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CHEMICAL EFFECTS OF HEAVY METALS ON THE HYDRATION OF CALCIUM SULPHOALUMINATE $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$

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Abstract

The system $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$–$CaSO_4{\cdot}2H_2O$–$Ca(OH)_2$ was hydrated in the presence of ten dopants, specifically soluble salts of heavy metals.

When added in 10% amount, the effect of each salt is strongly evident at shorter curing times, the hydration kinetics being more favoured in the order $Pb(NO_3)_2<K_2CrO_4<Cd(NO_3)_2<Zn(NO_3)_2\approx Mn(NO_3)_3\approx K_2MoO_4<Ni(NO_3)_2<Cu(NO_3)_2<Cr(NO_3)_3<Fe(NO_3)_3$. At longer curing times the differences among the systems decrease significantly.

The 28-day compressive strength is almost the same for all the systems except those containing $Pb(NO_3)_2$, K_2MoO_4 and K_2CrO_4.

Keywords: calcium sulphoaluminate, ettringite, hazardous wastes, heavy metals, solidification/stabilization

Introduction

Many industrial processes generate solid inorganic hazardous wastes containing heavy metals. Unsafe disposal of these wastes may result in environmental contamination due to possible release of metal species into waters and soil. Solidification/stabilization (*S/S*) processes give the opportunity to avoid harmful effects by physical containment and/or chemical fixation of pollutants [1].

Most commonly practised inorganic *S/S* processes are cement or pozzolanic based. They owe their effectiveness to the formation of a calcium silicate hydrate matrix. In these systems heavy metals may interact in a number of ways, that is adsorption, chemisorption, chemical precipitation, ion exchange, surface complexation, microencapsulation, chemical incorporation in the hydrated neoformed phases, diodochy and isomorphic substitution. The last two phenomena may preferentially take place when calcium trisulphoaluminate hydrate $6CaO{\cdot}Al_2O_3{\cdot}3SO_3{\cdot}32H_2O$ (ettringite) is among the hydration products. This is proved by the occurrence of ettringite-like minerals

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– sturmanite $Ca_6(Fe,Al)_2(SO_4)_2(B(OH)_4)OH_{12}{\cdot}26H_2O$
– bentorite $Ca_6(Cr,Al)_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$)
and also by the synthesis of ettringite derivatives reported by many authors [2–7].

In the field of systems able to generate ettringite increasingly high attention has been paid in the last few years to calcium sulphoaluminate $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ based cements. The reason for this is that sulphoaluminate clinker can be synthesized at a temperature 200–300°C lower than that required for portland cement clinker. In addition, industrial waste materials and by-products such as chemical gypsum, blast furnace slag, coal fly-ash, bauxite fines and so on can be successfully employed for the synthesis. These systems can be classified as low-energy cements.

Applications of calcium sulphoaluminate based binders in *S/S* processes were also studied, and, as for other *S/S* processes, chemical effects of waste components on the behaviour of the system and on the properties of the final product must be understood. Heavy metals ions and oxyanions are among the inorganic species which have such effects.

In this work ettringite was synthesized by hydration of a mixture containing $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, $CaSO_4{\cdot}2H_2O$ and $Ca(OH)_2$ in stoichiometric ratio. The effects of soluble nitrates of Cd(II), Cr(III), Cu(II), Fe(III), Mn(III), Ni(II), Pb(II), Zn(II) as well as K_2CrO_4 and K_2MoO_4 on the hydration properties of such a system were investigated.

The work was carried out by means of thermal analysis and quantitative determination of chemically combined water and the 28-day compressive strength. Thermal analysis was performed by means of a NETZSCH STA 409 apparatus.

