrO_4·$4H_2O$	27.1	61.8	25.3	12.9
	$Na_2Cr_2O_7$·$2H_2O$	25.3	64.5	26.0	9.5
	$CrCl_3$·$6H_2O$	27.8	77.0	18.2	4.8
	$Pb(NO_3)_2$	27.9	74.9	17.5	7.6
	$Zn(NO_3)_2$·$6H_2O$	28.2	71.8	21.7	6.5
	$ZnSO_4$·$7H_2O$	27.2	70.7	22.4	6.9
	$CdCl_2$·5H2O	24.5	68.0	24.8	7.2

case of CSA1, the quantities of Cr^{6+} present in the leachate were lower than those observed at 28 days of age. The quantities of Cr^{6+} collected from the leaching of CSA2 were higher than those observed at 28 days of age: 2.6 times higher for dichromate and 2.3 times higher for chromate, respectively. The behaviour of the two binders is shown in Fig. 6: CSA1 exhibits better fixation of Cr^{6+} than CSA2.

Degree of metal stabilization for each paste is given in Fig. 7, which indicates that well over 99% of the metals cadmium, lead, and trivalent chromium are stabilized in the pastes. Stabilization of Cr^{6+} depends upon the binder used:

— it is greater than 98.2% for CSA1,
— it is in the range of 65 to 93% for CSA2.

3.2. Microstructural investigation

3.2.1. Results of XRD

The phases detected by X-ray diffraction were unreacted yeelimite and gypsum, and ettringite. The intensity of the main peak of ettringite was higher in CSA2 paste, and especially when chromium was introduced under either sodium dichromate or chromate forms (Fig. 8).

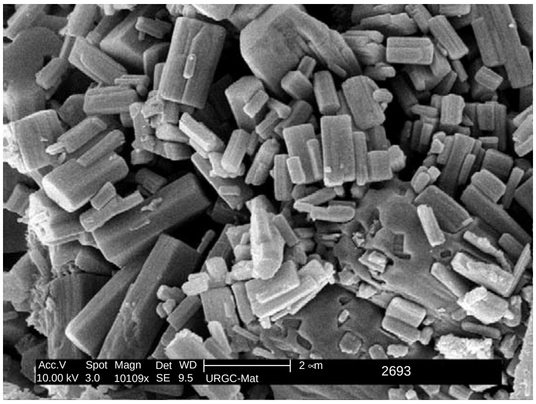

Fig. 10. CSA2 doped with sodium chromate.

3.2.2. Results of thermal analysis

The quantity of ettringite obtained after 28 and 90 days of hydration was assessed by means of thermal analysis. The mass loss obtained from TGA curves in the range of 100 to 150 °C allowed the calculation of the theoretical quantity of ettringite that was formed in each paste. The results are presented in Tables 2 and 3.

In CSA1, the quantity of ettringite was in the range of 33% to 36% at 28 days and 34% to 38% at 90 days. The differences observed between the different pollutants were small.

In CSA2, the quantity of ettringite was in the range of 35% to 50% at 28 days and 38% to 52% at 90 days. In this binder, there was a drastic increase in the ettringite content when sodium dichromate and, especially, sodium chromate were introduced in the paste. Studies conducted by Ogawa and Roy [14] have shown that the presence of sodium accelerated the reactivity of yeelimite and the dissolution of calcium sulfate, thus leading to higher production of ettringite. The higher the presence of gypsum, the higher

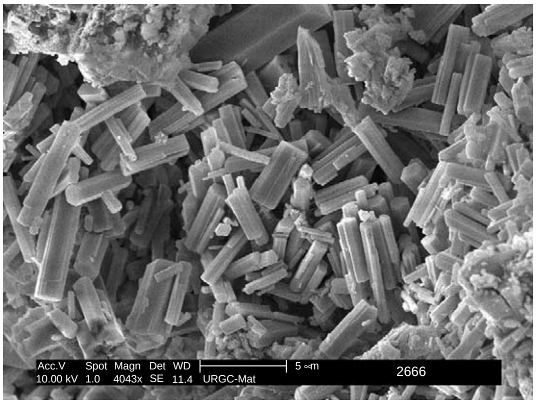

Fig. 9. CSA2 doped with sodium dichromate.

Fig. 11. CSA2 doped with chromium chloride.

the precipitation of ettringite. This explains the differences between CSA1 and CSA2. These results were confirmed by the conductivity study.

