

An FTIR, SEM and EDS investigation of solidification/stabilization of chromium using portland cement Type V and Type IP

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Abstract

The characterization of chromium-doped ordinary portland cement (Cr-OPC) before and after leaching has been carried out using Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM). Evidence is presented from FTIR results for the mutual interaction between the dopant chromium and the calcium silicate hydrates (C-S-H). Atmospheric carbon dioxide, as well as the dopant chromium, were found to have significant effects on the chemical state of the silicates. Morphological information obtained from SEM analyses indicates that the solidified Cr-OPC mass retains most of its physical integrity even after exposure to the leaching solution. Examination of the bulk of the Cr-OPC matrix reveals that chromium is dispersed in the bulk rather than on the surface of OPC grains. Possible mechanisms of solidification/stabilization of chromium in cement-based systems are discussed.

Introduction

Cement-based solidification/stabilization (S/S) processes using ordinary portland cement (OPC), pozzolanic substances and fly ash have been used as a potentially viable technology for safe disposal of industrial wastes [1-5], as well as for treating residues from other technologies. Cement-based materials have also been used in the immobilization of nuclear wastes [6]. There is, however, a considerable disagreement about the mechanism of such S/S processes, and in many cases the physical and chemical changes that take place when S/S substances are combined with wastes are yet to be delineated. The hydration of OPC involves a series of complex dynamic chemical reactions; the two most important chemicals produced from the hydration of tricalcium sil-

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icate (C_3S) and β -dicalcium silicate are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). The poorly crystalline C-S-H is produced on the surface of the hydrating cement grains. Both C-S-H and CH may undergo further reactions with atmospheric carbon dioxide during setting and hardening of the cement paste. However, hydration of cement particles and formation of C-S-H has been reported to be retarded in the presence of certain heavy metal wastes [7-14]. The mutual interaction of metal wastes and the cement are now being actively studied to establish a detailed mechanism of the S/S process. It may be envisaged that this type of interaction may involve exchange processes on the surface of cement particles with the release of H^+ ions or other cations and subsequent adsorption and/or complexation of M^+ ions on the high surface area of C-S-H (typical surface area of C-S-H is 10-100 m^2/g when measured by N_2 adsorption as compared with 20-50 m^2/g for cement clinkers [15]). These processes must also be dependent on the pH, redox status of the medium and chemical characteristics of the surface.

In our continuing efforts [16-26] to gain understanding of the microchemical mechanisms of S/S of hazardous metal pollutants using OPC, we now present some FTIR, SEM and EDS results on the leaching effects on chromium-doped OPC and the effect of carbonation during setting and hardening.

Experimental

Ordinary portland cement Type V and Type IP used in this investigation are sulfate-resisting cements received from Texas Industries, Inc. Type IP is blended with 20% by weight of fly ash. A 10% (w/w) chromium solution was prepared from chromium nitrate in deionized water and slowly added to the cement while mixing thoroughly. A water-to-cement ratio of 0.40 was maintained. The samples were then stored in air at room temperature under laboratory atmospheric conditions for a period of at least twenty-eight days before analyses. Some selected samples were also stored in an argon-rich atmosphere to see the effect of carbonation on the hydration of Cr-doped cement. The leaching tests using acetic acid and sodium acetate buffer (pH 4.85) were carried out for two hours only to investigate the leaching characteristics and leaching effects on the solidified system.

The FTIR spectra were recorded by an IBM Model FTIR 44 instrument using potassium bromide pellets prepared by a constant sample-to-KBr ratio (1.0 mg sample/100 mg of KBr) and total weight (50.0 mg). Usually, 32 scans were recorded. Some measurements were also carried out by Nicolet FTIR 500 instrument. The FTIR absorption spectra were recorded over the range 400-4000 cm^{-1} with 2 cm^{-1} resolution.

The SEM and EDS analyses were carried out on a JEOL-6400 scanning electron microscope (SEM) equipped with a Tracor-Northern Series 2 EDS system with a germanium detector and diamond window. Prior to analysis,

both leached and unleached samples were dry-cut using an Isomet low speed saw with a diamond studded blade. The sample slices were mounted using double-sided tape. Energy dispersive X-ray spectra were taken separately on the unleached and leached layers.

