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IMPACT OF CARBON DIOXIDE ON THE IMMOBILIZATION POTENTIAL OF CEMENTED WASTES: CHROMIUM

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ABSTRACT

Portland cement and blended cements containing blast furnace slag afford both physical and chemical immobilization of chromium. Chromium occurs in aqueous solutions in two oxidation states, Cr(III) and Cr(VI). Slag-containing cements are very effective at removing Cr(VI) from the internal pore fluid, probably by reducing Cr(VI) to less soluble Cr(III). Carbon dioxide attack, or carbonation, is probably the most common form of concrete environmental attack and it promotes changes to the cement chemical composition and physical properties that can affect the long-term retention of heavy metals. In the present paper the effect of carbonation on the immobilization of Cr(III) and Cr(VI) has been studied in both Portland cements and blended cements containing blast furnace slag. The results show that although Portland cements matrices are more resistant to carbonation than slag-containing cement matrices, the increase of chromium content in pore solution is more marked for Portland matrices. After 60 days the pore fluid of carbonated Portland cement spiked with 50000 ppm Cr(III) or Cr(VI) contains 20 or 40000 ppm respectively, whereas after carbonation of slag blends for the same time, the corresponding pore fluid Cr contents are 1 and 16000 ppm respectively. © *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 cement-based stabilization/solidification processes have been used and patented for conditioning a number of wastes before disposal (1). Plain Portland cement or Portland cements containing slag, pozzolans and/or other additives, afford chemical as well as physical immobilization potential for conditioning of hazardous heavy metals. However, evaluation of the retention of metals in Portland cement and fundamental studies of the chemical conditioning process have been preferentially carried out on freshly stabilized, solidified samples and less attention has been paid to the influence of cement deterioration due to environmental attack on metal immobilization matrices.

Carbonation is probably the most common form of concrete environmental attack. Carbonation promotes changes to the cement chemical composition and physical properties that can affect the long-term retention of heavy metals. Carbonation of cements results in a slightly increased strength and a reduced permeability (2) that would in principle be a desirable attribute for a matrix used to confine toxic wastes. However carbonation neutralizes the alkaline nature of the hydrated cement paste and thus chemical fixation of waste in cement-based materials, attributed to the solubility reduction of metals at high pH, can be vitiated. Recently, Bonen and Sarkar (3,4) have determined the adverse effects of attack of water containing carbon dioxide on the carbonation rate of pastes doped with cadmium, nickel, lead and mercury. These authors concluded that lead was best retained, but nickel and cadmium were mobilized; metal concentrations in the leachates approached several ppm and exceeded the 1.0 mg/L guideline for cadmium.

The effect of carbonation on the immobilization of chromium in two cement matrices are presented. Chromium occurs in aqueous solutions in two oxidation states, Cr(III) and Cr(VI). The later is more toxic and more difficult to fix into solids. Previously (5,6), we characterized the mechanism of immobilization of chromium in cement and demonstrated that S^{2-}, a constituent of slags, reduces Cr(VI) to Cr(III).

Experimental

Paste cylinders doped with chromium in the mix water were prepared with Portland cement (OPC) and Portland cement with granulated glassy blast furnace slag (BFS). These were subjected to accelerated carbonation in a pure CO_2 atmosphere at 100% R.H. The pastes had a water:solid ratio of 0.5 (weight).

TABLE I
Chemical Composition of Cement Binders

wt% Oxide Component	Ordinary Portland Cement (OPC)	Ground, Granulated Blast Furnace Slag (BFS)
CaO	64.03	43.21
SiO_2	19.82	34.90
Al_2O_3	4.89	13.84
Fe_2O_3	3.51	0.40[a]
MgO	2.58	7.93
SO_3	3.01	b
Na_2O	0.14	0.37
K_2O	0.28	0.21

[a] Probably present as FeO and Fe_2O_3.