3.2.3. Results of mercury intrusion porosimetry

The results of mercury intrusion porosimetry are presented in Table 4. CSA2 pastes presented higher porosity than CSA1 pastes. They also showed higher amounts of macropores, especially when they were doped with chromate or dichromate ions. This explains why the quantity of leached Cr^{6+} was higher in CSA2 pastes.

3.2.4. Results of SEM investigations

SEM investigations showed different morphologies of ettringite. CSA2 paste doped with sodium dichromate presented numerous short hexagonal crystals of ettringite (Fig. 9). In CSA2 paste doped with sodium chromate, crystals of ettringite were larger (Fig. 10). It seems that the growth of needle-like ettringite microcrystals is hindered in the CSA2 paste doped with sodium dichromate or dichromate. Larger crystals appear leading to the destruction of the sample. This corresponds to the precipitation of swelling delayed ettringite, as reported by Wang et al. [15] and Kasselouri et al. [16]. When ettringite precipitates after the matrix has reached some rigidity, it cannot develop according to long fine prismatic crystals. Vacant spaces within the paste are not sufficiently available to allow complete development of crystals. Thus, shorter and larger crystals are formed, exerting pressure on the existing microstructure and leading to cracking as shown in Fig. 1.

Hollow and more elongated ettringite crystals were present in the CSA2 paste doped with chromium chloride (Fig. 11).

3.3. Conductimetry and solution analysis

The conductimetry curves are presented in Fig. 12. The level of conductivity is lower than in Portland cement and the curves do not present the same shape according to the composition of the CSA cement.

In the control cement composed of 70% CSA clinker and 30% phosphogypsum (CSA2), once the maximum con-

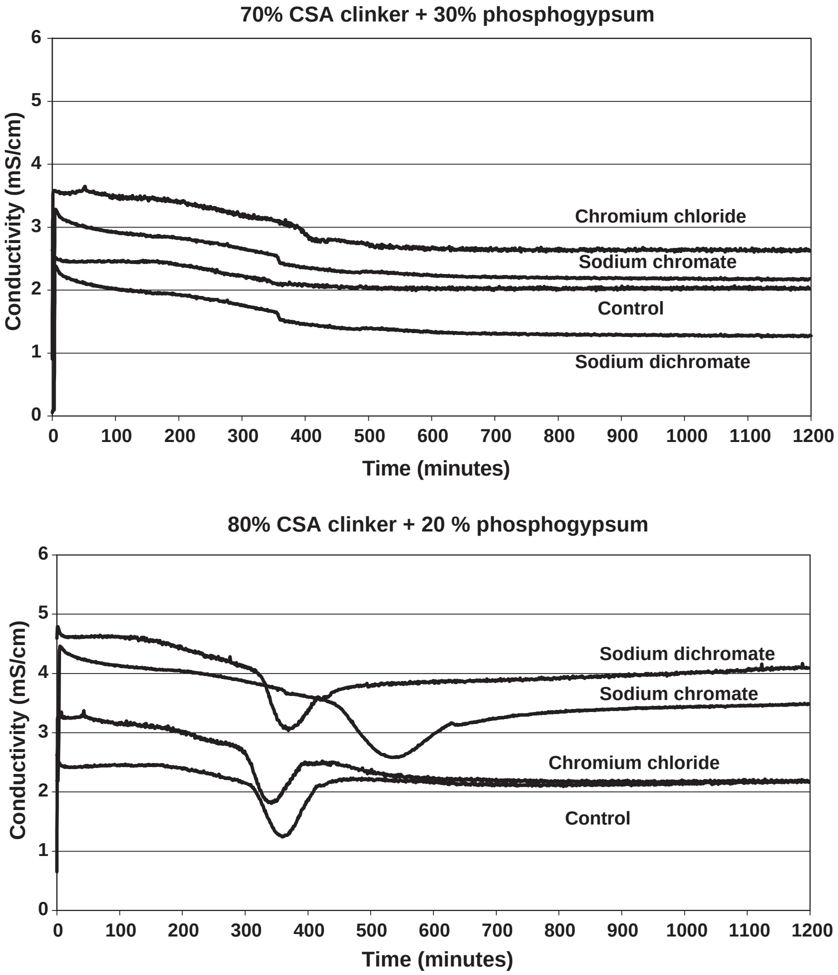

Fig. 12. Conductimetric curves obtained for suspensions ($W/S=4$).

ductivity reached, the level of conductivity remains constant for 150 min and then decreases, due the precipitation of ettringite. When this cement is polluted, the shape is relatively the same but the period of constant conductivity disappears and the conductivity decreases after the initial peak of conductivity.