Experimental

Calcium sulphoaluminate $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ was synthesised by firing a stoichiometric mixture of analytical grade $CaCO_3$, $CaSO_4{\cdot}2H_2O$ and Al_2O_3 at 1300°C for two plus one hours with intermediate grinding of the product to pass a 45 μm sieve. These reaction conditions were found in a previous work [8]. The quality of the product and the reaction yield were checked by X-ray diffraction analysis and chemical extraction of unreacted CaO (Franke method [9]), respectively. The product was found to be virtually pure $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, as only traces of $3CaO{\cdot}Al_2O_3$ were found after firing. Chemical conversion of the reactants was almost complete, as the amount of unreacted CaO was found to be 5% after 2 h firing and only 0.7% after 2+1 hours firing with intermediate grinding.

Hydratory mixtures were prepared containing $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, $CaSO_4{\cdot}2H_2O$ and $Ca(OH)_2$ in stoichiometric ratio for the following ettringite synthesis reaction:

$$4CaO{\cdot}3Al_2O_3{\cdot}SO_3 + 8(CaSO_4{\cdot}2H_2O) + 6Ca(OH)_2 + 74H_2O \rightarrow$$
$$\rightarrow 3(6CaOAl_2O_3{\cdot}3SO_3{\cdot}32H_2O)$$

The water to solid ratio was 0.6, slightly in excess of the stoichiometric ratio equal to 0.54. The liquid, aqueous phase was pure CO_2-free water in the case of the undoped system, while in the case of the ten doped systems, soluble nitrates of Cd(II), Cr(III), Cu(II), Fe(III), Mn(III), Ni(II), Pb(II), Zn(II) as well as soluble K_2CrO_4 and K_2MoO_4 were dissolved in pure CO_2-free water in such amounts to have 10% of each salt at a time referred to the total amount of unhydrated $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$–$CaSO_4{\cdot}2H_2O$–$Ca(OH)_2$ mixture.

Hydration was carried out at 25°C and 100% R. H. Small samples (2 g) were taken after 1, 3, 7, 14, 28 h, 3, 7, 14 and 28 days of curing. Chemical reaction was stopped by grinding under acetone followed by washing with diethyl ether. Stopped samples were stored in a desiccator and used for thermal analysis and chemically combined water determination. Larger samples (50 g) were cured up to 28 days for compressive strength measurement. In these samples the reaction was stopped by immersion into acetone for 24 h.

Results and discussion

The interpretation of DTA results was made on the basis of literature data [10, 11], as well as on the basis of previous results obtained with a similar system [12]. Particularly, endothermic peaks were detected at 127±22°C for et-

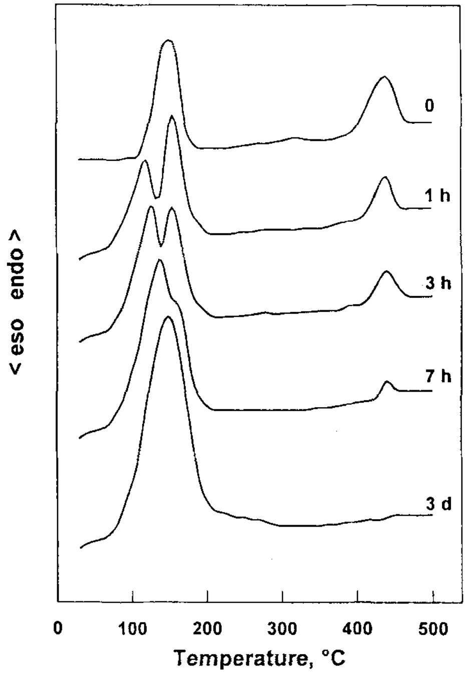

Fig. 1 Thermal curves of samples of the undoped system at 0, 1, 3, 7 h and 3 days

tringite, at 265±5°C for calcium monosulphoaluminate hydrate, at 305±15°C for calcium aluminate hydrate, at 170±10°C for gypsum and at 417±27°C for hydrated lime.

