Pergamon

Cement and Concrete Research, Vol. 26, No. 3, pp. 377-385, 1996
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0008-8846/96 $15.00 + .00

PII S0008-8846(96)00010-5

EFFECT OF LARGE ADDITIONS OF Cd, Pb, Cr, Zn, TO CEMENT RAW MEAL ON THE COMPOSITION AND THE PROPERTIES OF THE CLINKER AND THE CEMENT

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(Refereed)
(Received November 8, 1995; in final form January 2, 1996)

ABSTRACT

The addition of important quantities of Cd, Pb, Cr, Zn to raw meals of Portland and calcium aluminate cement modifies the mineralogical composition and the properties of the final cement. Portland cement can absorb a large amount of Cd, and Zn.This absorption leads to an increase of setting time and a decrease of strengths of the cement. It also can trap chromium with a short setting time and high strengths. Calcium aluminate cements easily trap Cd and Cr with a delayed setting and good strength but also Pb with normal setting time and strengths. Large quantities of zinc oxide have a deleterious effect on calcium aluminate strengths.

RESUME

L'addition d'importantes quantités de Cd, Pb, Cr, Zn au cru de ciment Portland et alumineux modifie la composition mineralogique et les propriétés du ciment final. Le ciment Portland peut absorber de grandes quantités de cadmium et de zinc. cette absorption conduit à une augmentation du temps de prise et une diminution des résistances du ciment. Il peut aussi piéger le chrome avec un temps de prise plus court et de hautes résistances. Les ciments à base d'aluminates de calcium piégent facilement Cd et Cr avec un temps de prise plus long et de bonnes résistances, mais aussi Pb avec un temps de prise et des résistances normales. De grandes quantités d'oxyde de zinc ont une action néfaste sur les résistances des ciments d'aluminates de calcium.

Introduction

The utilisation of hydraulic binders to solidify and to stabilize industrial wastes and municipal garbages is presently recognized as one of the solutions to the problems of the environment protection. Consequently many researches have been and are still undertaken on these subjects. The results are widely published (1 to 6).

The first action is the pH increase which allows the precipitation of several metal hydroxides. The second action is the introduction of toxic elements such as chromium (7) or cesium (8) into the structures of the hydrated compounds of the cements, specially calcium aluminates or cal-

TABLE 1

Amount of Minor Elements in OPC Clinker and After Leaching (14)

Element	Concentration (ppm) in OPC	Concentration in solution after leaching (µg/l)	Threshold of detection	Legal limits
Mn	107/922	< 1	1	50
As	13/117	< 1	1	50
Cd	0.1/1.7	0.7	0.1	5
Cr	60/155	21	1	50
Hg	0.03/0.1	< 0.5	0.5	1
Ni	18/49	< 1	1	50
Pb	8.7/171	5	1	50
Zn	21/290	7	2	5000

cium sulfoaluminates (ettringite) (9). On the other hand, the use of the energetic potential of many wastes (tyres, used oil, papers, rice husk . . .) leads to an other solution for fixation of elements in the anhydrous products, i.e. the clinker itself.

This technique presents two advantages. In one side, a save of energy by the use of the wastes combustion heat and on the other side, the fixation of toxic elements in a crystallised structure. This technique has been studied to stabilize nuclear wastes constituents (10). In contact with water during the hydration reaction, the compound will be either inert (and the toxic element will be definitely trapped in the crystal of the anhydrous compound) or hydraulic, giving rise to an hydrated compound of the same type as those previously described (the toxic element being trapped in the structure of the hydrates).

The first mechanism of the solidification can be written in a simplified way as:

$$A + B + H_2O \rightarrow H(M)OH_2$$

AB = anhydrous binder
M = element (Metal) to be trapped
H(M)OH2 = Hydrated compound containing M

The second mechanism will be AB + M → AB(M)

AB(M) = represents the anhydrous compound containing M

In a first hypothesis, AB(M) is inert and the element M is stabilized as a ceramic or glass type solid. In the second hypothesis AB(M) + H2O → H(M)OH2 and we are again in the first mechanism of stabilization through an hydrated compound.

