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CHARACTERIZATION OF CEMENT-STABILIZED Cd WASTES

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ABSTRACT

Portland cement affords both physical and chemical immobilization of cadmium. The immobilization has been studied analyzing the pore fluid of cement samples and characterizing the solid pastes by X-ray diffraction.

The influence of cadmium on the cement hydration and on its mechanical properties has been also studied by isothermal conduction calorimetry and by the measure of strength and setting development.

Finally, the effect of cement carbonation on the immobilization of cadmium has been analyzed. © *1997 Elsevier Science Ltd*

Introduction

Waste disposal has become a major concern in most industrial countries because of limited sites and strict environmental standards for landfilling. A wide range of portland cement-based stabilization/solidification processes have been used and patented for the conditioning of a number of wastes before disposal (1). However, it appears that the scientific basis for conditioning wastes is not well documented. Because each chemical element has a unique chemistry, its interaction with cement must be studied separately. In the present study we describe interactions between cadmium and Portland cement.

Cadmium is known to be toxic to most living organisms including humans, and long-term exposure causes cancer and hypertension (2). Electroplating is the largest source of cadmium-bearing wastes.

Results on leaching studies (3,4) confirm that cadmium could be retained in cement. However, when the final pH of the leachant drops around 7, cadmium leaches out at a relatively high level. Besides, most of the tests to evaluate the retention of metals in Portland cement have been carried out in fresh stabilized-solidified samples and little attention has been paid to the influence of cement deterioration due to the environmental attack.

Carbon dioxide attack or carbonation is probably the most common form of environmental attack on concrete and it promotes changes in the cement chemical composition and physical properties that can affect the long-term retention of heavy metals. In the present paper we also study the effect of atmospheric carbonation on cadmium immobilization.

TABLE 1

Chemical Composition of Portland Cement

Oxide	**CaO**	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**MgO**	**SO_3**	**Na_2O**	**K_2O**
weight (%)	63.52	20.06	2.92	5.32	1.28	3.09	0.20	1.03

Experimental

Materials. The cement used was a type I Ordinary Portland Cement (OPC) with chemical analysis as shown in Table 1.

Control samples were prepared with distilled water at a w/c ratio of 0.5; other cylinders were prepared with mix water containing 5,000, 15,000, 30,000 or 50,000 ppm of cadmium added as nitrate salt.

Procedure. The paste cylinders (45 mm diameter, 80 mm height) were demolded after 24 h and placed in a chamber at 100% r.h. at 25°C during 1, 7, 30 or 90 days. At these ages, the cylinders where submitted to pore water extraction.

Pore water is the water contained within solid cement pores but not combined into solid hydration products. It was extracted by using a high pressure compression device (5). The pore water extracted was partly used for pH, determined by titration with HCl, and the remainder analyzed for other ions: cadmium, calcium and aluminum by atomic absorption; sodium and potassium, by atomic emission; and $SO_4^{=}$ and NO_3^- by ionic chromatography.

A limited number of cylinders spiked with 50,000 ppm of cadmium through which CO_2 gas was bubbling continuously throughout the experimental period. After 30 or 90 days the cylinders were submitted to pore water extraction.

The solid pastes were examined by X-ray diffraction with a Philips PW-1710 diffractometer.

Setting times were determined by the UNE 80102-88 standard method. The w/c ratio used was 0.32 for OPC plain samples and 0.34 for OPC + 50,000 ppm Cd samples, which is the w/c ratio experimentally calculated for a normal consistency paste.

Compressive and flexural strength were determined (UNE 80-101 standard method) at 2, 7 and 28 days in 10 × 10 × 60 mm samples with the same w/c ratio used in setting time evaluation specimens, previously cured at 100% r.h.

The hydration curves were produced using a JAF Isothermal Conduction Calorimeter operated at 25° C. Samples weighing 15g were mixed with 4.8 ml of distilled water or 5.1 ml of 50,000 ppm Cd solution outside the calorimeter and placed in the cells after approximately 5 mins.

Results and Discussion

Pore Solution Composition. Table 2 shows the results of pore fluid analysis for OPC pure samples and OPC samples mixed with a variable content of cadmium solution. Σz^+ and Σz^- are the calculated mass-charge balances of ions in solution. The overall charge balances are in good agreement; that means that all the species present in the pore solutions have been analysed.