[b] Contains about 1% S as sulphide (S^{2-})

Materials. The Portland cement used was very similar to an ASTM Type 1, and the slag is marketed commercially as a cement replacement material. It is an iron blast furnace slag with a high (>90%) glass content, water-granulated and ground. Table 1 lists the chemical analysis of these materials.

Control samples were prepared with distilled water; other cylinders were spiked with mix water containing 5000 or 50,000 ppm Cr(VI) as K_2CrO_4 or the same concentrations of Cr(III) using $Cr(NO_3)_3{\cdot}9H_2O$ as loadings typical of wastes.

Procedure. The paste cylinders (45 mm diameter, 80 mm high) were demolded at 24 hours and placed in a chamber at 100% R.H. through which wet CO_2 gas at ca 30l/hr was passed continuously throughout the experimental period. After 60 days the cylinders were submitted to pore water extraction.

Pore solution is the fluid that is contained within solid cement but is not combined into solid hydration products. It was extracted by using a high pressure compression device (7). In the extracted pore solution, typically 0.5-4 cm^3 for OPC and ~8 cm^3 for OPC + BFS, the pH was measured with a glass combined electrode and the chromium concentration determined. Total chromium was measured by atomic absorption; Cr(VI) was determined by a spectrophotometric method (8) based on the reaction of Cr(VI) with diphenylcarbazide in an acid medium to give a violet solution.

The solid pastes were examined by X-ray diffraction with a Philips PW 1710 powder diffractometer using monochromatized CuK radiation. Specimens for microstructural examination were embedded in an epoxy resin and polished with successively finer grades of diamond pastes down to 0.25µm. The flat, polished samples were coated with carbon and examined in a Cameca electron microprobe analyser with wavelength dispersive spectrometers.

TABLE II

Pore Fluid Analysis of Cements Specimens Carbonated for 60 days

Sample	carbonation front (mm)	pH	[Cr] total ppm	Cr(VI) ppm
OPC blank	<2	11.88	9.82	0.35
OPC + 5000 ppm Cr(III)	<2	10.60	6.06	3.41
OPC + 50,000 ppm Cr(III)	<2	11.72	18.94	12.59
OPC + 5000 ppm Cr(VI)	<2	13.16	547	415
OPC + 50,000 ppm Cr(VI)	<2	12.64	39,840	31,480
9:1 BFS/OPC blank	7	8.32	0.82	0.17
9:1 BFS/OPC + 5000 Cr(III)	T.C.[a]	6.83	0.13	0.17
9:1 BFS/OPC + 50,000 Cr(III)	T.C.	6.42	1.09	0.15
9:1 BFS/OPC + 5000 Cr(VI)	20	7.96	1.10	0.85
9:1 BFS/OPC + 50,000 Cr(VI)	4	11.20	15,944	12,080