Several questions arise about this last configuration. What are the maximum contents of this type of elements acceptable by the cements with a slight modification of its properties? What could be the processing problems connected with the use of wastes derived fuel (thermal profile modification, variation of the kiln atmosphere, gas or dust emission). The hydraulic binders are manufactured by firing at high temperature natural materials such as clay, bauxite, limestone and contain Ca, Si, Al, Fe, Mg, Na, K, S, O_2 as principal elements. Many other elements are brought by the fuel and the raw mix. They are called "minor" because of their low contents and thus, their supposed effect on the quality of the final product. In fact, in most of the cases the

TABLE 2

Chemical Composition of the Cements

Cement	SiO2	CaO	A1203	Fe2O3	MgO	TiO2	LOI
OPC	14.13	43.52	3.66	1.82	0.84	0.06	35.97
CAC	4.14	25.49	29.63	11.69	0.29	1.47	27.29

effect is more important than it could be predicted only by the content of the element. The increasing use of waste tends to increase the proportion of these elements and also bring some others.

The first step has been to identify the elements found usually in Portland cement. This has been done by numerous researchers (11/12/13) and summarized in the Table 1.

The second column of Table 1 shows the range of concentration of several minor elements found in Portland cement clinker (statistically found in 200 clinkers and given in ppm)

The second step has been to evaluate the stability of these elements in industrial cements and particularly their behavior during standart leaching tests. These results are presented in the third column of the Table 1 as a sum of the leaching tests after 1 day, 1 week, 1 and 9 months, and given as microgramme/liter (14).The forth column shows the limits of detection of the measurement techniques, and the last one reminds us the legal limits according to the European regulations relevant to water potability (14).

The results of these studies show that the leaching solution of standard cement is no more concentrated in toxic elements than natural rocks such as granite or basalt. Three cements, enriched in Cr, Cd, Pb, have shown important leaching concentration of chromium. The ratio between the released fraction of calcium over these of heavy metal remain constant: the authors conclude that the dissolution of heavy metals occurs by dissolution of the cement paste itself due to the high pH. Only a part of these metals goes into solution, the remaining being precipitated as hydroxides.

The target of the present work is to estimate the ability of industrial cements to trap the most commun pollutant elements found in industrial or domestic wastes (Cd, Pb, Cr, Zn) during the production of the binders and to study the stability of the final product during and after hydration. The cement are calcium silicates based cements (Portland cements) and calcium aluminates containing cements. In order to be situated in a difficult case of fixation, we have chosen metal salts having high surface tension such as chlorides.

Experimental Procedures

Two industrial cements raw mix corresponding to Portland cement and calcium aluminate cement have been mixed with 10% $PbCl_2$, $CdCl_2$, 2.5 H_2O, $ZnCl_2$, $CrCl_3$, $6H_2O$ of respective purity 99%, 98%, 99% and 96%. The Table 2 shows the chemical analysis of the raw meals. These mixtures, after homogeneisation have been burned in a muffle kiln at 1450°C during one hour.

The resulting products have been examined by X ray diffraction and by scanning electron microscopy (SEM) on polished sections. The bulk analysis of Pb, Cd, Zn, Cr, Cl have been done by ICP (inductively coupled plasma).

After burning, the OPC clinker was coground with 5% gypsum at 350 m^2/kg fineness and the cement was mixed with water at W/C = 0.4. The calcium aluminate clinker was ground at the

TABLE 3

Retention Efficiency for Portland and Calcium Aluminate Cements

Cement	OPC	OPC	OPC	OPC	CAC	CAC	CAC	CAC
Addition	Cd	Pb	Cr	Zn	Cd	Pb	Cr	Zn
% fixation	22%	0%	84%	53%	48%	53%	74%	28%

same fineness and mixed with water at W/C = 0.4. The setting time and hardening behavior are estimated. After 28 days of storage the prisms have been stored in water at W/C = 10

Results and Discussion

The Table 3 shows the percentage of fixation for a given element (ratio between the amount of element remaining in the clinker over the amount of the same element in the raw mixture, tacking into account the loss of ignition)

In Table 4, are shown the mineralogical compositions determined by X ray diffraction and by SEM. (The meaning of phases called X, Y, is given in the relevant discussion). The distribution of the added elements in the different phases has been also determined and published elsewhere (15). In the last columns, we note qualitatively the setting time and the 24 hours compressive strengths of the cements (the signs -, o, +, mean respectively longer, equivalent and shorter setting time than the setting time of the standard cement and lower, equivalent or higher strengths than the standard cement).

The Table 5 shows the metal content of the solution after a month leaching at W/C = 10

Effect of Cadmium. In Portland cement, cadmium occurs in various concentrations in the raw materials and fuels as a trace elements and is mainly trapped by the alite and belite of the clinker (16/17).

