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THE INFLUENCE OF HEAVY METALS ON THE HYDRATION OF BINDERS OF INTEREST FOR CHEMICAL GYPSUM STABILISATION *

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ABSTRACT

The effects of the presence of some heavy metals on the hydration processes of binders useful for waste stabilisation have been investigated. The specific types of waste to which our attention has been directed are the chemical gypsums formed as by-products in a number of industrial processes.

Experiments have been carried out with hydratory model systems containing a binder (blast-furnace slag or fly ash–lime mixture), pure gypsum and a heavy metal compound ($Cr(OH)_3$, K_2CrO_4, $Mn(OH)_3$, $Fe(OH)_3$, $Ni(OH)_2$, $Cu(OH)_2$, $Cd(OH)_2$ or $Zn(OH)_2$).

The results have shown that in most cases the hydration processes are substantially unchanged or even favourably influenced. Retarding effects were only observed in the presence of Zn and (to a lesser extent) Cu.

INTRODUCTION

The entrapment of hazardous wastes within a cement-like matrix is a technique widely used to avoid environmental contamination. Among the binders which can be usefully employed, fly ash (mixed with lime) and blast-furnace slag are particularly attractive inasmuch as they are themselves industrial by-products and give hydration products of high durability and adequate mechanical strength [1–5].

It is clear that a specific waste can be successfully disposed of provided that some proper criteria are applied to determine the compatibility of the waste with the binding matrix. In this regard, it is of primary importance to confirm that the waste components do not negatively influence the hydration processes of the binder.

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Waste chemical gypsums are obtained in huge amounts in a number of industrial processes, such as the production of mineral acids, the neutralisation of acid waters by means of lime or limestone, the desulphurisation of flue gas, etc. These wastes, particularly when they contain heavy metals, require stabilisation.

The use of binders, such as fly ash–lime mixtures or blast-furnace slags, is promising, because they contain calcium and aluminium oxides that can convert the main component of chemical gypsum (calcium sulphate) into calcium trisulphoaluminate hydrate (TSH) [6–8]. This is produced in addition to the main binder hydration product, calcium silicate hydrate (CSH), and is characterised by satisfactory physical, mechanical and chemical properties [9–11].

On the other hand, minor components and impurities can significantly influence the hydration processes within the binder–waste mixture. In this connection, very little is known about the effects of heavy metals on the hydration of binders such as fly ash–lime mixtures and blast-furnace slags. In order to determine these effects, the behaviour of hydratory model systems containing one of these binders, pure gypsum and a heavy metal compound has been investigated.

EXPERIMENTAL

The binder : gypsum : metal-compound composition ratio employed was 70 : 24 : 6.

Blast-furnace slag or a 60 : 40 fly ash–lime mixture was used as binder. 0.5% $Ca(OH)_2$ was added to the slag to promote its hydraulic behaviour. The chemical compositions of the slag and fly ash are reported in Table 1. The lime and gypsum were analytical grade reagents.

TABLE 1

Chemical composition of slag and fly ash (wt.%)

	Blast-furnace slag	Fly ash
SiO_2	34.6	50.0
Al_2O_3	11.8	26.8
Fe_2O_3	1.6	6.3
CaO	42.7	1.9
MgO	4.3	1.2
K_2O	n.d.	2.5
SO_3	n.d.	0.8
S	1.0	n.d.
Mn_3O_4	0.6	n.d.
Loss on ignition	3.0	7.0

n.d., Not detected.

Hydroxides of Cr^{III}, Mn^{III}, Fe^{III}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} were freshly precipitated from solutions and characterised for chemically bound water by thermogravimetric analysis. Chromium was added as potassium chromate in an additional system.

The water/solid ratio in the pastes was 0.6. Curing times were up to 182 days at 25 °C and up to 91 days at 40 °C. The reaction was stopped by grinding under acetone, followed by washing with ether. The hydrated samples were then stored in a desiccator in the presence of P_2O_5.

The hydration products were characterised by thermal analysis, using a Netzsch STA 409 and a Stanton STA 780 apparatus. The heating rate was 10 K min^{-1}, which gives a linear temperature scale during the analysis, except at the beginning of the run. Systems containing slag were analysed between 25 and 280 °C, while those containing fly ash–lime mixture were analysed between 25 and 600 °C.

Quantitative data were obtained by determining the amount of non-evaporable water by ignition at 1000 °C. Systems containing fly ash–lime mixture were analysed for unreacted lime by the Franke method [12].

RESULTS AND DISCUSSION

The systems investigated are identified as shown in Table 2.

Figure 1a shows the results of thermal analysis for systems containing slag aged 28 days at 25 °C. System SG displays two endotherms: that at the lower temperature is related to TSH, while the other is due to the presence of unreacted gypsum [13]. The same effects are present in all the other systems.