T.C.[a] = Totally carbonated

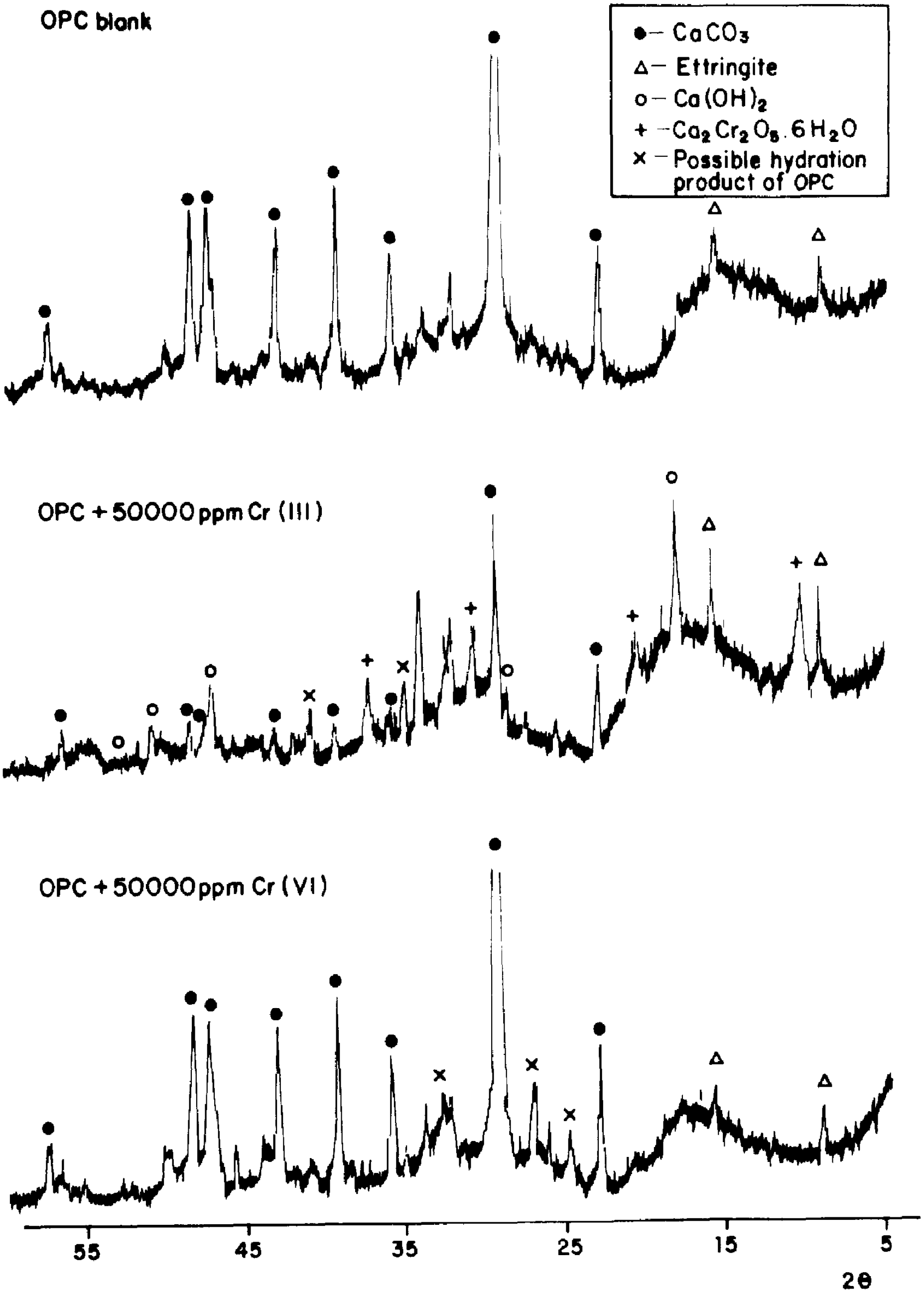

Fig. 1

X-ray diffraction spectra of cured OPC specimens carbonated for 60 days.