Results

FTIR has been found to be a powerful tool [16,20,25,27] in examining the vibrational aspects of hydrating/hydrated cement and provides insight into the structure of the solidified matrix. Morphological and compositional information have been obtained from SEM and EDS analyses.

FTIR spectroscopy

Typical FTIR spectra for the dry clinkers of OPC Type V and hydrated OPC are presented in Figs. 1(a) and 1(b), respectively. Since no discernible differences were observed in the FTIR spectra of the chromium doped Type IP cement as compared to the Type V, we shall present only the results of Type V and concentrate subsequent discussion on this system, although it will apply as well for Type IP.

The major vibrational bands identified from the dry clinkers (Fig. 1a) are: ν_3 SiO_4^{4-} , (asymmetric Si-O stretching), ν_4 SiO_4^{4-} , (out-of-plane Si-O bending), and ν_2 , SiO_4^{4-} (in-plane Si-O bending) centered at around 935, 525 and 458 cm^{-1} , respectively. Possible substitution of the Si by Cr would be expected to affect these stretching and bending modes differently. The triplet bands appearing at 1101–1157 cm^{-1} are due to the ν_3 modes of SO_4^{2-} and the weak bands at 658 and 598 cm^{-1} are due to ν_4 modes of SO_4^{2-} . The broad band near 3435 cm^{-1} is due to symmetric stretching water (ν_1) and the one at 1638 cm^{-1} is assigned to ν_2 deforming bending mode of water. The sharp band appearing at 3640 cm^{-1} is due to asymmetric stretching vibration of OH-groups. The band assignments are in good agreement with those reported by others [28,29].

When dry clinkers are hydrated and cured in air (Fig. 1b), two intense, but poorly resolved bands appear at 1435–1430 cm^{-1} due to ν_3 CO_3^{2-} and a sharp band appears at 875 cm^{-1} corresponding to ν_2 CO_3^{2-} . The ν_3 SiO_4^{4-} peak appearing at 935 cm^{-1} in the dry clinkers is shifted to the higher energy field centered between 1087–1032 cm^{-1} and obscures the sulfate bands. The decrease in intensities of the SiO_4^{4-} bands between 450–510 cm^{-1} and the shifting of ν_3 of SiO_4^{4-} to the higher energy field is indicative of polymerization of the orthosilicate units, SiO_4^{4-} , present in cement matrix and is attributed to the formation of C-S-H [30]. Close examination of the spectrum of argon-cured hydrated OPC (Fig. 1c) reveals that the ν_3 of SiO_4^{4-} peak has been shifted to the higher energy field by only 40 (cm^{-1}) wavenumbers as compared to 150 (cm^{-1}) wavenumber units in air-cured samples. Also the relative intensities of ν_4 and ν_2 of SiO_4^{4-} vibrations in argon-cured samples have remained mostly

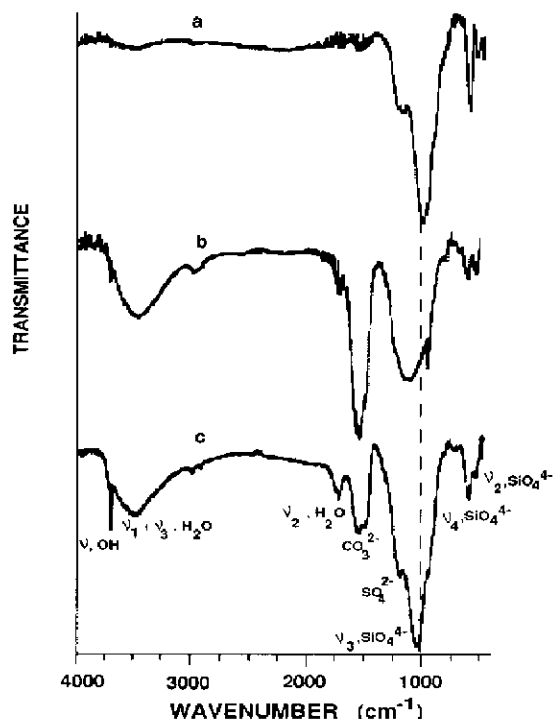


Fig. 1. FTIR spectra of (a) dry clinkers, (b) OPC paste cured in air and (c) OPC paste cured in argon.

unchanged, which is indicative of a lower degree of polymerization in the argon-cured sample. As can be seen, the sulfate region has not been obscured (Fig. 1c) due to the lower degree of polymerization.

