Potential application of ettringite generating systems for hazardous waste stabilization

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Abstract

The potential of ettringite generating systems in hazardous waste stabilization processes is studied by means of a mixture of anhydrous calcium sulphoaluminate and anhydrite doped with the nitrates of the six heavy metals Cu, Cr, Cd, Pb, Zn and Fe. The study has been carried out by means of differential thermal and X-ray diffraction analyses, infra-red spectroscopy, scanning electron microscopy coupled with an energy dispersion system and three different leaching tests. The presence of the metals has only a small negative effect on the hydration kinetics. The hydrated samples retain their structural integrity when submitted to the dynamic leaching test in water and pH 4 HNO_3 solution, while they are disintegrated when the leachant is a pH 4.74 acetate buffer. The sulphoaluminate phases can partially accommodate any metal in the crystal lattice, thus giving rise to chemical entrapment.

1. Introduction

Interest in hazardous waste stabilization processes based on the formation of ettringite (calcium trisulphoaluminate hydrate $6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$) has grown steadily in the last few years [1–5].

Ettringite-based stabilization systems offer certain advantages over traditional cement-based ones for a number of reasons which can be summarized as follows.

From a chemical point of view, it is well known that trivalent ions such as Fe^{3+},

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Cr^{3+} and Mn^{3+} can replace Al^{3+} in the ettringite crystal lattice. In fact, totally and partially substituted ettringite derivatives occur as minerals (sturmanite $Ca_6(Fe,Al)_2(SO_4)_2(B(OH)_4)(OH)_{12} \cdot 26H_2O$ and bentorite $Ca_6(Cr,Al)_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) and have also been artificially synthesized [6].

Other cationic substitutions can occur, as bivalent ions such as Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} can replace Ca^{2+} in the crystal lattice to a variable extent [7].

In addition, anionic substitution has been reported with regard to SO_4^{2-} replacement by CO_3^{2-}, NO_3^- etc. [1,8–11]. Evidently, ettringite-based stabilization systems can take advantage of this chemical characteristic regarding wide ionic substitution potential.

From a technological point of view, a wide range of raw materials, including industrial wastes and by-products, can be employed for the formulation of ettringite-based stabilization systems. Furthermore, at least two different processes can be developed for the formation of ettringite.

Materials such as coal fly-ash, blast furnace slag, chemical gypsums and bauxite wastes can be used in addition to commercial lime, limestone, alumina and natural gypsum [12–21].

Hydrothermal processes requiring temperatures no higher than 85°C can be adopted for the so-called direct ettringite synthesis process [12–14,17,21]. On the other hand, the high-temperature synthesis (1200–1300°C) of anhydrous calcium sulphoaluminate, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, gives a reactant that, when hydrated at room temperature with calcium oxide and/or sulphate, gives ettringite via the so-called indirect synthesis process [15,16,18–20].

The physico-mechanical characteristics of hydrated ettringite-based products vary considerably depending on the type of process.

Pre-formed building elements with 28 days compressive strength ranging from 9.1 to 47.3 MPa have been produced via direct synthesis [21]. On the other hand, hydraulic binders based on anhydrous $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ have been produced with 28 days compressive strength up to 78 MPa [20].

In this paper a mixture made of anhydrous calcium sulphoaluminate and anhydrite has been studied in order to understand the influence that six heavy metals have on the hydration kinetics, and to characterize the stabilizing properties by means of three dynamic leaching tests.

As any heavy metal has a unique chemistry, its interactions with a stabilizing matrix must necessarily be studied separately before using real and more complex systems. For this reason the study has been carried out with six model systems made of the stabilizing matrix doped with 3.34×10^{-4} mol/g of the nitrate of Cu, Cr, Cd, Pb, Zn and Fe.