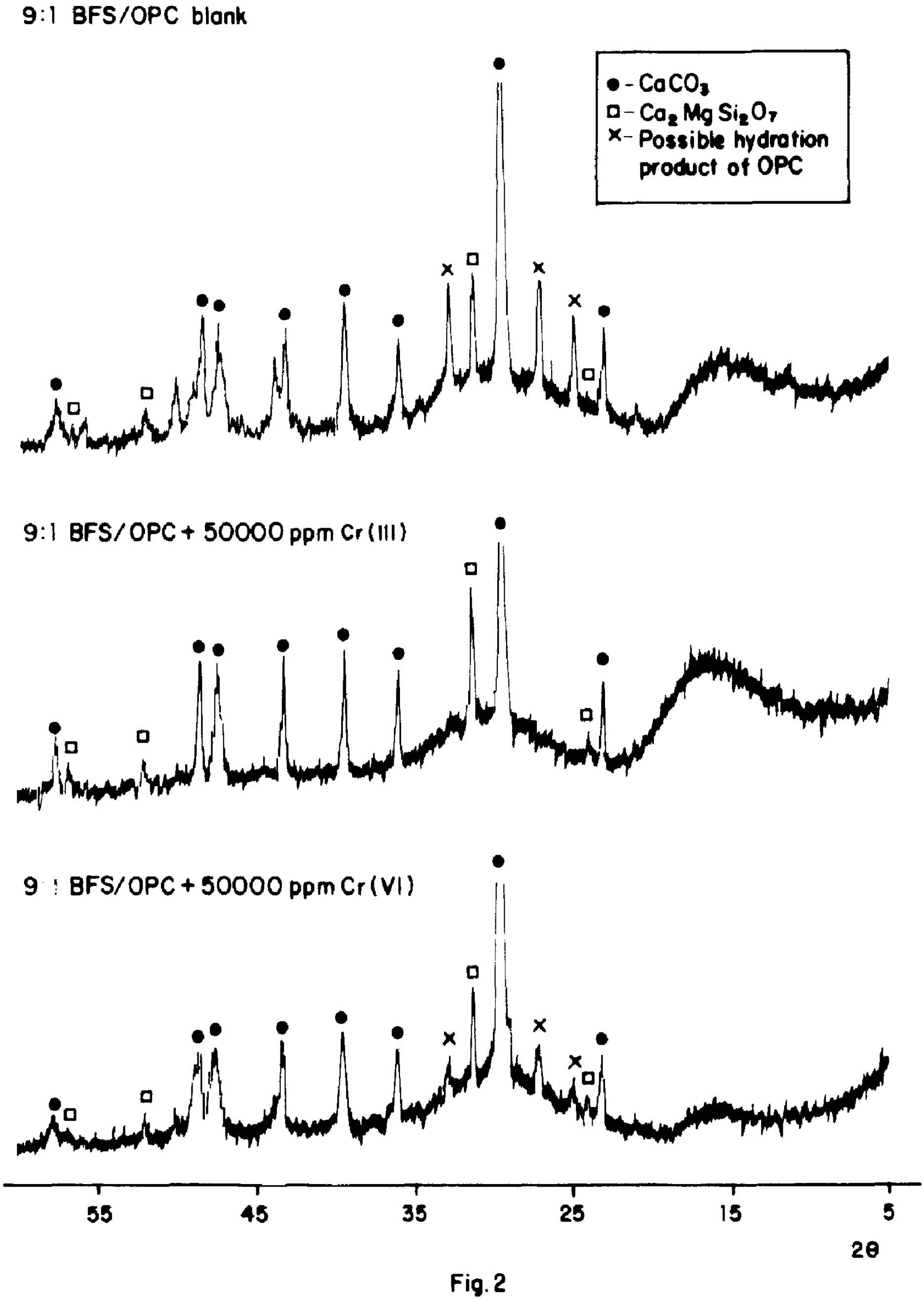

Fig. 2

X-ray diffraction spectra of cured 9:1 BFS/OPC specimens carbonated for 60 days.