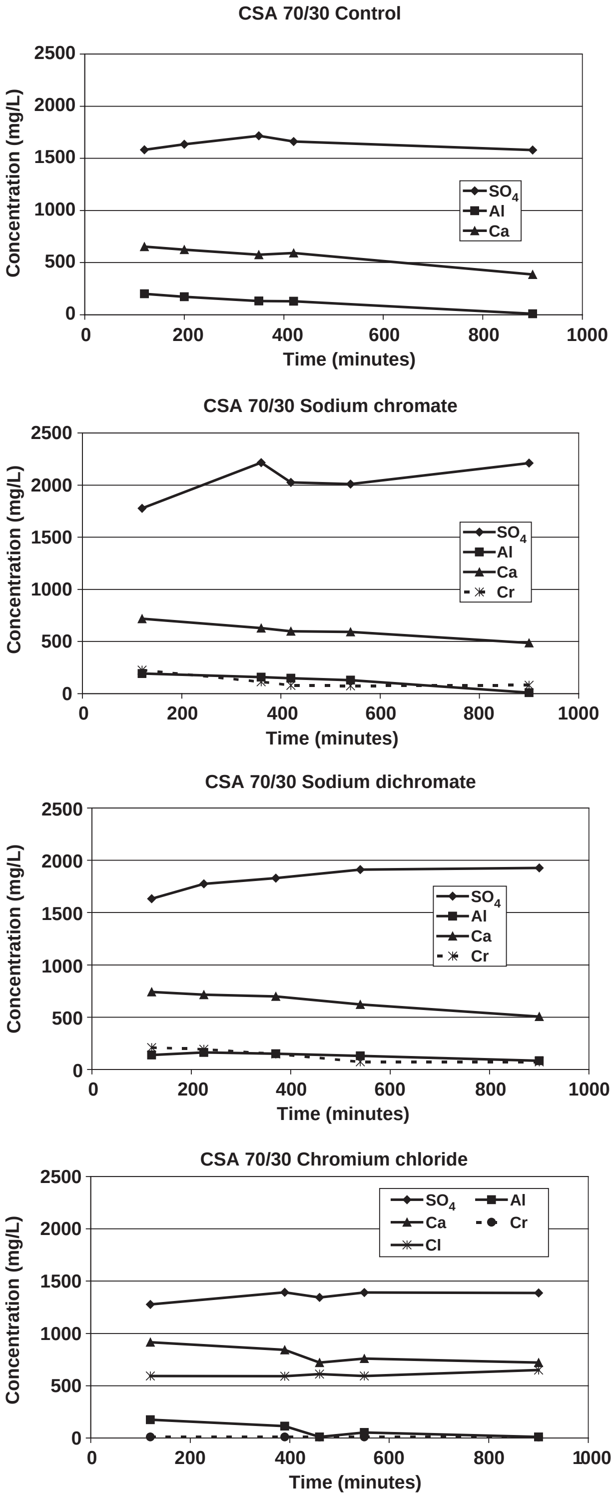

Fig. 13. Analysis of solutions. CSA2.