2. Experimental

2.1. Materials

The reactant system is made of a stoichiometric mixture of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $CaSO_4$ in the molar ratio 1:2. Upon hydration it gives ettringite and $Al(OH)_3$ gel according to the following reaction:

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 2CaSO_4 + 38H_2O$$
$$= 6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O + 4Al(OH)_3 \qquad (1)$$
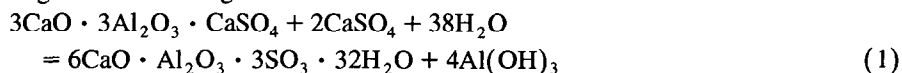
The stoichiometric mixture of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $CaSO_4$ was produced by firing at 1300°C for two hours starting from analytical grade $CaCO_3$, $CaSO_4 \cdot 2H_2O$ and Al_2O_3. The raw mix was ground and passed through a 125 μm sieve. Sieving was repeated three times to ensure good homogenization. X-ray analysis showed that the fired product contained only very small quantities of unreacted CaO. Increasing the firing time at 1300°C did not raise the yield of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, while sulphate decomposition made the quantity of free CaO increase.

Calcium sulphate is present in the form of anhydrite instead of gypsum to avoid the formation of expansive ettringite.

2.2. Hydration

Six model systems were prepared by adding the nitrate of Cu, Cr, Cd, Fe, Zn and Pb to the $3CaO \cdot 3Al_2O_3 \cdot CaSO_4 - CaSO_4$ mixture in amounts equal to 3.34×10^{-4} mol/g. The undoped system and the systems doped as above were hydrated at 25°C and 100%R.H. for 1, 3, 7, 14 and 28 days with a water/solid ratio equal to 0.66, which was the optimum value to ensure good workability and avoid solid particle segregation. Samples were taken at pre-fixed hydration times and the hydration was stopped by grinding under acetone to wash off the water, with a final washing with diethylether to facilitate drying.

2.3. Analysis

The samples in which the chemical reaction was stopped as described above were submitted to a series of analyses in order to investigate the hydration kinetics from both the qualitative and quantitative points of view. Neo-formed hydration products were identified by means of differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis. Metal speciation was investigated by means of infrared spectroscopy (FTIR) and surface elemental analysis carried out with a scanning electron microscope coupled with an energy dispersion system (SEM/EDS). The amount of non-evaporable water was determined by means of loss on ignition (LOI) at 1000°C.

2.4. Leaching tests

In addition to the samples required for investigation of the hydration kinetics, other monolithic samples were prepared for each doped system in order to carry out three different leaching tests. These monolithic samples were cured for 28 days under the same conditions as before. They were cylindrical in shape with $d \times h = 2 \times 3$ cm^2. The three dynamic leaching tests employed made use of the following leachants: (a) distilled water; (b) HNO_3 solution at pH 4, and (c) 1M acetic acid plus 1M sodium acetate buffer solution. In each case, seven leachant renewals were ensured at the times 1, 4, 7, 24, 31, 48 and 72 h. At the end of each leaching step, leachate metal concentration and pH were measured. It was not possible to carry out test (c) for times greater than 24 h because of matrix disintegration. In any case, the solids obtained at the end of each leaching test were submitted to DTA and XRD analysis.

3. Results and discussion

3.1. Hydration

The neo-formed hydration products were identified through DTA from data in the literature [22,23].

Fig. 1 shows three typical thermograms of samples of the undoped system and those containing $Zn(NO_3)_2$ and $Cd(NO_3)_2$ cured for 14 days. Thermogram (a) refers to the undoped system and shows three endotherms labelled E, M and A as the temperature increases. Endotherm E is due to the presence of the main hydration product, ettringite. The presence of the other reaction product, alumina gel, is indicated by endotherm A. The formation of small amounts of calcium monosulphoaluminate $(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O)$ is indicated by the presence of endotherm M.

The influence of the metals Zn, Cu and Fe on hydration is shown by thermogram (b) in Fig. 1 which refers to the system containing $Zn(NO_3)_2$. Each of the above metals has the same two-fold effect, although to a variable extent. They have a catalytic effect on the hydration of anhydrite to gypsum (endotherm G is due to the presence of gypsum), but a retarding effect on the formation of ettringite.

