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INERTIZATION OF TOXIC METALS IN CEMENT MATRICES: EFFECTS ON HYDRATION, SETTING AND HARDENING.

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ABSTRACT

The effect of the addition of four toxic metals added as chloride solutions and suspensions to a cementitious matrix, consisting of white cement paste and mortar, was studied.

To such purpose variations in the physical-mechanical properties of the cement mixes, the development of the heat over time and the evolution of the phases formed during hydration were observed.

Introduction

Processes based on cement binders for the inertization of wastes containing heavy metals have been commercially available for several years (1- 2).

The international scientific literature offers a number of studies useful in assessing the performance of inertization matrices, often determined by interpreting the results of leaching tests (3-5). Limited attention, however, has been given to how hydration, and the characteristics associated with this, such as setting times and hardening behaviour, are influenced by the addition of toxic elements.

As it is known, hydration processes are more or less markedly influenced by the presence of heavy metal salts. Metal cations in concentrations of between 0.2 - 4%, delay the setting and hydration times of the cement (6, 7); anions such as chlorides, bromides, nitrates and sulphates accelerate the hydration reactions (7, 8). For this reason, the global effects on cement hydration must be interpreted as the combined action of the cation and the anion. In this work, metal elements were added to a white cement in the form of chlorides to study the combined effect of an accelerating anion and a retarding cation.

The hydration heat development was measured, and the results obtained correlated with the setting time. The evolution of the phases during hydration of the cement was determined by means of X- ray diffraction (XRD), and the results obtained were correlated with the compressive strength measurements at different curing times.

The metal elements added were cadmium, chromium, lead and zinc, because these are among the most widespread and characteristically found in industrial wastes.

Materials

Cement

The tests were conducted using a CEM I 52.5 R white cement, whose composition is reported in table 1.

White cement was used because this type of cement has a very limited ferric oxide content, and consequently its mineralogical composition is simplified by the presence of only three main compounds (C_3S, C_2S, and C_3A). The cement utilized belongs to the 52.5 MPa compressive strength class, and consequently ranks as the highest clinker content cement commercially available. For this reason, as well as for the fact that it contains practically only three compounds, this cement, even though it is an industrial product, is the closest thing to a mixture of pure compounds.

TABLE 1

Potential Composition According to Bogue of White Cement Utilized.

Compound	C_3S	C_2S	C_3A	C_4AF
% in Weight	58	19	12	1

Toxic metals

The aqueous solutions of cadmium, chromium and zinc, the lead suspension had a concentration equivalent to 4% in weight of the element considered. The solutions were prepared using distilled water: cadmium, chromium and zinc chlorides were completely dissolved, lead chloride only partially dissolved at the above said concentration.

Mortars and mixes dosed solely with distilled water and without the addition of the pollutants were used for comparison, and are indicated below by the term "control".

Tests and Results

Setting Times

The setting times were measured using the Vicat needle (UNI EN 196 Part 3^a); the measurements were taken under non-standard conditions, utilizing pastes having a constant solution/cement weight ratio of 0.5 by weight. It was considered advisable to proceed in this manner rather than with mixes of similar consistency, so as to obtain indications regarding the capability of the metal elements to accelerate or retard the cement setting times at the same water/cement and pollutant/cement ratios. The water/cement ratio adopted is rather high compared to that required when working at equivalent consistency, as envisaged by the standard, but this choice was prompted by the fact that certain pollutants, causing rapid solidification of the mix, would have interfered with the execution of the test.

The results of initial and final setting times for the different mixes are reported in Table 2.

TABLE 2

Setting Times with Different Toxic Metals

Pollutant	Control	Cadmium	Chromium	Lead	Zinc
Initial, min	210	260	150	640	25
Final, min	385	280	195	770	120

Calorimetric Measurements

A Tam Thermometric isothermal conduction calorimeter was used, utilizing the maximum range value of 3000 μW. The results given by the calorimetric tests are summarized in Fig. 1, which shows the instant heat developed (mW/g) in function of time for the metal elements considered; zero time in the graph corresponds to 10 minutes after addition of the solutions to the cement.