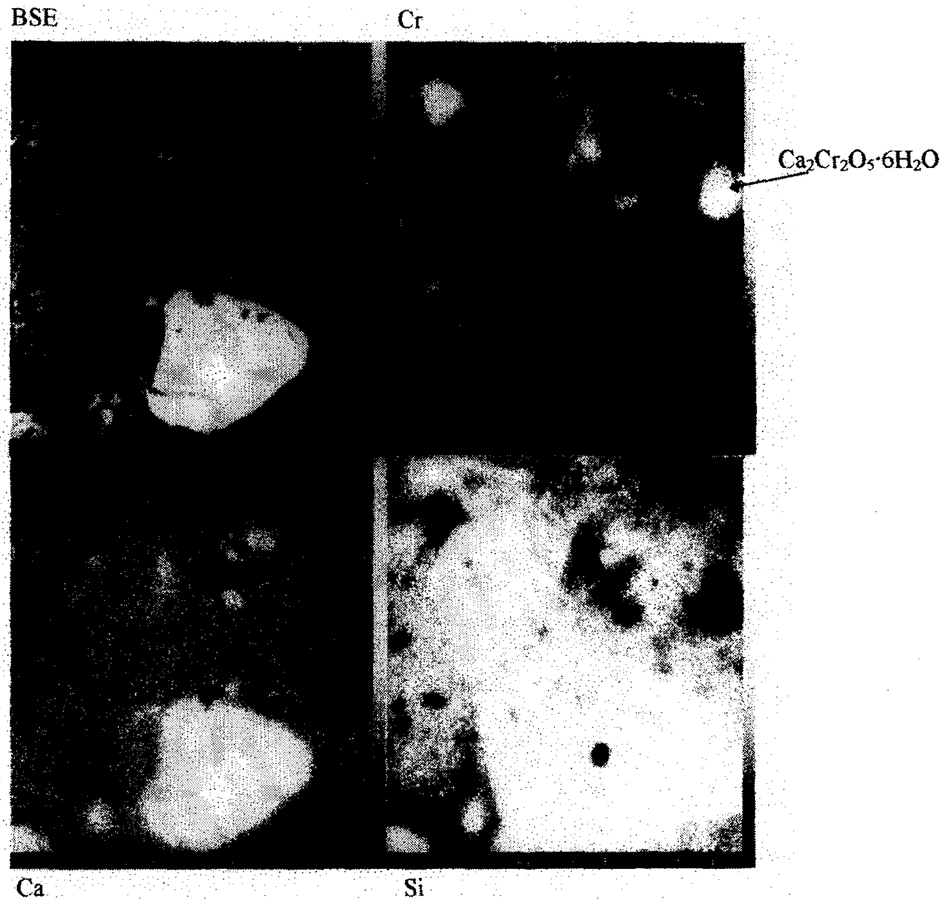

FIG.3.
EPMA images of OPC + 50,000 ppm Cr(III) sample after 60 days carbonation.

Results

Table 2 shows the results of pore fluid analyses of cement samples carbonated for about 60 days. This Table also shows the depth of carbonation measured by spraying a phenolphthalein solution on a fresh fracture surface before pore fluid extraction.

This test discloses that under these conditions 9:1 BFS/OPC mixes are more easily carbonated than plain OPC specimens, in which carbonation depth is less than 2 mm for both blank and spiked samples. The presence of chromium leads to a decrease or an increase in carbonation rate depending on the speciation of the metal. Thus, Cr(III) increases the carbonation rate whereas Cr(VI) decreases it. This behavior can be attributed to the different pH of the $Cr(NO_3)_3·9H_2O$ and K_2CrO_4 solutions: the first is acidic (pH< 3) while the second is slightly basic (pH> 8).

The pH of pore fluid correlates with the carbonation depth of the samples, varying from 13.16 for an OPC with Cr(VI) to 6.42 for 9:1 BFS/OPC containing Cr(III).

FIG. 4.
EPMA images of 9:1 BFS/OPC + 50,000 Cr(III) sample after 60 days carbonation.

The concentration of soluble chromium in the Portland cement pore fluid increases from zero chromium in the mix water to 9.82 ppm in the sample carbonated for 60 days, of which 0.35 ppm is present as Cr(VI).

When the chromium content of the cement paste is enhanced to 5000 ppm by spiking with Cr(III), the Cr content of the pore fluid decreases to 6.06 ppm for the same carbonation period and is only increased to 18.94 ppm when 50,000 ppm Cr was added. This chromium content is present mostly as Cr(VI). When the same quantities of Cr are added as Cr(VI), soluble chromium remains high, up to ~500 ppm and ~40,000 ppm for the two spiking levels tested: the chromium again persists as Cr(VI).