Chromium has no effect when present in hydroxide form, but significantly accelerates the formation of TSH when present as chromate, as

TABLE 2

Symbols of systems investigated

Metal compound	Binder	
	Blast-furnace slag	Fly ash–lime mixture
–	SG	ALG
$Cr(OH)_3$	$SGCr^{III}$	ALGCr
K_2CrO_4	$SGCr^{VI}$	–
$Mn(OH)_3$	–	ALGMn
$Fe(OH)_3$	–	ALGFe
$Ni(OH)_2$	–	ALGNi
$Cu(OH)_2$	–	ALGCu
$Zn(OH)_2$	SGZn	ALGZn
$Cd(OH)_2$	SGCd	–

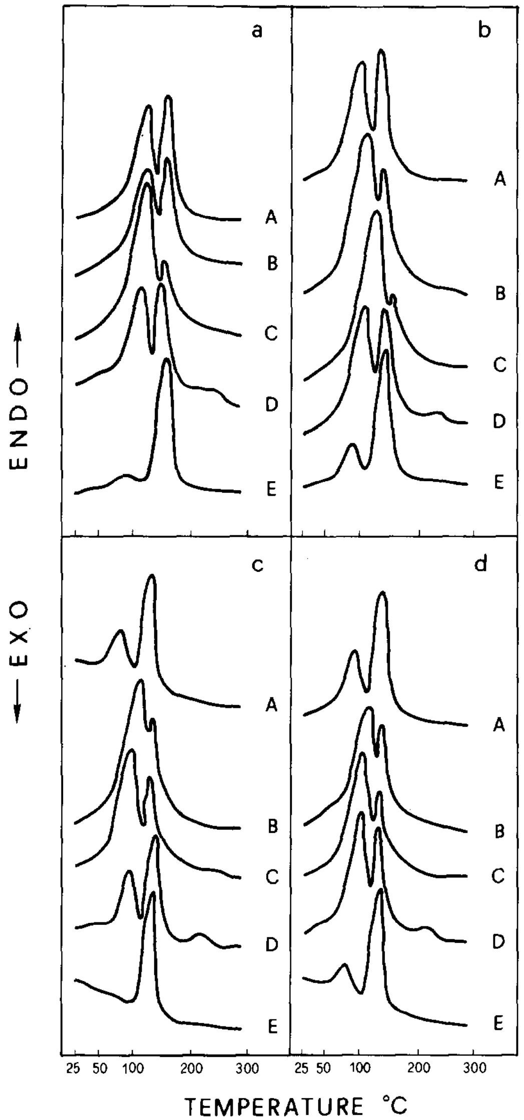

Fig. 1. Thermograms of samples containing slag: a, 28 days, 25 °C; b, 91 days, 25 °C; c, 7 days, 40 °C; and d, 28 days, 40 °C. A, SG; B, $SGCr^{III}$; C, $SGCr^{VI}$; D, SGCd; and E, SGZn.

demonstrated by the different relative intensities of the corresponding endotherms relative to this reaction product. The shoulder on the rising slope of the TSH peak reveals the presence of the main hydration product of slag, CSH [6]. Cadmium does not seem to significantly affect hydration at this stage. Lastly, the strong retarding effect of zinc is evident.

Figure 1b shows the thermograms of systems containing slag aged 91 days at 25 °C. The degree of hydration is generally not much higher than that at 28 days, with the exception of system $SGCr^{III}$, which reaches a conversion

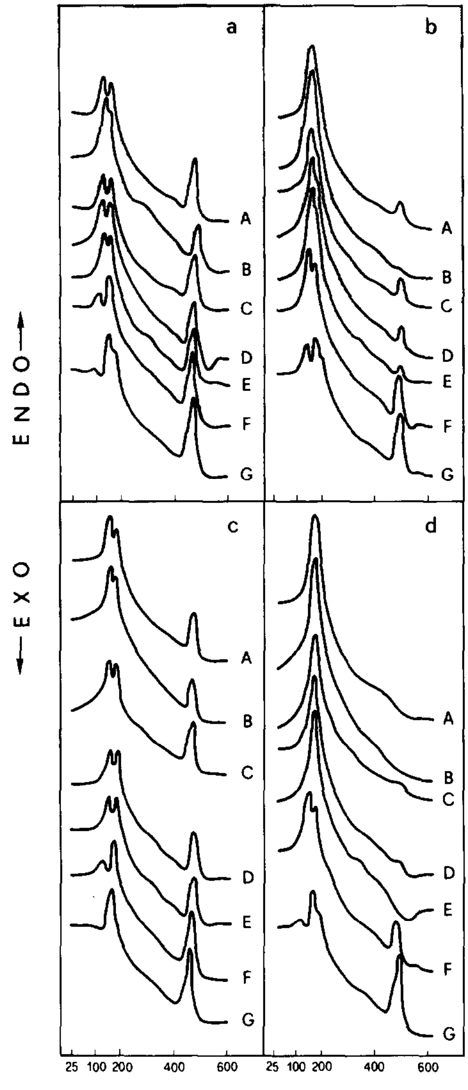

Fig. 2. Thermograms of samples containing fly ash–lime mixture: a, 28 days, 25 °C; b, 91 days, 25 °C; c, 7 days, 40 °C; and d, 28 days, 40 °C. A, ALG; B, ALGCr; C, ALGFe; D, ALGMn; E. ALGNi; F. ALGCu; and G, ALGZn.