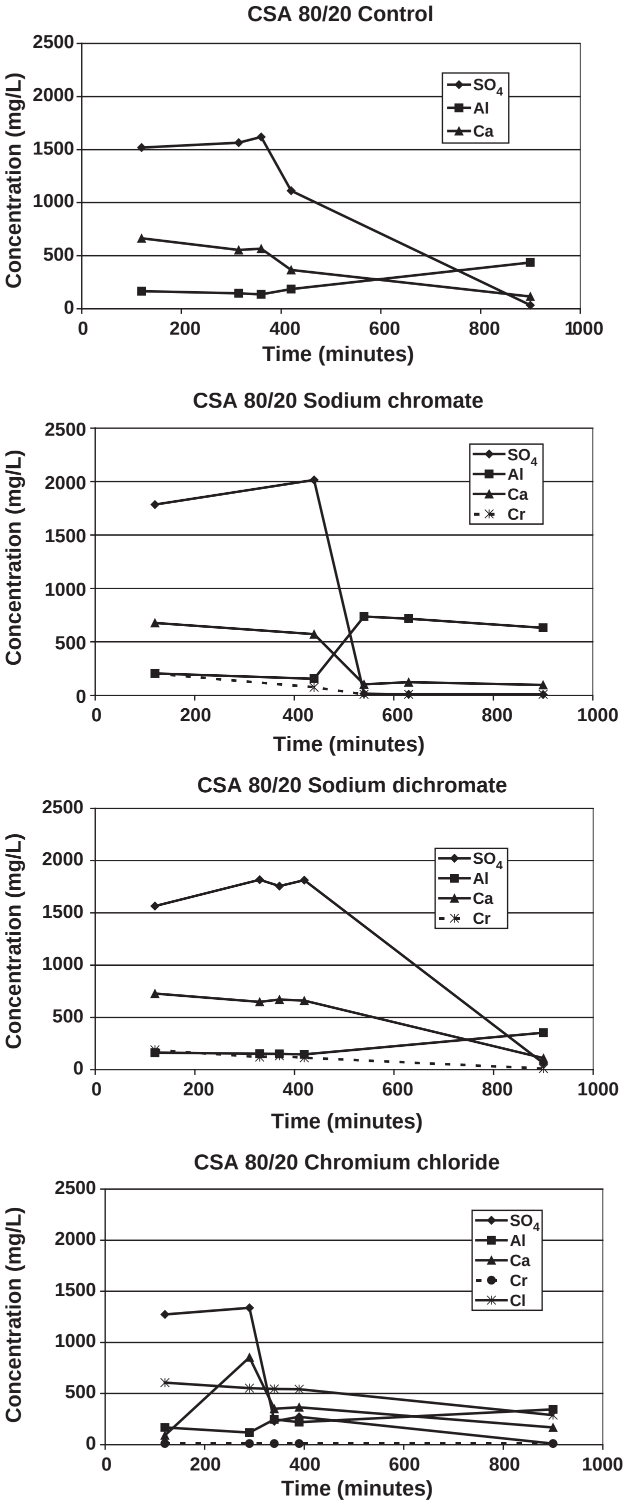

Fig. 14. Analysis of solutions. CSA1.

In the control cement composed of 80% CSA clinker and 20% phosphogypsum (CSA1), once the maximum conductivity reached, the level of conductivity remains constant for 200 min and suddenly decreases to reach the minimum value after 360 min, due the precipitation of ettringite. Then, the conductivity increases and remains constant. The addition of chromium chloride and sodium dichromate does not modify the shape of the curve. The addition of sodium chromate retards the precipitation of ettringite and the minimum value of conductivity is reached after 540 min.

The analyses of solutions are shown in Figs. 13 and 14. In the solution of the control cement composed of 70% CSA clinker and 70% phosphogypsum (Fig. 13), the quantity of aluminum and calcium ions decreases slowly versus time, showing progressive precipitation of ettringite in the paste, while that of sulphate ions increases due to the dissolution of gypsum.

In presence of sodium chromate, the concentration in sulphate ions is initially higher but decreases after 325 min and chromate, aluminium, and calcium ions concentrations decrease, characterizing the precipitation of ettringite integrating chromate ions. The same phenomenon is observed with sodium dichromate.

In presence of chromium chloride, the precipitation of ettringite is well marked after 400 min. The chloride ion concentration remains constant: this ion is not integrated in the structure of ettringite. In this cement, the presence of pollutants does not significantly modify the precipitation of ettringite, as proved by the shape of the conductimetric curve (Fig. 12).

In the solution of the control cement composed of 80% CSA clinker and 20% phosphogypsum (Fig. 14), important precipitation of ettringite occurs after 360 min, corresponding to the minimum value of conductivity (Fig. 12). The precipitation of ettringite is delayed in presence of sodium chromate and dichromate: the depletion in sulfate ions only appears after 420 min. The presence of chromium chloride has an accelerating effect on the precipitation of ettringite. In the polluted solutions, chromium and chloride ions are consumed versus time and thus integrated in the structure of ettringite.

4. Conclusions

The stabilizing matrix based on calcium sulfoaluminate cement shows a behaviour in leaching tests that can be very different depending on the nature of both the CSA binder used and the pollutant. Regardless of the quantity of gypsum present in the cement, the stabilization of zinc nitrate and sulfate, lead nitrate, cadmium chloride, and chromium chloride is excellent.

In presence of sodium dichromate or chromate, the lower the quantity of gypsum the better the retention of chromium (Cr^{6+}). This is explained on the basis of different microstructures developed in the cements. Delayed ettringite precipitates in the cement containing 30% phosphogypsum (CSA2), leading to higher porosity and cracking.

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