BFS/OPC matrices, carbonated to neutral pH pore fluid, show much lower chromium contents in both sets of samples, blank and Cr-spiked samples with Cr in both (III) and (VI) states. For example for the Cr(III) sample spiked with 50,000 ppm, the chromium content in pore fluid decreased to 1 ppm; for 5000 ppm Cr(VI), it had fallen to about 1 ppm in the BFS-containing sample. This contrasts with OPC spiked with 5000 ppm Cr(VI) where pore fluid Cr remains at ~500 ppm. The sample spiked with 50,000 ppm Cr(VI) show only slightly decreased levels. This shows that BFS/OPC blends have only a limited capacity to immobilize Cr(VI) by a reductive process.

Figures 1 and 2 shows the X-ray diffraction spectra of OPC blank, BSF/OPC blank and chromium spiked samples. $CaCO_3$ can be detected in all samples. OPC samples also show the presence of ettringite and BFS/OPC samples the presence of a melilite type phase, $Ca_2MgSi_2O_7$, which is also present in unhydrated BFS. Other reflections, probably from an hydration product of OPC or of OPC in BFS/OPC blends were found (product x, not identified). All BFS samples give rise to an asymmetric, diffuse band extending from about 20° to about 37° and centered at about 30° 2: this glassy scatter is attributed to unreacted slag.

In the BFS/OPC samples spiked with Cr(III) or Cr(VI) it is not possible to find crystalline phases other than those already present in hydrated blank samples. However, in the OPC sample spiked with 50,000 ppm Cr(III) the reflections of $Ca_2Cr_2O_5 \cdot 6H_2O$ are readily distinguished. This compound was previously synthesized (5) as a reaction product of $Ca(OH)_2$ with chromium (III) nitrate at 25°C. This X-ray diffractogram arises from a zone not yet totally carbonated, as the presence of $Ca(OH)_2$ corroborates. This detection is noteworthy as it validates the mechanism of fixation for chromium which was previously deduced from pure phases.

Figure 3 shows EPMA images of OPC + 50,000 ppm Cr(III) sample after 60 days carbonation. The EPMA analysis shows a generally interstitial distribution for chromium: it is not found in inner C-S-H product which is very dense. Some small particles with Ca signals approximately equal to Cr occur which could correspond to $Ca_2Cr_2O_5 \cdot 6H_2O$, detected by X-ray, or its solid solution with the corresponding aluminate.

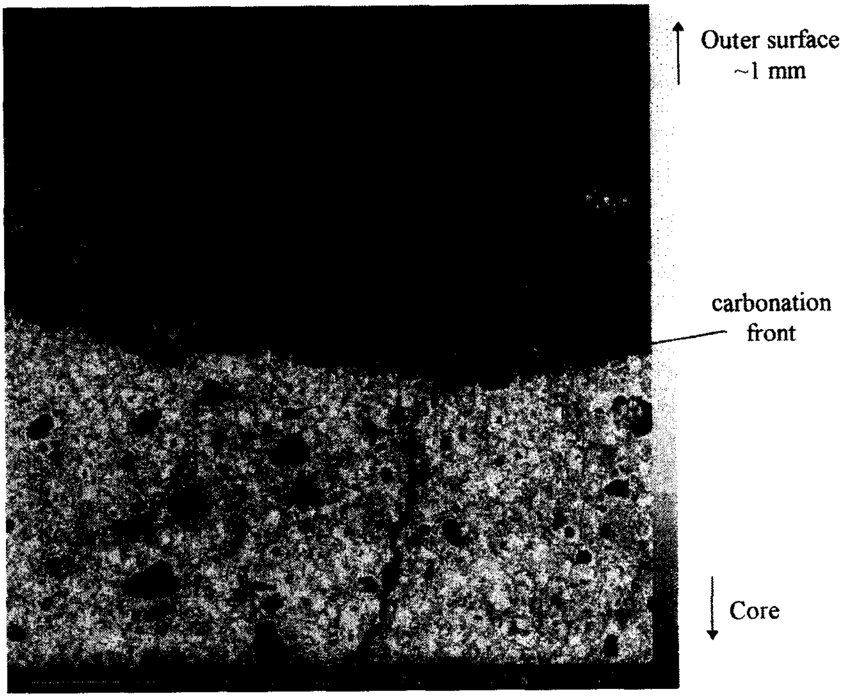

Fig. 5.
EPMA map of Cr in an OPC + 50,000 ppm Cr(VI)paste, cured and then carbonated 60 days.