The prominence of the OH-band (Fig. 1c) in an argon-cured sample over that in an air-cured sample (Fig. 1b) provides evidence for the reaction of CO_2 with CH. Thus, it appears that both C-S-H and CH are competing for atmospheric CO_2 .

Effect of chromium doping

Additional peaks in the FTIR spectrum shown in Fig. 2 of the chromium-doped portland cement (Cr-OPC) at 1387 cm^{-1} (s, s) and 1353 cm^{-1} (sh, w) are due to $\nu_3\text{ NO}_3^-$ and $\nu_1\text{ NO}_3^-$ vibrational bands.

The appearance of poorly resolved bands at around $1048\text{--}1001\text{ cm}^{-1}$ and the overlapping of ν_4 and $\nu_2\text{ SiO}_4^{4-}$ bands invokes the possibility that either Cr^{3+} ions have been incorporated with the C-S-H or the polymerization of the silicates have been affected by the reactions and/or adsorption of chromium on the components of OPC. The possibility of Cr(III) substituting for Si(IV) must be considered.

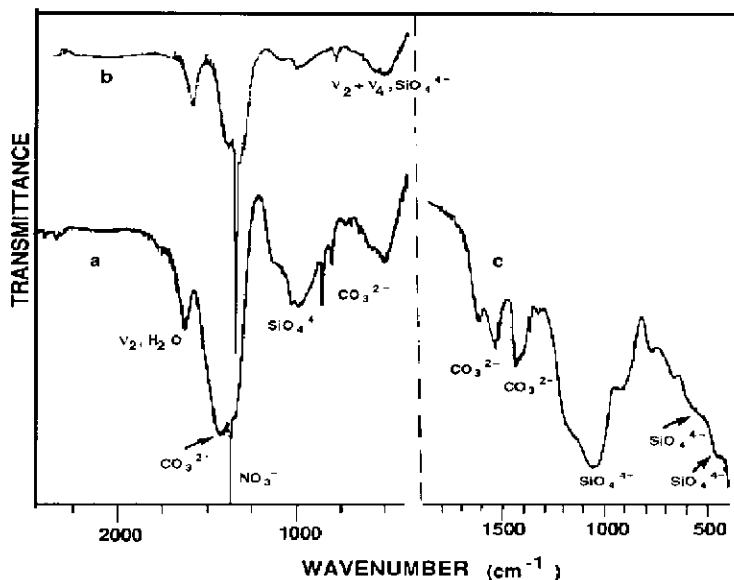


Fig. 2. FTIR spectra of: (a) Cr-OPC, air cured; (b) Cr-OPC, argon cured; and (c) Cr-OPC, leached.

Effect of leaching

The FTIR spectra of the leached Cr-OPC sample (recorded by Nicolet FTIR 500) is shown in Fig. 2(c). The reduced intensities of the two carbonate bands centered at 1560 and 1455 cm^{-1} are attributed to the dissolution of carbonates in acidic leaching solution. A strong and broad band due to $\nu_3\text{ SiO}_4^{4-}$ appears at 1060 cm^{-1} and the bands due to ν_2 and ν_4 vibrations appearing between 525 – 450 cm^{-1} have also been resolved. Close examination of the silicate bands between the unleached (Fig. 2a) and leached (Fig. 2c) Cr-OPC samples reveals some critical differences caused by the leaching procedure. The SiO_4^{4-} band in the silica phase has now been shifted up by about 110 wavenumber units in the leached sample and the relative intensities of the ν_2 and ν_4 vibrations have also been significantly reduced in relative intensity. It can, therefore, be concluded that C-S-H has been attacked by the acidic solution and that the silicate groups undergo an enhanced degree of polymerization.

