

## Analysis of Chemical State Change of Heavy Metals in Incineration Ash of Urban Refuse by Heat Treatment

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### Introduction

Recycle of the incineration ash of urban refuse has been intensively investigated by many researchers. In the recycle process the hazardous heavy metals such as Cr, Pb, Cd, Hg, As, Se are derived from the incineration ash, and their elution to the environment is a great care. Many treatment methods have been proposed to inhibit the elution, e.g., mixing with chelating agent, and heat treatment after addition of inorganic agent. In the present study we focus on the heat treatment method after addition of the mixture of siloxane and silanol salt and aim at elucidating the chemical state change of Zn by the treatment.

### Experimental

XANES measurements were performed on untreated fly ash, heat-treated one, and standard samples ( $\text{ZnCO}_3$ ,  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{ZnO}$ , Zn). The heat treatment was carried out at 900 °C for 30 min after mixing with 10% of siloxane and silanol salt mixture. X-ray fluorescence spectra (9.33 keV -11.18 keV) corresponding to Zn-K edge absorption were measured using a 19-element detector at BL38B01.

### Results and Discussion

Fig. 1 shows near edge spectra from the Zn K-edge of the samples. The concentration of the total Cr was estimated at ca. 8000 ppm from the rise around 9.68 keV by comparison with the standard sample. The small sharp peak observed for  $\text{ZnCl}_2$  at 9.677 keV on the left side of the main peak is specific to  $\text{ZnCl}_2$ . The intensity of this peak was decreased by the heat-treatment with the agent. This indicates that  $\text{ZnCl}_2$  contained in the

incineration ash of urban refuse transformed into the other compound. It is considered that the trace Zn and Cl in  $\text{ZnCl}_2$  were incorporated into the glass framework formed by heat treatment of siloxane and silanol salt mixture, and stabilized as solid solution. Our result indicates that the treatment inhibits the elution by stabilization. In the previous work it has been reported that the treating agent suppresses dioxin generation in incinerators by incorporating its precursors such as chlorides, chlorinated organic compounds. Our result also supports this feature.

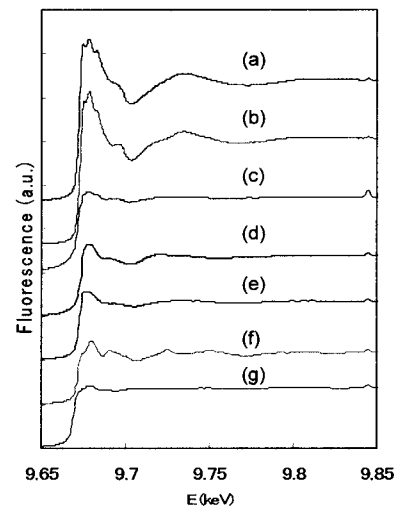


Fig. 1 Near edge spectra from Zn K-edge of (a) untreated fly ash, (b) treated fly ash, (c)  $\text{ZnCO}_3$ , (d)  $\text{ZnSO}_4$ , (e)  $\text{ZnCl}_2$ , (f)  $\text{ZnO}$ , and (g) Zn.

## Chemical State Analysis of Trace Amounts of Heavy Metals in Cement

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### Introduction

Cement has been widely employed to stabilize and solidify waste materials containing the heavy metals, and the long-term leachability of the cement-stabilized residues is the important factor associated with landfilling.<sup>1)</sup> In recent years, techniques to manufacture cements from the incineration ash of urban refuses and sewage sludge have been developed. We should pay much attention 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 chemical states during hydration in order to assess a potential environmental risk. In this study, we focused on the XAFS analysis of the behavior of trace Zn in normal Portland cement.

### Experimental

XAFS measurements were performed on normal Portland cement samples at the age of 0, 7, 35, 76, 294 days, and standard samples ( $\text{ZnSO}_4$ ,  $\text{ZnO}$ , Zn,  $\text{ZnCl}_2$ ,  $\text{ZnCO}_3$ ). The concentration of Zn in cement was 205.1 ppm. X-ray fluorescence spectra (9.33 keV -11.18 keV) corresponding to Zn-K edge absorption were measured using a 19-element detector at BL38B01.

### Results and Discussion

Fig. 1 shows near edge spectra from the Zn K-edge of the samples. We found that the peak inherent to  $\text{ZnO}$  (indicated by arrow) decreases with hydration. This is the first evidence that trace amounts of Zn existing as oxide coordinated

by four oxygens changes to the other chemical state with the hydration of cement. Our results at least shows trace amounts of Zn changes its chemical state in cement matrix during hydration, i.e., when used as construction materials. The EXAFS analysis based on FEFF 8 simulation is currently in progress.

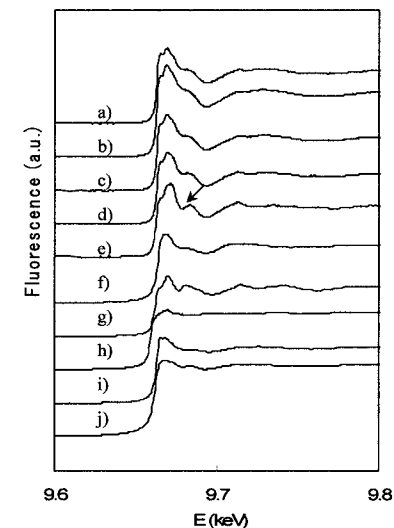


Fig. 1 Near edge spectra from Zn K-edge of (a) 294 days, (b) 76 days, (c) 35 days, (d) 7 days, (e) unhydrated, (f)  $\text{ZnSO}_4$ , (g)  $\text{ZnO}$ , (h) Zn, (i)  $\text{ZnCl}_2$ , and (j)  $\text{ZnCO}_3$ .

Reference 1) Ziegler, F.; Scheidegger, A. M.; Johnson, C. A.; Dähn, R.; Wieland, E. *Environ. Sci. Technol.* **2001**, *35*, 1550.