

CHEMICAL STATE ANALYSIS OF TRACE HEAVY METALS IN NORMAL PORTLAND CEMENT USING X-RAY ABSORPTION FINE STRUCTURE

Cement has been widely used to stabilize and solidify waste materials containing heavy metals, and long-term leachability of the cement-stabilized residues is an important factor when assessing potential hazards. Elution of hexavalent chromium from cement itself has also become an environmental problem, because cement contains trace amounts of chromium derived from raw materials such as iron slag and refractory bricks. Techniques to manufacture cements from the incineration ash of urban refuse and sewage sludge have been developed [1]. We should pay close attention to the use of 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 chemical states during hydration in order to assess a potential environmental risk. We present here the chemical state changes observed for trace amounts of chromium [2,3] and zinc by X-ray absorption fine structure (XAFS) [4].

A normal Portland cement sample was supplied by the Japan Cement Association. The cement paste sample had a water /cement ratio of 0.5. The concentrations of hexavalent chromium, total chromium, and zinc were determined by conventional wet analysis at 6.4 ppm, 58.4 ppm, and 205.1 ppm, respectively. These chromium and zinc properties are intrinsic to cement materials and are supposed to be derived from the natural raw materials and the refractory bricks.

XAFS spectra were recorded at beamline **BL38B1**. An Si(111) double-crystal monochromator was used, and higher harmonics were eliminated

with Rh-coated mirrors. The spectra of unhydrated and hydrated cement samples were collected in the fluorescence mode using a Ge 19-element SSD (GL0110S, Canberra Industries Inc.).

Figure 1 shows Cr *K*-edge XANES spectra of cement and reference materials. A peak due to hexavalent chromium was observed at 5993 eV in the pre-edge region of the spectrum in **Fig. 1** (indicated by an arrow). We used the intensity of the Cr *K* pre-edge peak for quantitative analysis of the hexavalent chromium (Cr(VI)) in cement matrix. We found that the peak area due to the hexavalent chromium decreased monotonically with the

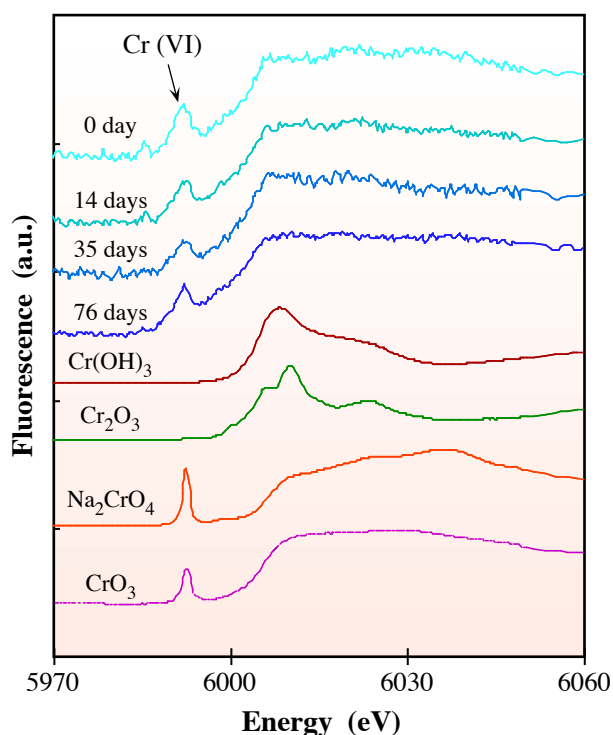


Fig. 1 Cr K-edge XANES spectra for normal Portland cement at the age of 0, 14, 35, and 76 days, along with Cr(OH)₃, Cr₂O₃, Na₂CrO₄ and CrO₃ for reference.

material's age, *i.e.*, with the cement hydration (Fig. 2). This indicates that the trace hexavalent chromium intrinsically contained in cement is gradually reduced to trivalent chromium during the hydration process and thus its toxicity and solubility decreases with time. This suggests that the reduction of the hexavalent chromium to the trivalent chromium is involved in the hydration reaction.