Scanning electron microscopy

The morphology of the unleached, leached and leached-unleached front of the Cr-doped is distinctly visible (Fig. 3). The unleached sample (Fig. 3a) seems to possess a compact structure with very little cracks and holes, and some flakey substances can be seen scattered all over the matrix. The leached sample (Fig. 3b) shows sharp contrast with the unleached sample. The solidified cement has been transformed into an amorphous structure with cavities, holes and cracks due to exposure to the acidic leaching solution. The cavities are filled with loosely bound flakey materials of varying particle sizes. The

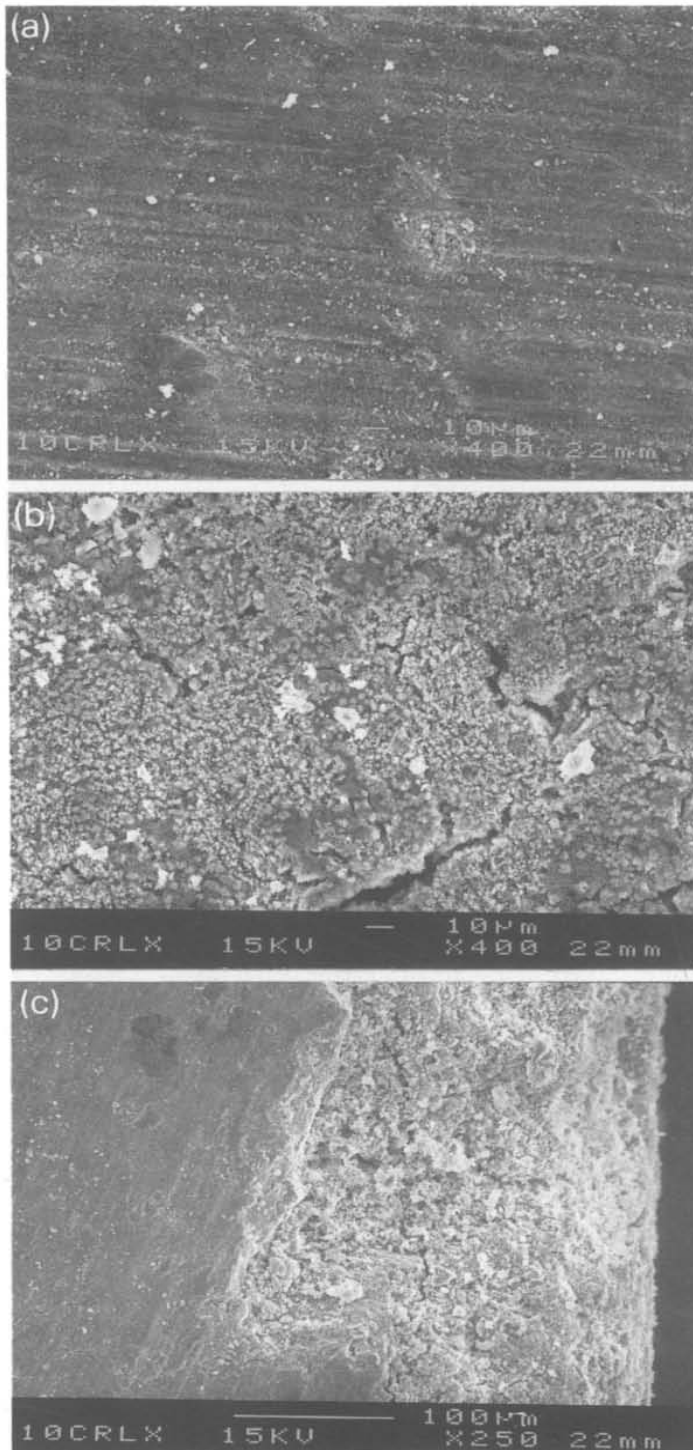


Fig. 3. SEM micrographs of chromium doped portland cement: (a) unleached, (b) leached and (c) leached-unleached fronts.