TABLE 2

Pore Solution Analysis of Cement Samples

		mmol·L^{-1}					ppm	meq·L^{-1}		
Days	**pH**	**SO_4^{2-}**	**NO_3^-**	**K^+**	**Na^+**	**Ca^{2+}**	**Cd^{2+}**	**Σz^+**	**Σz^+**	**E(%)**
Control Samples										
1	13.5	4	2	540	63	1	0.10	605	544	11
7	13.5	5	0	567	76	2	0.06	647	527	3
29	13.7	5	1	528	68	1	0.11	598	594	1
97	13.6	6	0	571	72	1	0.07	645	566	13
Samples with mix water spiked with 5,000 ppm Cd^{2+} form nitrate salt										
7	13.5	3	10	589	84	2	0.09	676	658	3
29	13.7	4	12	543	71	1	0.09	616	605	2
97	13.6	5	49	553	74	1	0.09	629	525	18
Samples with mix water spiked with 15,000 ppm Cd^{2+} form nitrate salt										
1	13.5	3	129	578	64	1	0.09	643	610	5
8	13.6	2	116	540	72	1	0.09	615	646	5
Samples with mix water spiked with 30,000 ppm Cd^{2+} form nitrate salt										
1	13.5	3	306	690	76	1	0.09	767	738	4
8	13.6	3	236	650	84	1	0.09	736	772	5
Samples with mix water spiked with 50,000 ppm Cd^{2+} form nitrate salt										
1	13.3	1	521	717	85	5	0.09	811	761	6
7	13.4	2	302	596	45	2	0.13	644	702	9
30	13.8	4	419	802	101	1	0.08	904	928	13
97	13.4	3	599	754	94	1	0.08	850	953	11

The pore solutions extracted from OPC samples have high pH values, above 13.5 as it is well-known. Addition of cadmium nitrate decreases pore fluid pH for 50,000 ppm solution. The presence of NO_3^- ions in aqueous phases leads to an increase of mostly Na^+ and K^+ levels.

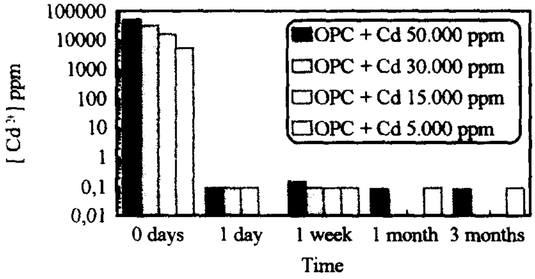

FIG. 1.
Evolution of Cd concentration in pore water.

The concentration of soluble cadmium in pore fluid of portland cement is about 0.1 ppm (as Cd^{2+}). If the Cd content of the cement is much enhanced by adding even 50,000 ppm in mixing solution, the Cd content of the resulting pore fluid remains below 0.1 ppm, suggesting that a solubility-limiting mechanism operates. The good immobilization of Cd in OPC matrices is enphasized in Fig. 1, in which, Cd content in the pore fluid is represented versus curing time.

The X-ray diffraction analysis of the solid phases revealed the presence of a compound similar to $Cd(OH)_2$ of poor crystallinity, with some calcium incorporation, probably a $CaCd(OH)_2$ type product.

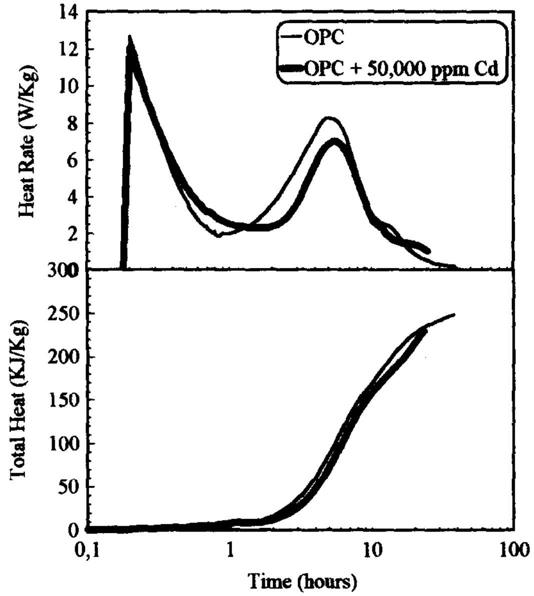

FIG. 2.
Isothermal hydration heat evolution curves.