On the other hand, the effect of the metals Cr, Cd and Pb is shown by thermogram (c) in Fig. 1 which refers to the system containing $Cd(NO_3)_2$. In this case also, the

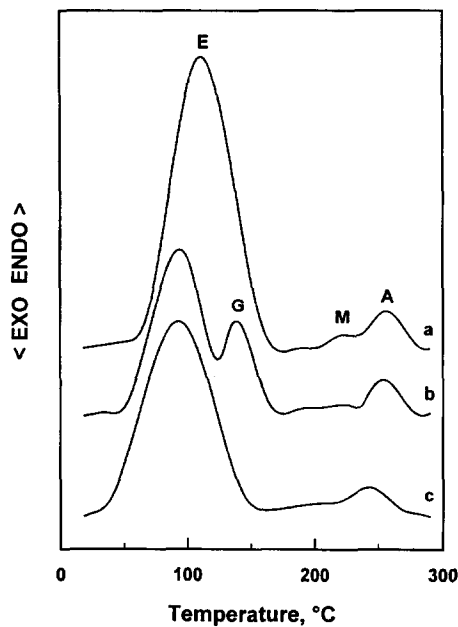Fig. 1. Typical thermograms of samples of hydrated systems. (a) Undoped system; (b) system containing $Zn(NO_3)_2$; (c) system containing $Cd(NO_3)_2$.

Table 1
Intensity of main XRD peaks, counts

Sulphate form	Metal present in the system					
	Zn	Cu	Fe	Cr	Pb	Cd
$CaSO_4 \cdot H_2O$	1100	500	330	280	0	0
$CaSO_4$	0	700	831	953	1100	1150

behaviours of the systems containing the above three metals are qualitatively similar. In actual fact, no significant difference is observed with regard to the undoped system.

Additional information on the hydration kinetics was obtained by means of the XRD analysis technique, which makes it possible to monitor the presence of unreacted sulphate in the form of both gypsum and anhydrite.

Table 1 shows the results of XRD analysis in terms of counts relative to the main diffraction peaks for gypsum and anhydrite after 28 days hydration. It is seen that unreacted sulphate is completely or partially present in the form of gypsum depending on the nature of the system. The catalytic effect on the hydration of anhydrite is seen to be as follows: Zn > Cu > Fe > Cr > Pb ≈ Cd.

The formation of gypsum is not favourable as far as durability is concerned, owing to its higher solubility compared to anhydrite. From the technological point of view, the possibility that the hydration to gypsum can take place in some systems is worth investigating.

Quantitative hydration data are reported in Fig. 2 in terms of non-evaporable water versus hydration time. It can be clearly seen that, after 14 and 28 days curing, all the doped systems have a very similarly behaviour and the almost constant degree of hydration is about 15% lower than that of the undoped system. Greater differences are observed after 1, 3 and 7 days curing. After 1 day curing the systems containing Cd, Zn and Pb show a very low degree of hydration, while the others show an increasing degree of hydration in the order Cu < Cr < Fe. Significant differences are still observed only for Zn and Cu after 3 and 7 days curing. It should be pointed out that very slow hydration kinetics should be of concern, as in an actual application the setting time could be negatively affected.

3.2. Leaching

The cumulative amounts of metals released in the leaching tests carried out with distilled water and pH 4 HNO_3 solution are reported in Fig. 3. Here it can be clearly seen that the absolute quantities released are very small in both tests. This is also true in terms of quantities released as a percentage of the initial quantity present in the monolithic specimen. In the case of lead, which gives the maximum amount released, this quantity is about 2.5% of the initial quantity.