well above that of the reference system SG and close to that of system $SGCr^{VI}$. The presence of zinc again display a strongly retarding capacity.

Figure 2a shows the thermograms of systems containing fly ash–lime mixture aged for 28 days at 25 °C. Three main endotherms, referred to reaction products, unreacted gypsum and unreacted lime respectively, can be detected as the temperature increases. As in the systems previously described, the main reaction products are CSH and TSH. Here, however, it is

TABLE 3

Quantitative data

Days	SG	SGCr^{III}	SGCr^{VI}	SGZn	SGCd	ALG	ALGCr	ALGMn	ALGFe	ALGNi	ALGCu	ALGZn
Non-evaporable water at 25 °C (wt.%)												
1	2.4	5.1	6.0	0.8	2.6	0.9	0.0	0.0	0.0	0.0	0.6	0.0
3	4.0	6.0	8.8	0.9	4.1	0.9	0.0	0.4	0.6	0.0	0.9	0.0
7	4.6	5.0	11.0	1.0	6.8	3.1	1.7	1.5	1.2	2.8	1.2	1.2
14	5.7	7.2	14.2	1.9	6.3	3.9	4.7	3.2	2.5	4.2	2.1	2.1
28	7.6	8.4	17.3	2.2	8.7	7.4	9.1	6.5	4.8	8.1	4.6	3.1
56	8.0	12.6	19.7	3.3	9.0	12.5	14.4	11.1	8.6	13.5	8.3	5.2
91	9.2	14.7	20.6	4.9	10.0	16.4	19.2	13.8	12.3	16.5	12.3	6.6
182	–	–	–	–	–	24.2	28.8	18.8	20.8	20.9	15.8	12.0
Non-evaporable water at 40 °C (wt.%)												
1	2.1	4.0	5.0	1.0	4.1	1.7	0.0	0.0	1.5	0.0	1.2	0.0
3	3.0	12.3	6.3	1.1	5.0	3.0	1.2	1.8	1.7	2.1	1.5	0.6
7	6.1	17.0	8.5	1.0	6.3	9.1	6.2	5.1	6.1	7.1	3.7	0.6
14	6.2	25.3	21.0	1.2	7.1	12.1	12.1	9.7	9.2	11.1	7.1	1.2
28	8.2	18.1	32.3	2.0	29.5	19.1	19.0	15.1	15.0	17.5	11.5	2.8
56	27.1	17.7	42.5	11.3	36.0	31.8	25.9	20.6	25.5	22.0	16.0	7.8
91	–	–	–	–	–	34.5	30.7	27.9	31.1	27.8	18.5	14.0

Days	ALG	ALGCr	ALGMn	ALGFe	ALGNi	ALGCu	ALGZn
Reacted lime at 25 ° C (wt.%)							
1	11.1	10.6	9.5	9.8	7.0	6.5	6.0
3	9.5	10.4	10.9	11.4	9.6	8.5	5.5
7	15.0	16.2	14.8	14.8	10.3	9.3	2.5
14	20.4	24.4	20.4	19.6	19.1	10.7	1.0
28	31.7	34.7	29.0	26.4	27.6	18.2	2.2
56	45.3	56.0	41.5	41.8	43.3	29.1	5.5
91	57.0	61.6	50.7	47.5	53.9	36.2	15.4
182	67.1	73.4	61.4	58.6	63.5	49.4	34.3
Reacted lime at 40 ° C (wt.%)							
1	10.8	13.0	11.9	13.9	11.1	9.8	6.6
3	19.0	24.4	18.8	18.1	17.7	12.7	6.8
7	39.6	36.5	33.6	32.7	30.5	17.0	6.3
14	56.5	49.5	44.4	46.1	46.3	28.4	9.0
28	64.4	62.1	60.9	62.7	64.6	41.3	8.5
56	79.5	79.4	72.9	76.2	75.9	57.2	27.6
91	83.6	79.6	79.2	79.0	79.1	65.1	55.4

more difficult to distinguish their individual thermal effects because of considerable overlapping [8].

When compared to system ALG, ALGCr behaves better, ALGFe, ALGMn and ALGNi show similar hydration degrees, while ALGCu and ALGZn display considerably lower hydration degrees, the latter being worse.

