

# Chemical Speciation of Trace Zinc in Ordinary Portland Cement Using X-ray Absorption Fine Structure Analysis

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**Chemical change of trace zinc in ordinary portland cement (205.1 ppm) was investigated in hydration process using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Intensities of the peaks appearing at the same energy of ZnO in XANES spectra were decreased with cement hydration. The interatomic distances and the coordination numbers of the first and the second shells calculated from EXAFS spectra indicated that ZnO hydrolyzed to zincate ion  $[\text{Zn}(\text{OH})_4]^{2-}$  with cement hydration keeping their fundamental structure of  $\text{ZnO}_4$  tetrahedra.**

## I. Introduction

SPECIATION of toxic heavy metals in the environment using new analytical methodologies has attracted much attention in recent years, because comprehension of chemical forms of the toxic heavy metals in the environment is essential for assessing potential hazards.<sup>1</sup> The mobility, bioavailability, and treatability of the heavy metals are affected by the solubilities of the solid-phase and aqueous-phase metal species, and the toxicity is strongly dependent on their chemical forms.<sup>2</sup> Many researchers have reported on zinc speciation in environmental samples such as natural water, sediments, humic substances in soils using extended X-ray absorption fine structure (EXAFS),<sup>3–7</sup> and the reactions between zinc and calcium silicate hydrate (C–S–H) have been studied intensively.<sup>8,9</sup> Cement has been widely used to stabilize and solidify waste materials containing the heavy metals, and the long-term leachability of the cement-stabilized wastes is the important factor associated with landfilling. Ziegler *et al.* used X-ray absorption fine structure (XAFS) spectroscopy to elucidate the binding mechanism of Zn(II) to C–S–H and confirmed the presence of Si–O–Zn bonds.<sup>10</sup> Most of the early reports on cement, however, focused on the stabilization of the waste materials with cement and investigated the speciation of the heavy metals at rather high concentrations (ca. 0.2–3 wt%).

On the other hand, the existence of the heavy metals in cement has become an environmental problem. For example, elution of hexavalent chromium from cementitious soil stabilizer tends to exceed the environmental criteria of soil occasionally. Chromium is probably derived from raw materials such as iron slag and the refractory brick. Other toxic heavy metals are also derived from raw materials and assumed to be incorporated in cement clinker minerals as solid solution, because they are burned over 1400°C, at which chemical reactions through molten phases occur. This is

unlike the case with the cement-stabilized wastes with regard to the concentration and the chemical state. In recent years, techniques to manufacture cements from the incineration ash of urban refuse and sewage sludge have been developed.<sup>11</sup> Much attention should be paid in using such waste materials because trace heavy metals incorporated in cement may bring about a hazardous risk. Thus, it is essential to evaluate the behavior of trace heavy metals in cement by analyzing their local structures during hydration to assess a potential environmental risk.

We have already reported that trace hexavalent chromium (~6.4 ppm) in cement was gradually reduced to trivalent state during the hydration process in a specified condition using X-ray absorption near-edge structure (XANES) analysis.<sup>12,13</sup> In using the incineration ash of urban refuse and sewage sludge as the raw materials of cement, contamination with low-volatile heavy metals such as zinc and copper is supposed. In this study we focused on the XAFS analysis of the behavior of trace zinc in ordinary portland cement during the hydration process.

## II. Experimental Procedure

### (1) Samples

A standard sample of ordinary portland cement was supplied by the Cement Association of Japan. Hydrated cement samples were prepared by mixing with water in a sample bottle, and the cement paste had a water-to-cement ratio of 0.5. The sample bottles were sealed and cured in an incubator at 20°C for 7, 35, 76, and 294 days. Reference samples containing 20 mg of Zn were prepared using Zn, ZnO, ZnCl<sub>2</sub>, ZnSO<sub>4</sub>, and 2ZnCO<sub>3</sub>·Zn(OH)<sub>2</sub>, respectively. Each reference sample was mixed with 100 mg of BN (boron nitride) and was pressed into pellet of 13-mm  $\phi$  at 80 kN for 10 min.