The results in water and pH 4 HNO_3 solution are, unexpectedly, very similar, in spite of the great acidity difference between the two leachants. The explanation for this is given in Table 2, which shows the values of pH measured in every test at the end of
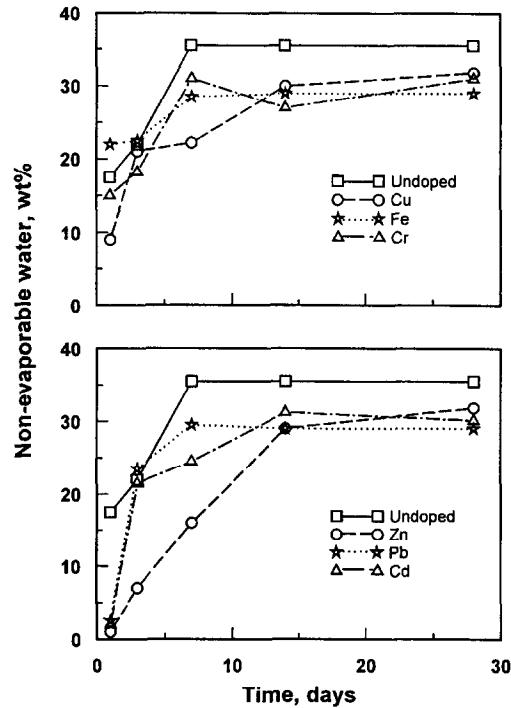
Fig. 2. Non-evaporable water in terms of wt.% of the initial solid weight vs. hydration time for all the systems investigated.

each leaching step. Only the minimum and maximum values are given, irrespective of the metal, as the measured values were not very different in each case. It must be stressed that the acid neutralization capacity of the matrix makes the pH reach alkaline
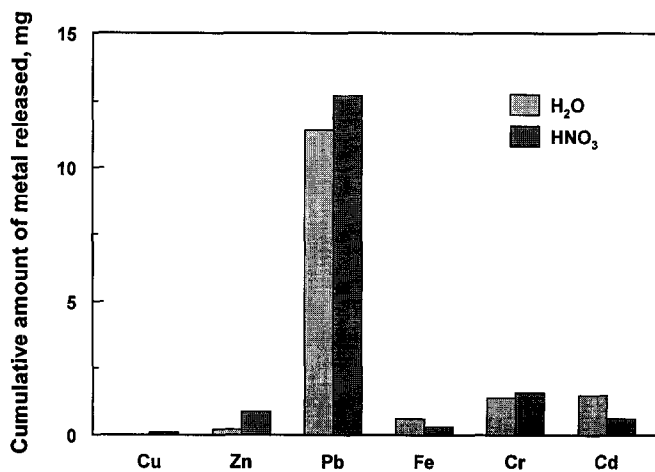

Fig. 3. Results of leaching tests in H_2O and in pH 4 HNO_3 solution.

Table 2
pH values at the end of leaching test steps

Leachant	Leachant renewal						
	1	2	3	4	5	6	7
H_2O	6.8–8.5	7.0–8.6	7.2–8.4	7.9–9.5	9.0–9.4	9.2–9.6	9.9–10.2
HNO_3 pH 4	7.8–8.3	7.2–8.5	6.8–8.3	7.8–9.3	8.9–9.5	9.1–9.6	9.4–9.8

values almost independently of the nature of the leachant. In these conditions the solubility of metals is low and this explains the results of Fig. 3.

The behavior of the stabilized system in the leaching test carried out in the acetic buffer is very different, as can be seen in Fig. 4. In comparison to the previously discussed tests, the quantities released increase by up to two orders of magnitude.

Iron and chromium are both released in much lower quantities than the other metals. It is worth remembering here that the leaching test in the acetic buffer was carried out up to 24 h with four renewals because of matrix disintegration. In spite of this, iron and chromium were released in very small fractional amounts. In the other cases, the percentage of metal retained ranged between about 45% and 85%. Matrix disintegration does not, therefore, imply total metal solubilization.
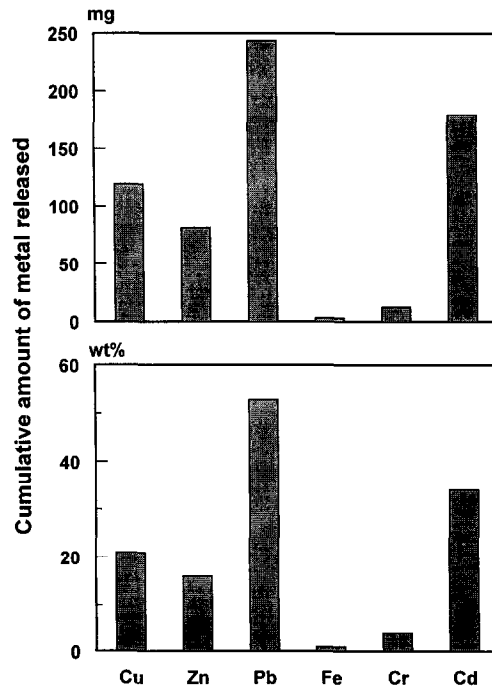