Figure 2b shows the thermograms of systems containing fly ash–lime mixture aged for 91 days at 25 ° C. As well as a general increase in the degree of hydration, the following observations can be made: in system ALGCr, calcium sulphate and hydroxide are almost completely converted, while in the cases of ALG, ALGMn, ALGFe and ALGNi, they show small effects; the hydration degree in systems ALGCu and ALGZn is again much lower.

Figure 1c shows the thermograms of systems containing slag aged for 7 days at 40 ° C. System SG shows the endotherms related to TSH and unconverted gypsum. The same effects are present in all the other systems except SGZn, in which the hydration is so strongly retarded that no reaction product is observed.

At this higher temperature, chromium, both hydroxide and chromate, significantly accelerates the formation of TSH, while cadmium and zinc are once again ineffective and strongly retarding, respectively.

Figure 1d shows the thermograms of systems containing slag aged for 28 days at 40 ° C. A general increase in the degree of hydration can be observed. When compared to SG, all the systems containing heavy metals behave in the same way as that observed at 7 days aging, with the exception of SGCd, which reaches a relatively higher hydration degree. Reaction in system SGZn is so slow that the degree of hydration is still lower than that of system SG at 7 days.

Figure 2c shows the thermograms of systems containing fly ash–lime mixture aged 7 days at 40 ° C. In relation to system ALG, ALGCr behaves similarly, ALGFe, ALGMn and ALGNi show slightly lower hydration degrees, and ALGCu and ALGZn are once more the least reactive.

Figure 2d shows the thermograms of systems containing fly ash–lime mixture aged for 28 days at 40 ° C. The hydration degree considerably increases for all the systems, and the following observations can be made: calcium sulphate and hydroxide are no longer detected in systems ALG, ALGCr and ALGNi, while they show small effects for both ALGMn and ALGFe (the sulphate has a shoulder on the right of the products peak); the hydration degree in systems ALGCu and ALGZn is again much lower.

Comparison between the behaviour of the systems containing slag, and that of the systems containing fly ash–lime mixture, leads to the following conclusions. When the binder is fly ash–lime mixture, the metals mostly produce effects ranging from nil to severe inhibition of hydration. Chromium has a slight favourable effect at 25 ° C only. When the binder is slag, the effects of the heavy metals are more differentiated. Chromium(III) and chromium(VI) improve the reactivity, cadmium tends to improve it only at the higher temperature and zinc strongly depresses it.

Differences in the rate of reaction of gypsum have also been observed; it is higher in the case of fly ash–lime mixtures.

Quantitative data regarding non-evaporable water and reacted $Ca(OH)_2$ are reported in Table 3.

The experimental results make it difficult to understand the reaction mechanisms leading to the differences observed in the behaviour of these systems. Nevertheless, mechanisms involving coating phenomena, adsorption processes, crystal nucleation and growth inhibition, as well as coprecipitation and ion substitution in the crystal lattices of the products, may play significant roles.

For example, it is known that octahedrally coordinated, trivalent ions and CrO_4^{2-} can replace Al^{3+} and SO_4^{2-} respectively in the crystal structure of TSH [14,15]. Moreover it is known from the chemistry of cement that metals such as Zn, Pb, Cu, Sn, Cd, As and Sb show retarding effects when added as soluble salts [5,16–19]. The reason for this is generally assumed to be the formation of gelatinous hydroxide coatings on the reactive particles in the strongly alkaline medium of hydrating cement.

However, different mechanisms must be invoked when, as in the present work, metals are in insoluble form. In this regard, Lieber [20] in a study on the retardation of cement by ZnO and PbO concluded that the effect of the former is due to the formation of crystalline calcium zincate coating. Tashiro et al. [21–23] investigated tricalcium silicate hydration in the presence of Cr_2O_3, Fe_2O_3, NiO, $Cu(OH)_2$, ZnO and PbO, and explained the retarding effect of copper, zinc and lead in terms of surface ion adsorption or complexation.

CONCLUSIONS

The influence of heavy metals on the stabilisation of waste gypsums depends on both the nature of the metal itself and the type of system used to generate the stabilising matrix. Chromium has a beneficial effect on the hydration of blast-furnace slag at both 25 and 40 °C. It is substantially ineffective at 40 °C only on the fly ash–lime system, as are iron, manganese and nickel at both temperatures. At 25 °C, chromium again has a beneficial effect on mixtures with slag. Cadmium is without influence on systems containing blast-furnace slag, except with later aging at 40 °C, when it enhances hydration; copper negatively influences the hydration of fly ash–lime mixture and zinc has a large retarding effect on the hydration of systems containing either blast-furnace slag or fly ash–lime mixture.

Understanding the mechanisms responsible for these behaviour patterns will require further more sophisticated experiments.

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