Figure 1 shows the results of thermal analysis for the undoped system. According to previous findings [12], ettringite is the only neo-formed product. Its formation is very fast, as after 3 days no unreacted $CaSO_4{\cdot}2H_2O$ and $Ca(OH)_2$ were detected. The thermal curves corresponding to curing times longer than 3 days are not shown as they are in no way different from that obtained for 3 days of curing.

The presence of a dopant may have a strong effect on the formation of hydrated phase as detected by DTA. Figure 2 shows the results of thermal analysis for all the doped systems after 3 h of hydration. A comparison of each of the curves in Fig. 2 with the curve of the undoped system (Fig. 1) at the same hydration time, allows the systems be divided into three categories. Systems containing $Pb(NO_3)_2$, K_2CrO_4 and $Cd(NO_3)_2$ show a lower reactivity with respect to the conversion of the reactants into ettringite. The worst system is the one containing $Pb(NO_3)_2$ and the reactivity decreases in the order $Cd(NO_3)_2 > K_2CrO_4 > Pb(NO_3)_2$. Within this group of systems, peculiarities are the formation of small

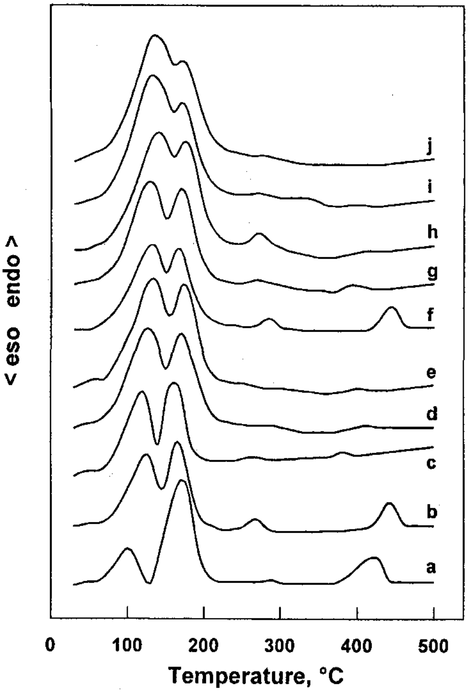

Fig. 2 Thermal curves of samples of doped systems aged for 3 h. Dopant: a) $Pb(NO_3)_2$; b) K_2CrO_4; c) $Cd(NO_3)_2$; d) $Zn(NO_3)_2$; e) $Mn(NO_3)_3$; f) K_2MoO_4; g) $Ni(NO_3)_2$; h) $Cu(NO_3)_2$; i) $Cr(NO_3)_3$; j) $Fe(NO_3)_3$

amounts of calcium monosulphoaluminate hydrate in the case of the system doped with K_2CrO_4 and the enhanced consumption of $Ca(OH)_2$ due to the formation of calcium aluminate hydrate in the case of the system containing $Cd(NO_3)_2$.

The systems containing $Zn(NO_3)_2$, $Mn(NO_3)_3$ and K_2MoO_4 show almost the same reactivity in terms of ettringite formation as the undoped system. Even within this group of systems some peculiarities are observed. Systems containing $Zn(NO_3)_2$ and $Mn(NO_3)_3$ show evidence of calcium aluminate formation, while calcium monosulphoaluminate hydrate is formed beside ettringite in the system containing K_2MoO_4.

Differently from other cases previously studied [13], the presence of Zn has no retarding effect.

The last group gathers systems doped with $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Cr(NO_3)_3$ and $Fe(NO_3)_3$ whose main effect is to enhance the formation of ettringite in the order $Fe(NO_3)_3 > Cr(NO_3)_3 > Cu(NO_3)_2 > Ni(NO_3)_3$. Once again, peculiarities are observed. In fact, systems containing $Ni(NO_3)_2$ and $Cu(NO_3)_2$ show evidence of formation of both calcium aluminate and monosulphoaluminate hydrates.