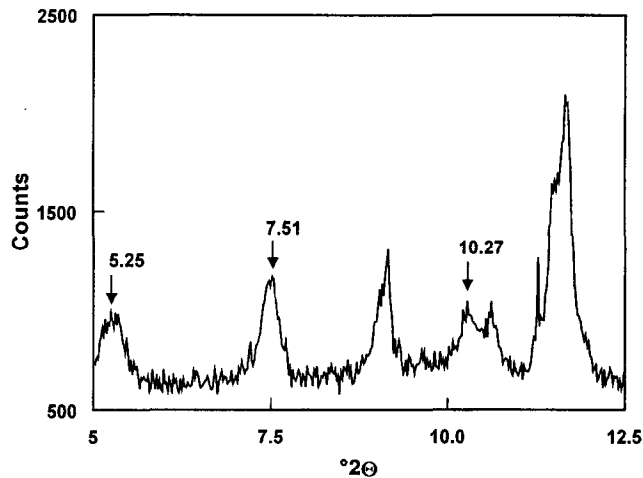Fig. 4. Results of leaching tests in pH 4.74 acetic buffer.

Fig. 5. Results of XRD analysis relative to the system containing $Zn(NO_3)_2$ after leaching test in acetic buffer.

DTA and XRD analysis carried out on the solids obtained after matrix disintegration made it possible to understand what happens during the test in the acetic buffer. Figs. 5 and 6 respectively show the results of XRD analysis and DTA in the case of Zn. The diffraction peaks at 5.25°, 7.51° and 10.27° 2Θ in Fig. 5 and endotherm CA at 60°C in Fig. 6 reveal the presence of calcium acetate pentahydrate [24]. The formation of this compound affects the solubility equilibrium of ettringite which decomposes giving off gypsum and aluminium hydroxide. This is clearly seen in Fig. 6, as endotherm E at 94°C, due to ettringite, is much less intense than that before leaching (see curve b in Fig. 1). On the other hand, the intensities of endotherm G relative to gypsum (135°C) and
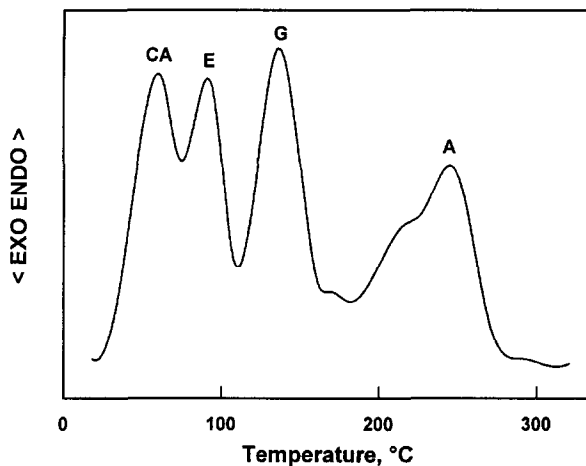

Fig. 6. Results of DTA analysis relative to the system containing $Zn(NO_3)_2$ after leaching test in acetic buffer.

endotherm A relative to aluminium hydroxide (248°C) are much greater than before leaching. This behavior has been observed in all cases.

The nature of the metal present in the system affects the extent to which ettringite solubilization and decomposition take place. Although a univocal relationship between the amount of residual ettringite and the amount of metal released has not been found, it is evident that the retainment of chemical integrity is the main factor that affects leaching in this case. The systems containing iron and chromium were those in which the residual amount of ettringite was much greater than in the others (2500–2800 counts vs. 1000–1200).