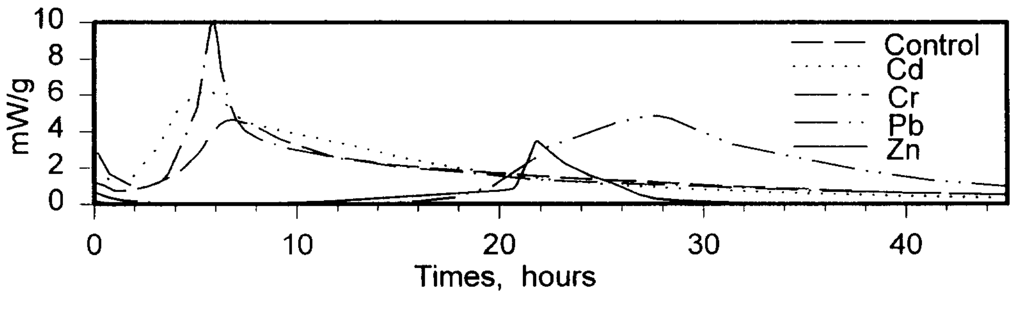

FIG. 1

Heat evolution rate vs. time for different pollutants and control

To measure the heat evolution rate, 400 mg of cement mixed with water and with the pollutant solutions or suspensions were placed in the measuring cell, at a fixed temperature of 25 ± 0.02°C. To facilitate mixing, the solution/cement ratio used was equivalent to 1; also, to maintain the same pollutant/cement ratio of the other tests conducted, the concentration of polluting metals in the liquid was reduced to 2%.

XRD Analysis

The white cement was hydrated in mixes with solution/cement ratio of 0.5. The reaction vessels, one for each reaction duration, sealed and placed in a glass container, were maintained at fixed temperature of 25 ±1°C.

At intervals of 1, 3, 7, 14 and 28 days, the samples were taken from the thermostatic containers and the hydration reaction was stopped by subjecting them to a rapid grinding in a mill together with ethyl alcohol and a subsequent washing with ethyl ether. The material was then filtered in a buchner using decarbonated air. The powders thus obtained were then kept in a drier in the presence of calcium chloride. These steps were taken so as to minimize carbonation, which nevertheless was observed in certain samples. The samples thus treated were then utilized for the XRD analyses.

The results of the tests conducted on the white cement control and on the four metals examined are given in Fig. 2. These graphs show the intensity, read from the spectra, of the characteristic lines of the cement phases (silicates) and of those of the new phases (cement gel, ettrigite, lime, chloroalluminates and carboalluminates). This was done in order to obtain a semi-quantitative evaluation of the development of the hydration products of the cement: the term "degree of hydration" in the following text is related to the intensity of the residual silicate lines at the different curing times.

Mechanical Tests

The compressive strength and flexural strength tests were conducted according to the italian standards (UNI EN 196 Part 1^a), on mortar prisms having a solution/cement weight ratio = 0.5 and an aggregate/cement ratio = 3. The mortar was produced using washed and selected siliceous sand qualifying as a UNI EN 196 Part 1^a sand grading.

The results reported in Table 3 regarding the curing intervals of 7 and 28 days, represent the mean values of four measurements for flexural strength and eight measurements for compressive strength.

TABLE 3

Flexural Strength and Compressive Strength at 7 and 28 days, MPa.

Pollutant		Control	Cadmium	Chromium	Lead	Zinc
Flexural,	7 days	5.5	6.1	6.3	6.4	4.5
	28 days	6.1	5.5	5.5	5.4	4.9
Compressive,	7days	48.4	52.0	57.1	54.3	44.5
	28 days	53.7	59.0	59.5	56.8	56.5

Discussion of Results

The results of the *calorimetric tests* show that the main heat evolution peak observed during hydration of the cement shifts considerably as a conseguence of the addition of the different elements to the mixes.

It was also observed that for the lead, the chromium and the cadmium, as well as for the control, the beginning of the heat evolution peak can be broadly correlated with the final setting time; it was noted in particular that the elements accelerating the setting of the cement (cadmium and chromium) accelerate the development of the main peak with respect to the control: in the case of lead (which retarded setting) also the main peak was delayed. The accelerators, as observed by Edwards (8), cause an increase in the maximum intensity of the peak, whereas in the case of lead the intensity of the peak is comparable to that of the control.

In all cases examined, the *compressive strength* of the white cement mortars at 28 days increased with the addition of the metal chlorides utilized. This is confirmed for chromium chloride, at the concentration levels utilized, by similar data in the literature (9), but is not confirmed for cadmium, lead and zinc, although in the comparable studies considered (10 - 11), these elements were not added to the inertization matrix as chlorides. This increase in the compressive strength is to be related to a greater degree of hydration of the cement at 28 days as compared with the control.