Figure 3 shows the results of thermal analysis carried out on all the doped systems after 3 days of curing. It is seen that at this longer age the behaviour of

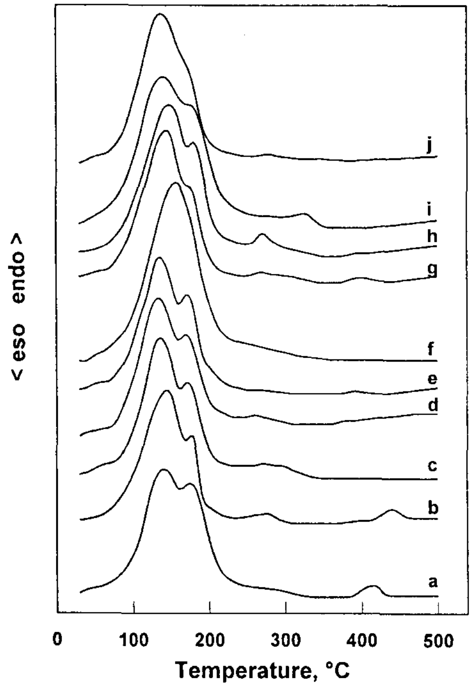

Fig. 3 Thermal curves of samples of doped systems aged for 3 days. Dopant: a) $Pb(NO_3)_2$; b) K_2CrO_4; c) $Cd(NO_3)_2$; d) $Zn(NO_3)_2$; e) $Mn(NO_3)_3$; f) K_2MoO_4; g) $Ni(NO_3)_2$; h) $Cu(NO_3)_2$; i) $Cr(NO_3)_3$; j) $Fe(NO_3)_3$

the doped systems in much more uniform with respect to ettringite formation, which is almost invariably retarded, the only exception being the system containing K_2MoO_4 in which the formation of ettringite reaches an extent similar to that of the undoped system. It is also seen that small amounts of unreacted $Ca(OH)_2$ are observed in the case of systems doped with $Pb(NO_3)_2$ and K_2CrO_4 and that the thermal curves only rarely show evidence of calcium aluminate and monosulphoaluminate hydrates persisting in the systems.

Quantitative data of chemically combined, non-evaporable water, are reported in Figs 4 and 5 for all the systems studied as a function of curing time.

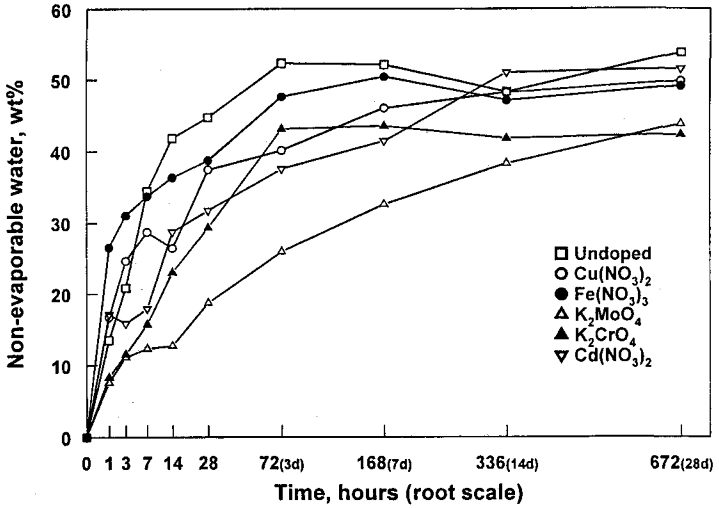

Fig. 4 Hydration kinetics in terms of non-evaporable water *vs.* curing time for the undoped system and some doped systems

By a careful examination of the data at 3 h and 3 days and after comparison with the results of Figs 1–3 (thermal analysis) it can be concluded that the qualitative and semi-quantitative results of thermal analysis, in terms of the kinetics of formation of hydration products, are confirmed by the quantitative data of Figs 4 and 5 for the non-evaporable water. The only exception is the system containing K_2MoO_4 which gives values for the non-evaporable water significantly lower than those for the undoped system both at 3 h and 3 days of curing (about 50% lower). On the other hand, the same system was found to produce hydrated phases to an extent similar to that of the undoped system at both 3 h and 3 days of curing when the results of thermal analysis were taken into account. The reason for this is not clear, but it may be supposed that the interactions between the dopant and the hydrating reactants are responsible for this behaviour. Anyway, at longer ageing times (28 days) the differences in non-evaporable water tend to decrease considerably.