In order to verify that matrix disintegration is due to acetate attack forming an insoluble hydrated calcium salt, a specimen of the system containing lead was kept in a controlled pH 4.7 HNO_3 solution for 2 weeks. This system, which showed the minimum amount of residual ettringite after the acetate buffer leaching, retained its structural integrity for the whole test time. At the end of this test the specimen was powdered in a laboratory mill and submitted to DTA and XRD analysis. The results of these analyses (not shown) were substantially unchanged with respect to those obtained before the test.

Acetic acid/sodium acetate buffer solutions are widely applied in many regulations for the assessment of long-term behavior of stabilized wastes [25,26]. However, it should be pointed out that this leaching medium cannot be used in the case of ettringite-based systems, for which alternatives should be found. One such alternative could be the use of continuously controlled pH 4.7 HNO_3 solution.

From the results of all the leaching tests carried out, it appears that the matrix under investigation owes its stabilizing properties not only to physical factors, but also to chemical ones. In this respect, the formation of partially substituted ettringite might play an important role.

Totally substituted ettringites have been synthesized by Bensted and Prakash Varma [6]. These products were also characterized by infrared spectroscopy. However the
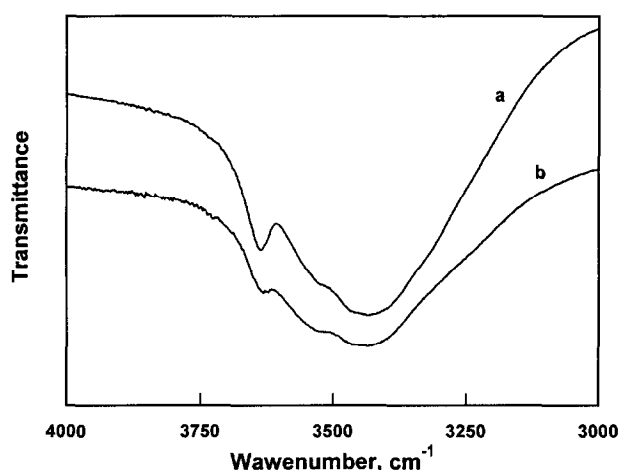

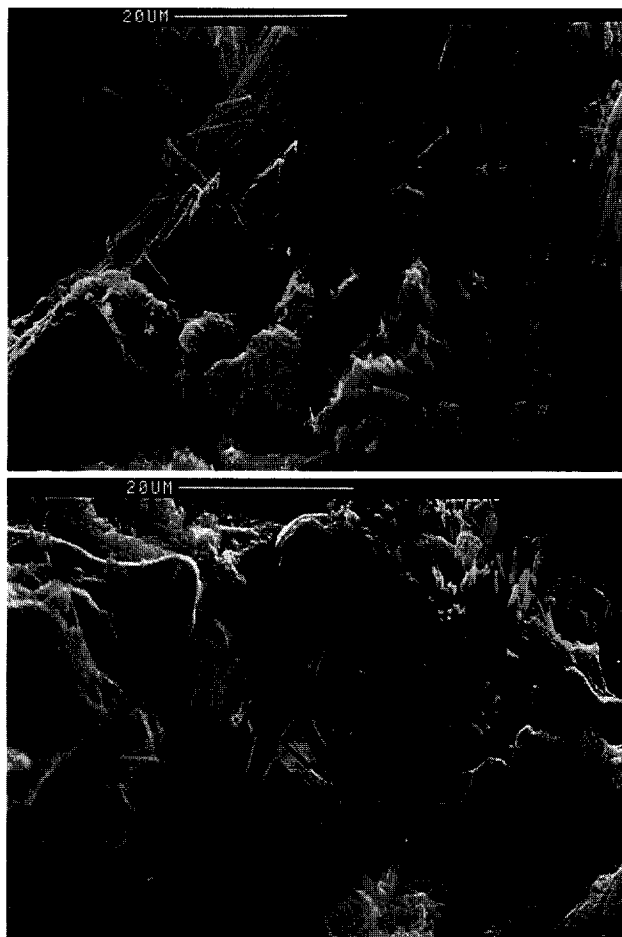Fig. 7. Results of FTIR analysis. (a) Undoped system; (b) system containing $Cd(NO_3)_2$.