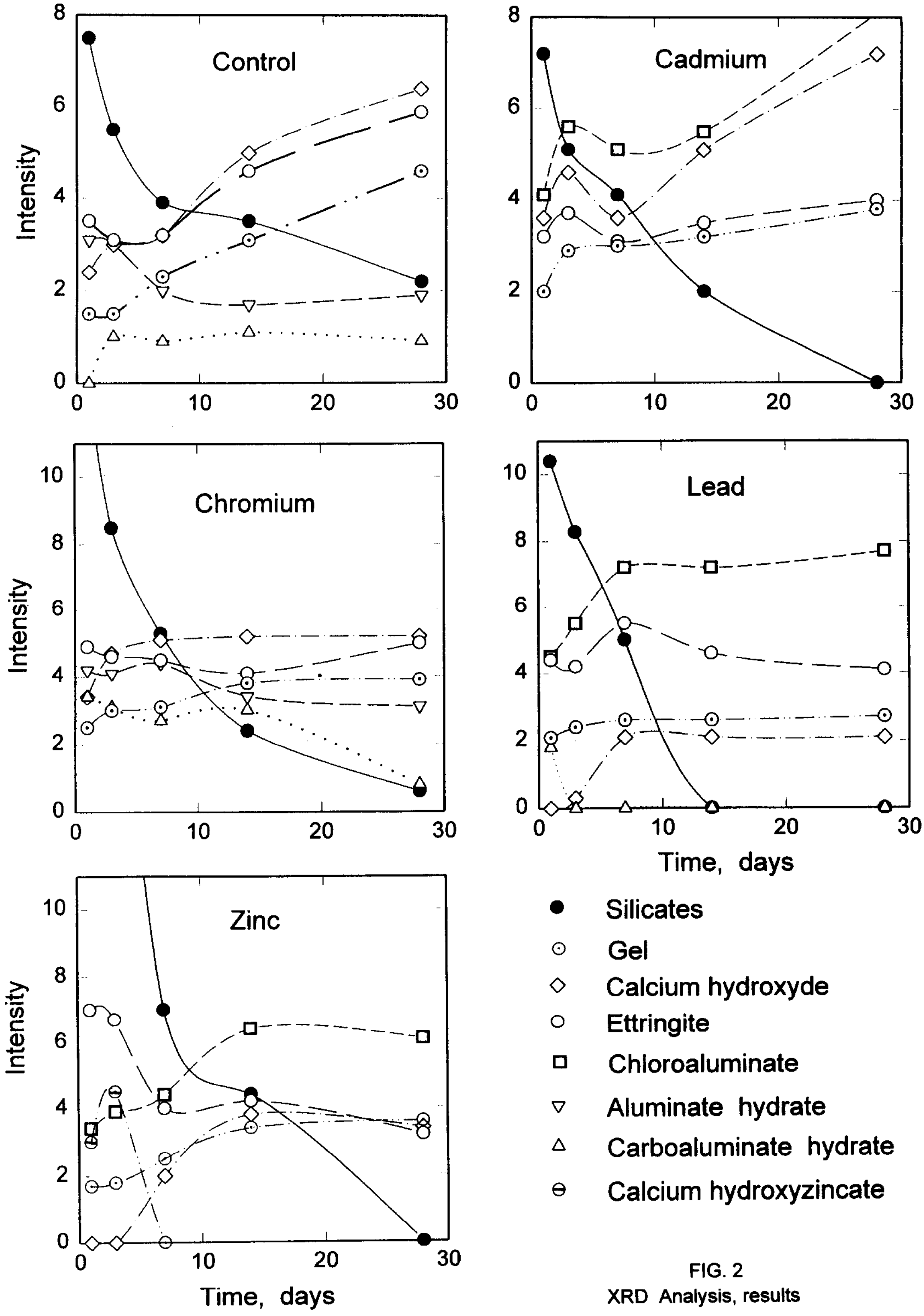

FIG. 2
XRD Analysis, results

Hydration in the presence of *cadmium* chloride proceeds up to 7 days at a rate comparable to that of the control, but then speeds up. In this regard Mollah (12) states that solutions of 10% cadmium nitrate retard cement hydration; this author also hypothesizes that the delay is due to the action of calcium hydroxycadmiate the presence of which, in our case, was not discerned by XRD.