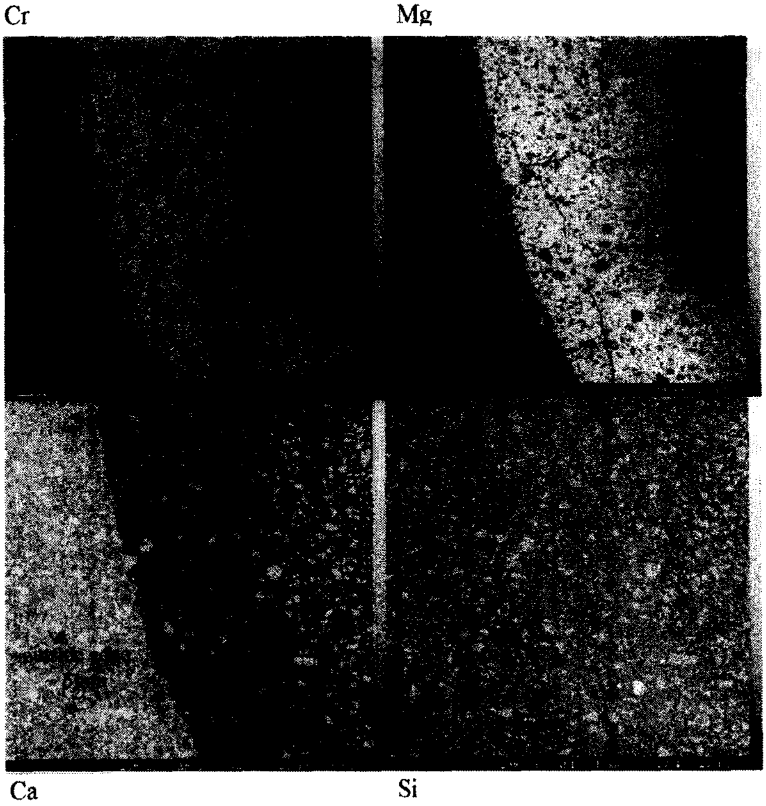

FIG. 6.
EPMA images of 9:1 BFS/OPC + 50,000 ppm Cr(VI) paste cured and carbonated for 60 days.

Chromium is preferentially distributed in the sample BFS/OPC + 50,000 ppm Cr(III) where it concentrates around former slag particles, the position of which is marked by relicts of $Ca_2MgSi_2O_7$: Figure 4. The nature of the Cr-rich precipitate is not known. Cr(VI) spiked samples show strong zoning associated with carbonation, as can be seen in Figures 5 and 6, showing respectively OPC + 50,000 ppm Cr(VI) and BSF/OPC 50,000 ppm Cr(VI) and carbonated for 60 days. The outer totally carbonated zone of the sample has a low chromium content; chromium, together with Mg and Si from hydrated slag, tend to migrate and become concentrated in the adjacent, uncarbonated alkaline zone. This migration also seems to affect the carbonation rate,which is decelerated.

Discussion

In a previous paper (5) the ability of Portland cement matrices to immobilize Cr-containing wastes was shown to depend on the oxidation state of the chromium. Cr(III) is most effectively incorporated into the solid phases, leaving low levels of Cr in the pore fluid of cements. Cr(VI) is less readily incorporated into cement hydrate phases, hence pore fluid from Cr(VI)-spiked cements contain relatively high levels of Cr. Slag blended cements have the

TABLE III
Pore Fluid Analysis of Uncarbonated Cement Samples (after ref. 5)