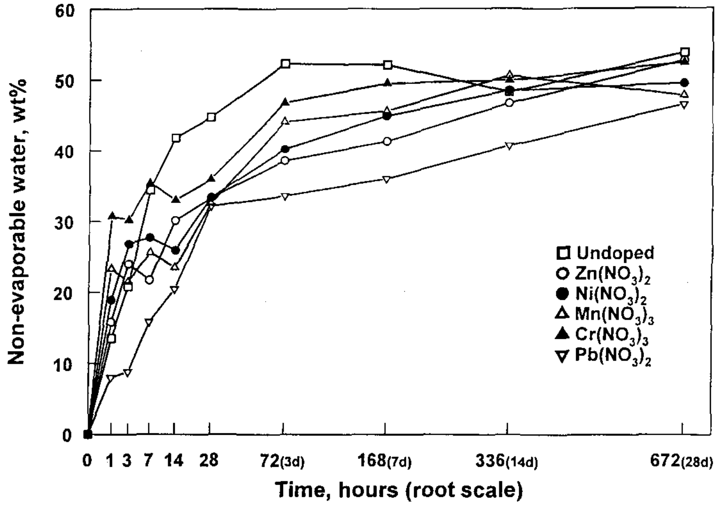

Fig. 5 Hydration kinetics in terms of non-evaporable water *vs*. curing time for the undoped system and some doped systems

Table 1 Compressive strength at 28 days ageing, MPa

System	Undoped		$Pb(NO_3)_2$	K_2MoO_4	K_2CrO_4	$Zn(NO_3)_2$
Strength	11.1		1.9	2.1	2.4	10.7
System	$Ni(NO_3)_2$	$Mn(NO_3)_3$	$Fe(NO_3)_3$	$Cr(NO_3)_3$	$Cd(NO_3)_2$	$Cu(NO3)_2$
Strength	10.9	11.0	11.3	11.4	11.6	11.8

Table 1 shows the results of compressive strength obtained with all the systems tested after 28 days of hydration.

It is seen that, with the exception of systems containing $Pb(NO_3)_2$, K_2MoO_4 and K_2CrO_4, all the doped systems give values of compressive strength very close to the value for the undoped system. The very low values observed in the cases of the systems containing $Pb(NO_3)_2$, K_2MoO_4 and K_2CrO_4 cannot be explained on the basis of a lower degree of hydration, as the data of Figs 4 and 5 show contents of non-evaporable water about 20% lower than the value for the undoped system. This difference cannot explain the much larger difference in mechanical strength. Other factors, such as morphology and microstructure, may have a strong effect and they can be active in some of the doped systems.

Conclusions

Chemical effects of soluble nitrates of Cd(II), Cr(III), Cu(II), Fe(III), Mn(III), Ni(II), Pb(II), Zn(II) as well as K_2MoO_4 and K_2CrO_4 on the hydration of the system $4CaO\cdot3Al_2O_3\cdot SO_3$–$CaSO_4\cdot2H_2O$–$Ca(OH)_2$ are mainly observed on the kinetics of hydration. These effects may be either depressing or enhancing and differences in behaviour are more evident at short curing times. As the curing time increases, such differences become smaller showing a common hydration thermodynamics.

The highly different behaviour observed in the mechanical properties cannot be explained in terms of the degree of hydration but other factors such as product morphology ad microstructure must be taken into account.

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