In the present case, 22% of cadmium is trapped in Portland cement and 48% in calcium aluminate. Alite, belite, calcium ferrite are detected while cadmium is concentrated in little

TABLE 4

Mineralogical Composition and Properties of OPC and CAC Containing Cd, Pb, Cr, Zn

Cement	Added elements	Mineralogical composition	Setting time	Hardening after 24 hrs
OPC	Cd	C3S/C2S/aluminate/Ferrite/X	-	-
OPC	Pb	C3S/C2S/Ferrites/C3A	-	-
OPC	Cr	C3S/C2S/C3A/Ferrite	+	+
OPC	Zn	C3S/C11A7CaCl2/Ferrite/ZnO	-	-
CAC	Cd	CA/C11A7CaCl2/C2AS/Ferrite/Y	-	o
CAC	Pb	C11A7CaCl2/C2AS/Ferrite/PbO	o	o
CAC	Cr	CA/C2AS/C11A7CaCl2/Ferrites	-	o
CAC	Zn	C11A7CaCl2/C2AS/Ferrite/Zn aluminates	o	-

TABLE 5

Composition of the Solution After Leaching Test

Cement	Added elements	Cd in solution	Pb in solution	Cr in solution	Zn in solution
OPC	Cd	< d.1			
OPC	Pb		0.1 mg/l		
OPC	Cr			25 mg/l	
OPC	Zn				0.5 mg/l
CAC	Cd	< d.1			
CAC	Pb		1 mg/l		
CAC	Cr			5.7 mg/l	
CAC	Zn				0.2 mg/l

bright sphere composed mainly of CdO and CaO (Phase X), as it can be proved by SEM (15). By X ray diffraction, free lime and $C_{12}A_7$ (instead of C3A) are detected.

Cadmium in the clinker retards the setting time and decreases slightly the compressive strengths. No cadmium is detected into the leaching solution after one month (Table 5).

The effect of cadmium on the hydration of Portland cement has been studied during the tentative of immobilisation of this compounds by cement matrix (18/19). These results cannot be directly compared with the presents findings because in the current study, cadmium is already in the clinker matrix. Nevertheless, it can be assumed that, after the dissolution period

FIG. 1.
Calcium aluminate cement containing cadmium: CA (a), C11ACaCl2 (b), C2AS (c), ferrite (d), phase Y (e).

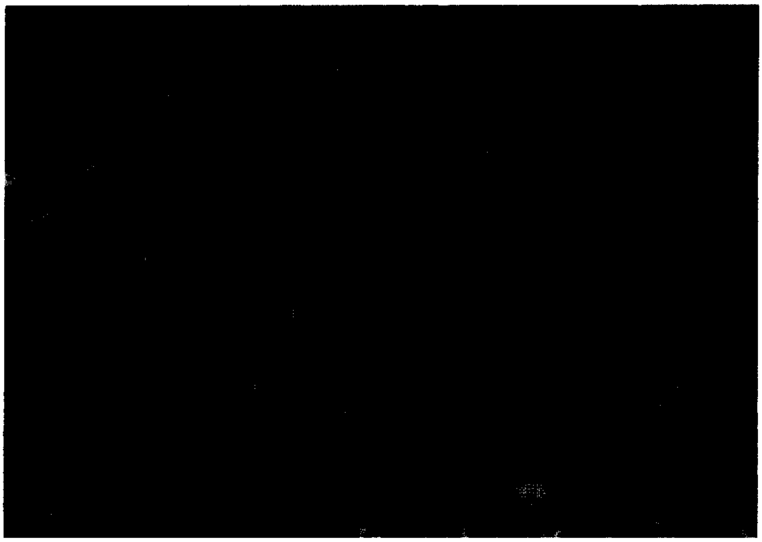

FIG. 2.
Calcium aluminate cement containing lead: gehlenite (a), C11A7CaCl2 (b), ferrite (c), lead oxide (d).

of the hydration, cadmium species which are released by the clinker are immobilized by physical entrapment of $Cd(OH)_2$ into the CSH.

In the case of calcium aluminate cements, monocalcium aluminate, calcium chloroaluminate, gehlenite, calcium aluminoferrite are detected. Cadmium is located in a phase (called Y in Table 4) which appears bright on the micrograph Figure 1 and which contains iron and cadmium oxide. It must be highlighted that the percentage of cadmium trapped in the calcium aluminate cement is twice that in the Portland cement. The presence of cadmium retards the setting time but does not modify the strengths after 24 hours. No cadmium is found into the leaching solution.