Sample	age (d)	pH	[Cr]total ppm	Cr(VI) ppm
OPC blank	34	13.6	0.24	-
OPC blank	250	-	2.2	2.1
OPC + 5000 ppm Cr(III)	41	13.5	0.24	-
OPC + 5000 ppm Cr(III)	250	-	0.4	0.35
OPC + 39,000 ppm Cr(III)	28	-	0.4	0.1
OPC + 5000 ppm Cr(VI)	250	-	71	70
9:1 BFS/OPC blank	24	13.1	<0.1	-
9:1 BFS/OPC + 5000 ppm Cr(III)	29	12.9	<0.1	-
9:1 BFS/OPC + 5000 ppm Cr(VI)	250	-	<0.01	-

ability to reduce Cr(VI) to Cr(III) which subsequently becomes incorporated into the cement hydrates. Consequently, the concentration of Cr in the pore fluid of slag blended cements, irrespective of its original speciation, is very low.

Table 3, from (5), gives a resume of chromium pore fluid contents of uncarbonated cements complimentary to those carbonated in the present paper. It can be deduced that even a slight carbonation of OPC leads to an increases of chromium level (three times higher) in the pore fluid. The same behavior takes place in the spiked chromium samples, in which chromium pore fluid levels go well above 1 ppm. However for BFS/OPC matrices the increase accompanying carbonation is less marked: about 1 ppm. Only the sample spiked with 50,000 ppm Cr(VI) gives high levels of chromium.

According to these results, BFS/OPC blends are the more suitable matrices for chromium-containing waste, being capable of maintaining chromium pore fluid contents below 1 ppm even in a completely carbonated state. Reasons for this are not yet known. Slags, by virtue of their slow hydration, continue to release S^{2-} ions which inhibit any tendency of chromium to oxidise to the VI speciation. It is known that in normal carbonation the calcium aluminate hydrates convert to carboaluminates, presumably by exchange of CO_3^{2-} for OH. At still higher carbonate activity, the carboaluminates convert to $CaCO_3$. However, nothing is known about the stability and resistance to carbonation of the Cr-substituted analogues or of intermediate (Al, Cr) solid solutions.

The development of a zonal structure, with separate Cr-rich and Cr poor zones, with overall depletion of Cr from the near-surface layers of carbonated but unleached samples, is a noteworthy feature which requires further study.

Conclusions

1. When carbonated, conditions BSF/OPC blends offer better performance than OPC in immobilizing chromium containing wastes.
2. Solubility-limiting phases predicted by laboratory phase studies, have been found to occur in cement matrices.

3. **Cr(VI) zoning related to carbonation has been observed. This affects carbonation rates and will have implications for the modeling of chromium leaching from matrices.**

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References

1. Conner, J.R. *Chemical Fixation Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York. (1990).
2. P.J. Dewaele, E.J. Reardon and R. Dayal, *Permeability and porosity changes associated with cement grout carbonation.* Cem. & Conc. Res. Vol. 21, pp.441-454, 1991.
3. Bonen and S.L. Sarkar. *The present state-of-the-art of immobilization of hazardous heavy metals in cement-based materials.* Advances in Cement and Concrete. Eds. M.W. Grutzeck and S. L. Sarkar. New York,1994.
4. D. Bonen and S.L. Sarkar. *The effects of simulated environmental attack on immobilization of heavy metals doped in cement-based materials.* Journal of Hazardous Materials, Vol. 40, pp. 321-335,1995.
5. Kindness, A. Macias and F.P. Glasser. *Immobilization of chromium in cement matrices.* Waste Management, Vol.14, No.1, pp.3-11,1994.
6. A. Macias, A. Kindness and F.P. Glasser. *Estabilización y solidificación de compuestos de cromo en matrices de cemento.* Solid and Liquid Wastes: Their Best Destination (II). Tenerife. December 1994.
7. S. Barneyback, Jr. and S. Diamond. *Expression and analysis of pore fluids from hardened cement pastes and mortars.* Cem. &. Concr. Res., Vol. 11, pp.279-285, 1981.
8. Z. Marczenko. *Separation and Spectrophotometric Determination of Elements.* Ellis Horwood, Chichester, England. 1986.