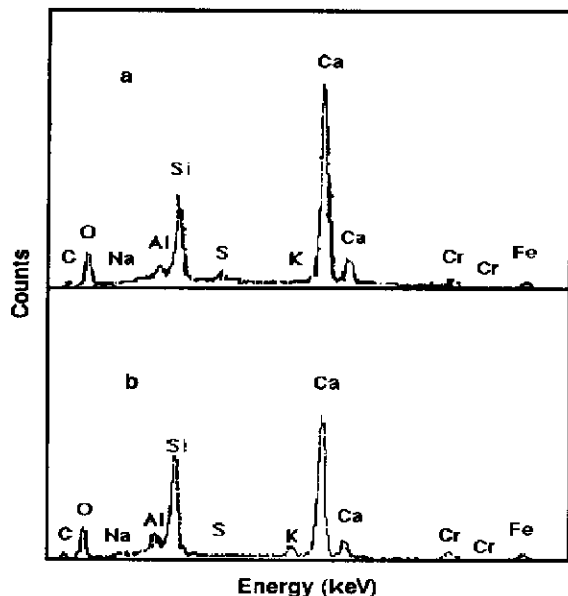


Fig. 4. EDS spectra of chromium-doped portland cement: (a) unleached sample and (b) leached sample.

characteristic morphologies of the leached and unleached phases (Fig. 3c) are quite clear. It is apparent that the unleached phase has similar morphology as the unleached sample (Fig. 3a), while in the leached phase, the flakey materials are loosely held together in small networks.

Energy dispersive X-ray spectroscopy

The leached and unleached samples were analyzed by the EDS technique (Fig. 4) for qualitative and semi-quantitative information concerning the leaching effects. The elements identified in both the unleached and leached samples are: carbon, oxygen, sodium (trace), aluminium, silicon, calcium, chromium and iron (trace). Potassium was found in the leached sample only, while sulfur was detected in the unleached sample but not in the leached sample. The sulfur is effectively removed by leaching.

It is interesting to note that the concentrations of chromium (Fig. 4a,b) in both the samples appear to be unchanged indicating that the leaching process did not have any significant effect on the chromium present in the bulk of the solidified matrix. Since EDS is not purely a surface sensitive technique [19] and has a penetration greater than $1\ \mu\text{m}$, this combined with the XPS evidence showing little surface chromium indicates that chromium is dispersed in the bulk of the medium. This is further supported by Cocke and co-workers [18], who showed using X-ray photoelectron spectroscopy (XPS) that in the unleached sample chromium is present mainly in the bulk of the medium, and a very low concentration of chromium was observed on the surface of Cr-doped

cement. Since calcium and silicon are the major components of cement, the compositions of Ca and Si in the unleached and leached samples can be calculated based on the normalization of Ca and Si peak areas only. The average compositions of Ca and Si in the unleached and leached samples are 69.0, 31.0 and 58.0, 42.0%, respectively. The Ca/Si ratio is slightly lower (1.4 vs. 2.3) in the leached sample as compared with the unleached sample, indicating Ca removal. The presence of potassium in the leached sample is attributed to an ion-exchange mechanism previously reported [19] by us. In addition, there appeared to be some enhancement of aluminum in the leached sample, which may also be due to density reduction, redistribution of the Al or to the ion-exchange mechanism as proposed for potassium.

Discussion

The silicate regions hold much of the information about the mutual interactions of the dopant metals and the silicate moiety present in OPC. The effect of carbonation on the polymerization of the orthosilicate units present in OPC and the influence of metal pollutants thereon is an important area of research and has broad implications on the S/S systems. We shall, therefore, concentrate our discussion on these two aspects only. In a previous report [25] we have discussed the mutual interactions of metal dopants and water.