The concentration of zinc in the unhydrated cement powder was determined to be 205.1 ppm (0.02051 wt% Zn) by conventional quantitative analysis using atomic absorption spectrometry. This zinc is intrinsic to cement materials and assumed to be derived from the natural raw materials.

### (2) XAFS Spectroscopy

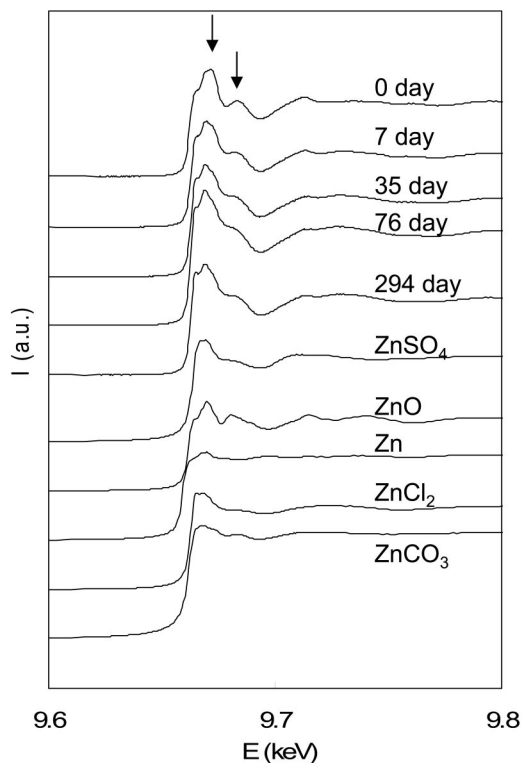
XAFS spectra were recorded at beamline BL38B01 of SPring-8 (Japan Synchrotron Radiation Research Institute, JASRI; West Harima, Hyogo). An Si-(111) double-crystal monochromator was used, and higher harmonics were eliminated with Rh-coated mirrors. Beam energy was calibrated by assigning the first inflection on the L3 absorption edge of a Pb foil to an energy of 13.035 keV. The spectra of unhydrated and hydrated cement samples were collected in fluorescence mode using a Ge 19-element SSD (GL0110S, Canberra Industries, Inc.). The spectra of the reference samples were collected in transmission mode using two ion chambers for  $I_0$  and  $I$ , both of which were filled with N<sub>2</sub>. The scan step was 0.4 eV. All scans were collected in triplicate and averaged to improve the signal-to-noise ratio. The samples were oriented at

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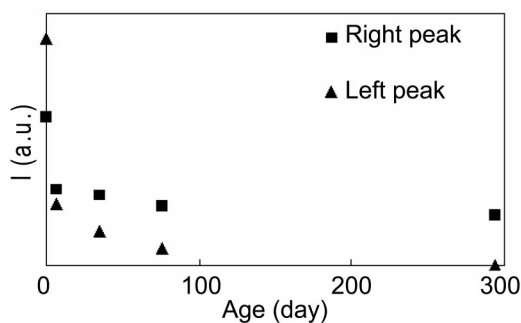
**Fig. 1.** Zn K-edge XANES spectra for ordinary portland cement at the age of 0, 7, 35, 76, and 294 days, along with  $\text{ZnSO}_4$ ,  $\text{ZnO}$ ,  $\text{Zn}$ ,  $\text{ZnCl}_2$ , and  $\text{ZnCO}_3$  for reference.

$45^\circ$  to the incident beam, and the measurements were conducted at room temperature to avoid transformation of cement materials.