Our results do not confirm the findings of Tumidajski at al (20) who claim that the presence of cadmium would inhibit the formation of C_3AH_6 hydrated phases. It could probably be only a delay in the formation of C_3AH_6 and not an inhibition.

Effect of Pb. Very little lead is trapped in Portland cement and the usual mineralogical composition is found by X ray diffraction and SEM. A small quantity of $C_{12}A_7$ is detected, probably stabilized by chloride ions. Belite is mainly found as isolated inclusions in the alite crystal and C_3A crystallises as special habit. According to Kirchner (21) most of the lead is found in the clinker. This discrepancy with our present results is probably due to the different lead salt introduced in the raw material and the absence of recycling phenomenon in our muffle kiln. Due to the presence of small amount of this element into the clinker, the effect on the hydration and the fixation is reduced. We note that the setting time is delayed in agreement with Sprung's results (22).

Calcium aluminate cement traps Pb with a better efficiency 53%).

The micrograph in Figure 2 shows the presence of gehlenite, $C_{11}A_7CaCl_2$, calcium aluminoferrite and lead oxide. Lead is mainly found as oxide but a little amount enters $C_{11}A_7CaCl_2$ and

FIG. 3.
Calcium aluminate cement containing chromium: CA (a), C_2AS (b), $C_{11}A_7CaCl_2$ (c), ferrite 1 (d), ferrite 2 (e).

gehlenite (15). In spite this amount of lead, the setting time and the hardening behavior are normal and only a very small quantity of lead is released after one month leaching.

Effect of Chromium. Portland cement clinker traps a large amount of chromium (84%). In the present experiment 1.2% and 3.25% of chromium are found respectively in alite and belite. These contents are higher than those previously found (0.57 and 1.11%) in the literature (23).

The setting time of the Portland cement is shortened and the cement hardens rapidly in agreement with previous results (24/25) which show that chromium leads to an increase of early strengths. It is also found in the literature that chromium deteriorates the 28 days strengths. This can be an explanation to the high amount of chromium released in the solution (Table 5).

Calcium aluminate cements also trap chromium with a good efficiency (74%). The micrograph in Figure 3 shows calcium aluminate, calcium chloroaluminate, gehlenite calcium chromate and two types of ferrites. Chromium seems to concentrate in calcium aluminate and in calcium ferrite. The setting time is delayed (as opposite as in the case of OPC), but the strengths are equivalent to the standard. The quantity of chromium released into solution is significative, although smaller than for OPC.

Effect of Zinc. In Portland cement clinker 53% of zinc is fixed and the usual phases, alite, (with a sign of decomposition), belite, C_3A and C_4AF are detected. Zinc oxide is also found by SEM. Alite size crystals increases with the ZnO additions, in agreement with the published literature (27). About 2% of alite is found in alite. ZnO retards the setting and reduces the strengths confirming the results previously found (28/29).

In the case of calcium aluminate matrix, gehlenite $C_{11}A_7CaCl_2$, ferrite and zinc aluminate are detected (Micrograph 4). Zinc is found in calcium ferrite and mainly crystallises as a complex zinc aluminate. The effect of zinc on the setting is less pronounced than for Portland cement

FIG. 4.
Calcium aluminate cement containing zinc: C_2AS (a), $C_{11}A_7CaCl_2$ (b), ferrite (c), phase 1 (d).

but the strengths are lower than the standard. In both cases (OPC and CAC), very little zinc is found in the leaching solution.

Conclusions

The matrices of calcium silicates and calcium aluminates are able to trap a large quantity of Cd, Pb, Cr, and Zn. Portland cement can accept Cd, Cr and Zn in its matrix with a modification of its hydration behavior (delayed setting and lower strength for Cd and Zn and shorter setting and higher early strengths for chromium).

Calcium aluminate cements have a good ability to trap lead without deleterious effect of its properties. In all cases very small quantity of the added elements are released in the leaching solution.

The results must be interpreted with precaution and the figures taken as an order of magnitude, because the efficiency of the fixation depends on the addition level compared to the saturation level, depends also on the thermal profile (burning temperature, residence time, gas partial pressures,..). It is worth noting the ability of calcium aluminate cements to fix chloride as $C_{11}A_7CaCl_2$.

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