For the *chromium*, the high compressive strength at 7 and 28 days can be related to the high rate of hydration of the silicates, indeed the absence of anhydrous silicates in the cement was observed at 14 days. In the course of the experiments conducted, the finding of Zamorani (9) was confirmed that the chromium chloride accelerates the cement hydration reactions. Likewise, Ivey (13), who utilized the nitrate salt instead of the chloride, found that the chromium had an accelerating effect on the cement hydration. Ivey associated this acceleration to the lack of ettringite formation; this observation was not confirmed in our experiments, however, since in the case of the chromium both the accelerating effect and ettringite formation were noted.

Lead sulphates and nitrates delay the hydration reactions (14 - 15); in the course of our tests we noted that in the case of lead chloride the hydration proceeds at about the same rate as for the control: we can hypothesize that this result is attributable to the strong accelerating action of the chloride ion, which counterbalances the retarding action of the lead. Moreover, in accord with the findings of Lieber (16) and Thomas (15) for lead, we noted no formation of crystalline phases containing this element.

As stated above in regard to the cadmium, chromium and lead, the end of the setting interval can be related to the beginning of the main heat evolution peak, and in the case of each of these elements both phenomena shift toward longer (retarded) or shorter (accelerated) times with respect to the control. For the *zinc*, on the other hand, we noted that setting shifted toward shorter times and the main peak toward longer ones with respect to the control.

As for the setting times, the result observed in the case of zinc contrasted with the indications in the literature; in fact, the addition of both the zinc chloride (17) and the zinc oxide (18) have been reported to have retarding effect on the setting.

As for the cement hydration, Edwards (8) has shown that the addition of zinc chloride has a retarding effect and the thermal peak intensity is reduced. This was confirmed in the calorimetry tests we conducted.

The XRD analyses performed at 1 and 3 days' hydration showed in the presence of zinc the formation of a crystalline phase, calcium hydroxyzincate, formed as a result of the reaction between the calcium hydroxide and the zinc hydroxide, in line with what has been pointed out by several authors (19 - 21).

Lieber (16), who utilized zinc oxide, noted that hydration started at about the time the calcium hydroxyzincate disappeared; in line with this result, our XRD analyses showed the disappearance of calcium hydroxyzincate at 7 days, and at the same time a reduction in anhydrous silicates and the development of lime. Arliguie (19 - 21), who did not measure the setting time, hypothesized that the prolongation of the dormant period is caused by the formation of an amorphous zinc hydroxide around the grains of C_3S, whereas the arrested hydration is due to the transformation of zinc hydroxide into calcium hydroxyzincate.

It would appear reasonable to assume that the chloride ion acts as to accelerate the initial and final setting times, and this occurs even if the hydration is rather limited (22); indeed, even the formation of zinc hydroxide on the surface of the granules could make a positive contribution to the setting. In turn, the formation of hydroxyzincate prevents further hydration of the cement, prolonging the dormant period, until the moment when the energic hydration of the cement itself starts, with the development of heat.

Since, as indicated above, the literature reports delayed setting in the case of zinc chloride and oxide, it was supposed that the reason for this discordance might lie in the use of white cement. To test this, we measured the setting times of a mix of ferric cement and the same zinc chloride solution: also in this case we observed an acceleration effect.

The mixture added with zinc chloride showed a slower rate of hydration than that of the control up to 7 days, at which point it then rose to a faster rate. These results agree with those obtained from the mechanical test, where the compressive strength at 7 days was less than that of the control, but at 28 days was greater.

Conclusions

Except in the case of zinc, the final setting times can be correlated with the calorimetric tests, with the elements which accelerate setting (cadmium and chromium) advancing the development of the main heat evolution peak with respect to the control, and the retarding elements (lead) delaying its development.

The zinc chloride accelerates setting and retards hydration of the white cement; the present report offers an interpretation of these contrasting results, based on the formation of zinc hydroxide and calcium hydroxyzincate.

The addition of metal chlorides does not retard hydration of the cement. It was observed, in particular, that with reference to the control, hydration in the presence of chromium is considerably faster, and in the presence of cadmium and zinc is in general faster, whereas hydration in the presence of lead proceeds at the same rate as that of the control.

The XRD analyses showed that for the elements in question there was no formation of new phases from the reaction between the metal elements and the cement pastes, except in the case of zinc. For this element we observed the formation of calcium hydroxyzincate in the first stages of curing (1-3 days).

The compressive strength of the cement mortars at 28 days slightly increased in all cases examined as a result of the addition of the metal chlorides utilized.

The heat evolution curves during cement hydration in the presence of metals do not show evident separation of thermal peaks due to different influences on the cement compounds; work is in progress to study C_3A and C_3S behaviour individually.

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