Figure 3 shows Zn K-edge XANES spectra of cement and reference materials. Two peaks peculiar to ZnO were also observed for cement, and their intensities monotonically decreased with the hydration of cement (indicated by arrows). This indicates that zinc atoms coordinated by four oxygen atoms decreased with the hydration of cement. It should be noted that zinc atoms intrinsically existing in the cement matrix change their chemical state drastically during hydration of the cement.

Our results indicate that chemical states of trace amounts of chromium and zinc are transformable with hydration of cement matrix. Monitoring of trace amounts of hazardous heavy metals by an automated routine analysis will be necessary in future for quality control in the cement industry and for hazard assessment of industrial wastes landfilling. We believe XAFS analysis will be a powerful tool for such purposes.

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References

- [1] H. Uchikawa *et al.*, World Cement **26** (1995) 33.
- [2] I. Tsuyumoto and H. Uchikawa, J. Ceram. Soc. Jpn. **111** (2003) 70.
- [3] I. Tsuyumoto and H. Uchikawa, accepted in J. Ceram. Soc. Jpn.
- [4] I. Tsuyumoto and H. Uchikawa, submitted in J. Am. Ceram. Soc.

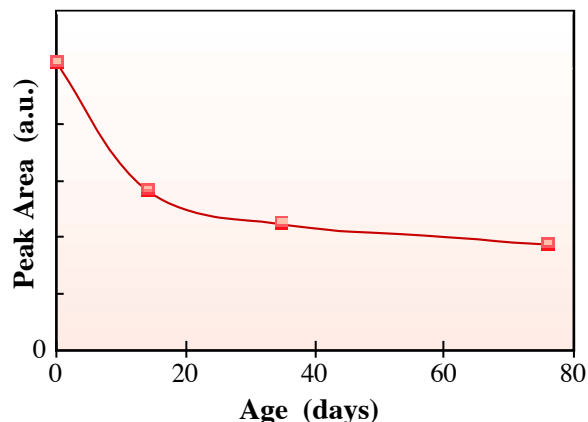


Fig. 2. Normalized area of the hexavalent pre-edge peak versus material age after mixing with water of the normal Portland cement. The curve is added to guide the eye.

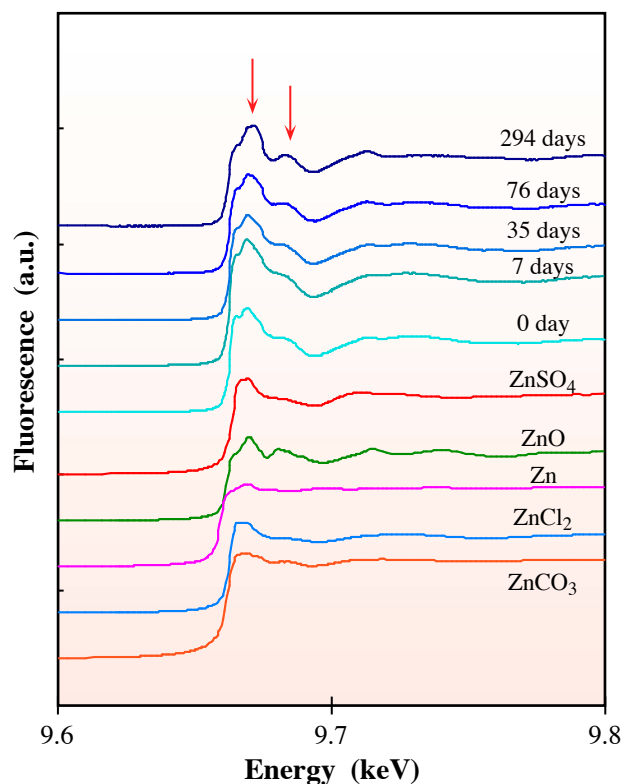


Fig. 3. Zn K-edge XANES spectra for normal Portland cement at the age of 0, 7, 35, 76 and 294 days, along with ZnSO₄, ZnO, Zn, ZnCl₂ and ZnCO₃ for reference.