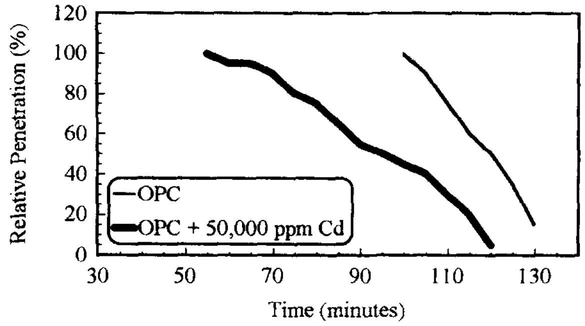

FIG. 3.
Relative penetration of the vicat needle during setting time test.

Effect of Cadmium on Cement Hydration and Physical Properties. The heat evolution curves for OPC and OPC + 50,000 ppm Cd are shown in Fig. 2. The hydration curve of OPC clearly illustrates the early, middle and late stages of cement hydration. The addition of cadmium affected the OPC hydration processes as it could be deduced from the shape of the curves obtained.

The heat evolution is enhanced during the first hour and the induction period is extended for the Cd spiked sample. This can be attributed to the $Cd(OH)_2$ precipitation that occur when the

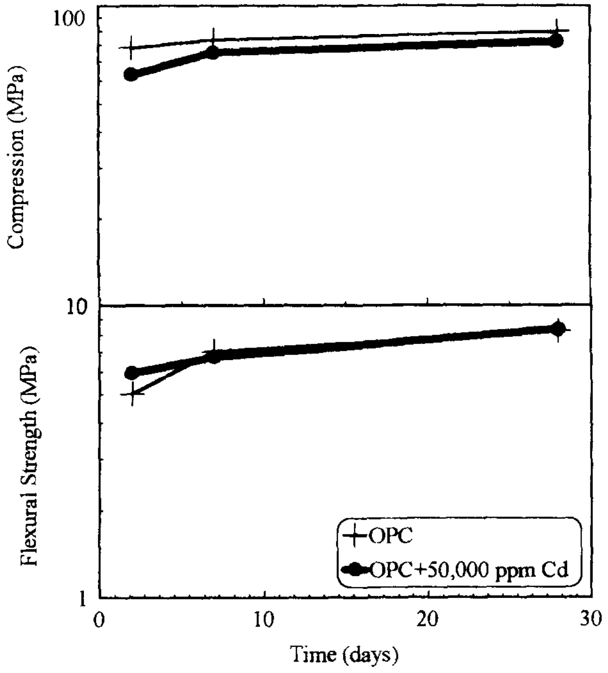

FIG. 4.
Mechanical resistances.

TABLE 3

Pore Solutions Analysis for Carbonated Cement Samples

Sample	time(days)	pH	[Cd](ppm)
OPC	30	13.19	0.09
OPC	97	7.22	0.03
OPC + 50,000 ppm Cd	30	12.95	0.11
OPC + 50,000 ppm Cd	97	7.58	0.09

cadmium nitrate solution is put in contact with cement, retarding the cement hydration reactions as other authors have previously discussed (6,7).

This modification of cement hydration caused by Cd presence has also implications in physical properties of cement. Thus, the data presented in Fig. 3 show that setting starts 35 min. before and finish 10 min. before in samples spiked with 50,000 ppm of Cd than that in the OPC plain ones.

The initial precipitation of $Cd(OH)_2$ induces a stiffening of the paste leading to a shortening of the initial setting time in sample containing Cd. The dilation of the induction period that takes place in presence of Cd causes an increase of plastic state time of the paste, but the final setting time is not altered.

The flexural and compressive strengths of OPC and OPC + 50,000 ppm Cd samples at 2,7 and 28 days are presented in Fig. 4. The results show that flexural strength is not significantly modified, and compression strength is only slightly decreased by Cd addition.

Effect of Cement Carbonation on Cd Immobilization. Table 3 summarizes the results of pore fluid analysis for OPC and OPC + 50,000 ppm Cd submitted to carbonation during 30 and about 90 days. At three months, carbonation of the pastes causes a decrease to neutral pH pore fluid in both control and Cd-spiked samples. The content of Cd in these samples is again below 0.1 ppm, thus it can be deduced that carbonation has no adverse effect on cadmium immobilization.

Conclusions

Portland cement gives good chemical immobilization for toxic wastes containing cadmium, when the Cd content of pore fluid is below 0.1 ppm even for a 50,000 ppm addition.

The presence of Cd has no negative influence on the physical properties of cement pastes when the final setting time and flexural and compressive strength are similar in both control and 50,000 ppm Cd containing pastes.

Degradation of the paste by carbonation does not interfere with the good immobilization of Cd in portland cement matrices.

Acknowledgments

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