Fig. 8. SEM photographs of samples of systems containing $Cd(NO_3)_2$ (above) and $Cr(NO_3)_3$ (below).

infrared spectra of ettringite and its derivatives containing Cr(III), Fe(III), Mn(III) only showed the same difference in the wavenumber range between 3000 and 4000 cm^{-1}.

FTIR analysis was carried out on samples of the whole set of systems and no significant difference was found among those containing the metals. However, these spectra were all slightly different from that of the undoped system. Fig. 7 shows a typical spectrum of a system containing metal and that of the undoped system. It can be seen that the difference between the two spectra occurs between 3000 and 4000 cm^{-1} and it can therefore be concluded that any metal is able to enter into the crystal lattice of ettringite.

SEM photographs of samples containing cadmium and chromium are shown in Fig. 8, where needle-like ettringite crystals can be clearly seen. Other plate-like and spongy crystals are also clearly visible. EDS analysis of the needle-like and plate-like spongy
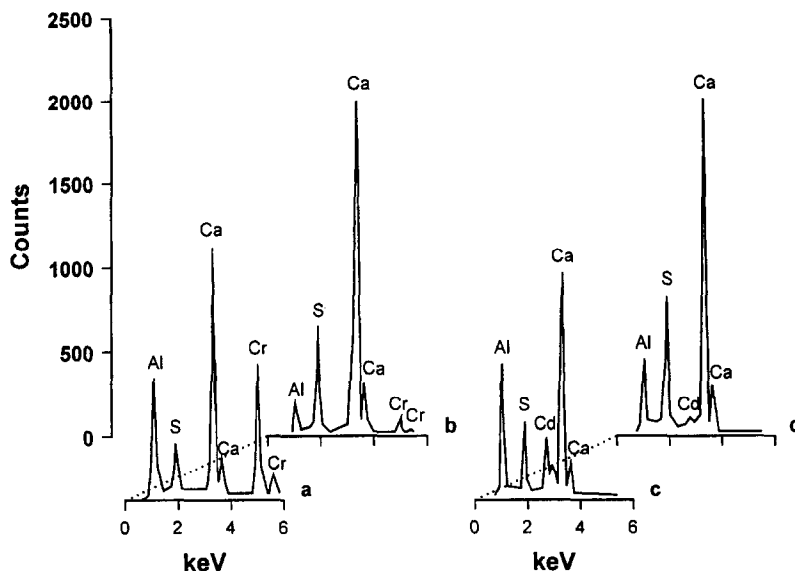
Fig. 9. Results of EDS analysis. (a) System containing $Cr(NO_3)_3$, plate-like crystals; (b) system containing $Cr(NO_3)_3$, needle-like crystals; (c) system containing $Cd(NO_3)_2$, plate-like crystals; (d) system containing $Cd(NO_3)_2$, needle-like crystals.

crystals is shown in Fig. 9. Here it can be seen that they can all accommodate calcium, aluminium and the metal. The calcium/aluminium ratio decreases, while the calcium/sulphur ratio increases when the electron spot moves from needle-like to plate-like spongy crystals, according to the compositions of the high and low forms of calcium sulphoaluminate hydrates. The albeit variable presence of metals in these crystals clear shows that the two forms of calcium sulphoaluminate are both able to accommodate the metals in the crystal lattice. From a quantitative point of view it can be said that calcium monosulphoaluminate hydrate is able to accommodate the metals to a greater extent than ettringite.

4. Conclusions

The experimental results indicate that the negative effects on hydration are limited to the reaction kinetics, and that the long-term hydration degree is not negatively affected.

The model systems studied retain both the metal and physical integrity when submitted to the dynamic leaching tests in water and in a pH 4 HNO_3 solution. The results of these tests indicate that the systems have a good acid neutralization capacity.

The formation of insoluble calcium acetate pentahydrate causes matrix disintegration during the acetate buffer leaching test. This test is therefore useless in the case of ettringite-based stabilization systems. However, the long-term stabilization capacity can be equally well ascertained by means of a controlled pH 4.7 HNO_3 solution.

Infrared analysis and SEM coupled with EDS analysis have shown that sulphoaluminate phase crystals are able to accommodate part of the metal in each case.

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