However, the solidification/stabilization of chromium will be greatly influenced by the aqueous chemistry of Cr^{3+} ions. The Cr^{3+} ion in aqueous medium is likely to be present as hydrated ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. The hexaquo ion is highly acidic ($\text{p}K_a$ 4) and may undergo deprotonation leading to the formation of hydroxy-bridged polymeric species of high molecular weight [31]. In an intermediate alkaline medium $\text{Cr}(\text{OH})_3$ may also be formed, which dissolves at high pH to form $[\text{Cr}(\text{OH})_6]^{3-}$ and $[\text{Cr}(\text{OH})_4]^-$ ionic species. Above pH 8 the CrO_4^{2-} ions may also exist in appreciable concentration [31]. These anions are unlikely to be adsorbed by the silicate surfaces, since cement paste is highly alkaline (pH 11 to 13) and is expected to have negative surface charges. It remains a mystery as to the mechanism of Cr incorporation into the C-S-H.

The FTIR results indicate some association of chromium with C-S-H, although it is rather difficult to predict the actual nature of chemical association from the present results alone. The degree of hydration in OPC will affect the intensities of the bending modes, ν_2 and ν_4 , and it is generally expected that the intensities of these vibrations will decrease with increased polymerization. If one closely examines the FTIR spectra of OPC (Fig. 1b), Cr-OPC (Fig. 2a) and Cr-OPC leached samples (Fig. 2c), it can be clearly seen that the two bending bands centered between 450–525 cm^{-1} in OPC, appear as a single peak centered at 520 cm^{-1} in Cr-OPC (Fig. 2a). The major band, ν_3 , shows some definite structure with two closely spaced peaks between 1000–1050 cm^{-1} in Cr-OPC. The overlapping of ν_2 and ν_4 bands of SiO_4^{4-} due to the addition of

chromium has not been observed for zinc, lead, cadmium or mercury doped samples. These changes may be due to the chromium ions being substituted for the silicon in the C-S-H. One could expect that the bending modes would be affected more than the stretching modes due to this substitution. Further work is required to confirm this on model samples with controlled substitution experiments. Similar chemical reactions of some heavy metals with synthetic hydrous calcium silicates, such as tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16} \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$), xonotline ($\text{Ca}_6\text{Si}_6\text{O}_{17} \cdot (\text{OH})_2$) and wollastonite ($\text{CaO} \cdot \text{SiO}_2$) have been reported by Komarneni et al. [32], but in most cases the cations are seen to substitute for Ca ions rather than silicon. The actual chemical speciation of Cr(III) in cement remains to be determined.

The leaching process seems to have reversed the situation, with ν_3 of SiO_4^{4-} now showing as an intense and broad peak centered at around 1060 cm^{-1} , and the ν_2 and ν_4 bands of SiO_4^{4-} have again been resolved. The ν_2 band is now centered at 460 cm^{-1} , while the ν_4 is barely visible as a shoulder. These vibrational changes are indicative of increased polymerization.

We have earlier reported [18], via EDS examination of unleached Cr-OPC systems, that chromium is dispersed in the bulk of the cement matrix. Examination of the unleached Cr-OPC sample by XPS confirmed [18] that chromium is present on the surface as Cr^{3+} oxidation state and the binding energy was found to be consistent with carbonate, silicate and hydroxides only and not of oxides. Results of EDS in the present studies also confirm that chromium is dispersed into the bulk of the OPC matrix. The leaching process did not significantly change either the Si or Cr, thus indicating that very little doped chromium has been dissolved into the solution due to leaching. Calcium and sulfur were leached significantly.

We have also reported [26] that the compact structures in Pb-OPC and Zn-OPC systems are completely destroyed due to leaching and the Ca/Si ratios are significantly reduced from 2.40 to 1.02 in the case of Pb-OPC and from 4.20 to 0.19 in the case of Zn-OPC systems due to leaching. In the present case the Cr-OPC mass retains most of its physical integrity even after exposure to the leaching solution and the Ca/Si ratio is only reduced from 2.30 to 1.40.

Conclusions

Dispersion of chromium below the surface of the OPC matrix and chemical interaction with C-S-H is revealed by EDS and FTIR examinations of the Cr-OPC systems. SEM micrographs clearly demonstrate that, unlike Pb-OPC and Zn-OPC, the Cr-OPC systems retain much of their mechanical strength after contact with a leaching solution. The results indicate that FTIR can be effectively used as a powerful tool in delineating the complexities of chemical reactions in dopant metal–cement systems.

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