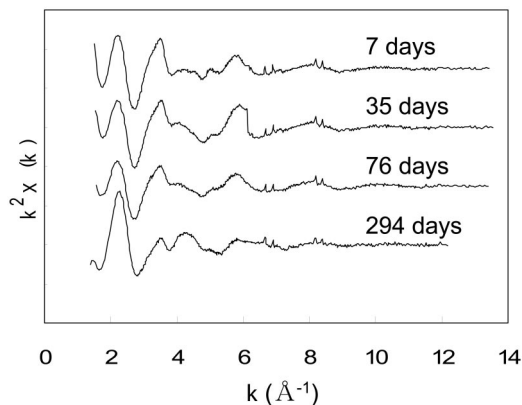
Data reduction was conducted using WinXAS 2.2 according to standard procedures.<sup>14</sup> The background offset was removed by subtracting a line fit to the pre-edge data, and the step heights were normalized to unity. The intensities of particular peaks appearing in XANES spectra were estimated by fitting with a sum of a Gaussian function and a Lorentzian function. The  $\chi(k)$  functions obtained from EXAFS spectra were weighed by  $k^2$  and Fourier transformed to attain radial structure functions (RSFs). The Fourier filtering range was between  $1.7$  and  $13.5 \text{ \AA}^{-1}$ , and a Bessel window with a parameter of 4 was used to suppress artifacts. Theoretical scattering paths for the fit were calculated with FEFF 8 using the wurtzite structure of  $\text{ZnO}$ .<sup>15</sup>

### III. Results and Discussion

The XANES spectra for the Zn K-edge of the cement at each age are shown in Fig. 1 along with the reference compounds. The



**Fig. 2.** Peak intensities of the XANES spectra for cement which appear at the same energy of the  $\text{ZnO}$  spectrum.

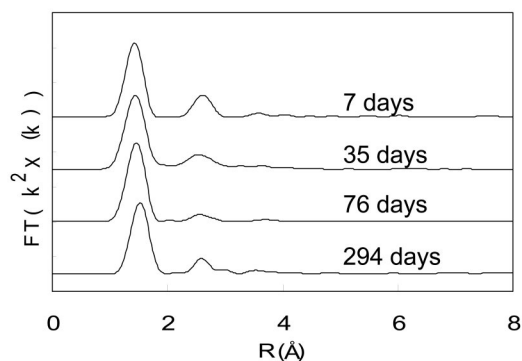


**Fig. 3.** EXAFS  $k^2\chi(k)$  function of zinc in cement.

two peaks which appeared in the spectrum of  $\text{ZnO}$  (depicted by arrows) were also observed in the spectra of cement, and these intensities were decreased apparently with hydration of cement. Figure 2 shows their intensities calculated by fitting, and it proves the decrease of the two peaks. This result indicates that the trace zinc in unhydrated cement has the same local structure as the wurtzite  $\text{ZnO}$ , in which  $\text{ZnO}_4$  tetrahedra were stacked. As hydration proceeds, the stacked structure is broken, and the wurtzite  $\text{ZnO}$  transforms into the other chemical form.

The background-subtracted, normalized, and  $k^2$ -weighted EXAFS spectra for Zn in cement at each age are shown in Fig. 3. The spectra suggest some change in the local structure around Zn with age. Figure 4 shows RSFs obtained by the Fourier transformations of the spectra in Fig. 3. The spectra are uncorrected for phase shift. All spectra showed a main peak around  $1.5 \text{ \AA}$ , which corresponded to the first coordination shell of Zn. The second peak appeared around  $2.6 \text{ \AA}$ , which corresponded to the second coordination shell of Zn. It is important to note that the intensity of the second peak was decreased with age.

The structural parameters calculated from EXAFS analysis are summarized in Table I. In the first coordination shell, the coordination number and the interatomic distance remained unchanged during hydration. Throughout the hydration process, Zn atom was surrounded by four O atoms, and the Zn–O distance was in the range of  $1.97$ – $2.05 \text{ \AA}$ . The obtained Zn–O distance corresponds with that of the typical  $\text{ZnO}_4$  tetrahedron in the wurtzite structure ( $1.80$ – $2.04 \text{ \AA}$ ). The results indicate the  $\text{ZnO}_4$  tetrahedra in cement keep their fundamental structure throughout the hydration process. In the second coordination shell, the coordination number was decreased drastically from  $N = 15.4$  of the unhydrated cement as hydration proceeded, whereas the interatomic distance was almost unchanged. This indicates the decrease of the Zn atoms located outside the vertices of the  $\text{ZnO}_4$  tetrahedra and, consequently, the transformation from the solid solution to an individual chemical



**Fig. 4.** RSF obtained by Fourier transformation of the EXAFS spectra in Fig. 3.

**Table I. Structural Parameters of Zinc in Cement Paste at Each Age Derived from EXAFS Analyses, Where  $R$  Is the Interatomic Distance,  $N$  Is the Coordination Number, and  $\Delta\sigma^2$  Is the Debye–Waller Factor**

Age (days)	Zn–O shell			Zn–Zn shell		
	$R$ (Å)	$N$	$\Delta\sigma^2$ (Å)	$R$ (Å)	$N$	$\Delta\sigma^2$ (Å)
0	2.01	4.71	0.0151	3.16	15.4	0.0086
7	1.98	4.51	0.0097	3.19	13.4	0.0032
35	2.03	4.09	0.0031	3.14	10.8	0.0072
76	1.97	4.46	0.0074	3.21	8.0	0.0049
294	1.98	4.48	0.0057	3.25	7.5	0.0042

species based on the  $\text{ZnO}_4$  tetrahedron. The individual chemical species meeting this condition is tetrahydroxozincate(II) ion  $[\text{Zn}(\text{OH})_4]^{2-}$ .

Zinc speciation in ordinary portland cement during hydration was elucidated as follows. In unhydrated cement, zinc exists as a solid solution in cement matrix, and its local structure is the same as the wurtzite  $\text{ZnO}$ . This trace zinc hydrolyzes to tetrahydroxozincate(II) ion  $[\text{Zn}(\text{OH})_4]^{2-}$  synchronously with the hydration of cement. The most stable phase of zinc at pH 12–13,  $E_h = 0$  V is tetrahydroxozincate(II) ion  $[\text{Zn}(\text{OH})_4]^{2-}$  from the Eh–pH diagram.<sup>16</sup> This corresponds with our results, and the zinc speciation is the same that has been expected thermodynamically. Ziegler *et al.* have investigated the sorption of Zn(II) to calcium silicate hydrate (C–S–H(I)) in aqueous suspensions by electron probe microanalysis (EPMA).<sup>17</sup> They have reported that zinc was observed to incorporate into the C–S–H(I) particles but did not appear to substitute for Ca or Si. These early reports are consistent with our results in this regard that zinc does not form solid solution after hydration of cement, though the origin of zinc is different. It is natural to assume that the  $[\text{Zn}(\text{OH})_4]^{2-}$  which was yielded by hydrolysis of solid solution of zinc is adsorbed on the surface or interlayer of C–S–H particles.

#### IV. Summary

XAFS analysis provides helpful information on the local structure of trace elements in cement matrix. In unhydrated cement, the intrinsic trace zinc exists at the same local structure as the wurtzite  $\text{ZnO}$ , in which Zn atoms are surrounded by four O atoms in the first-coordination shell. As the hydration of cement proceeds, only the coordination number of the second shell decreases, whereas that of the first shell and the interatomic distances of both shells remain constant. Our results elucidate that zinc exists as a solid solution in unhydrated cement, having the same local structure as

the wurtzite  $\text{ZnO}$ , and that this trace zinc hydrolyzes to tetrahydroxozincate(II) ion  $[\text{Zn}(\text{OH})_4]^{2-}$  with the hydration of cement keeping their fundamental structure of  $\text{ZnO}_4$  tetrahedra.

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