

### Chemical states of trace heavy metals in fly ash and bottom ash

M.Nagoshi\*(6097), H.Yamamoto<sup>1</sup>(6363), S.Ichikawa<sup>2</sup>(6106), T.Uruga<sup>3</sup> (0182), K.Sato, K.Nakahara<sup>1</sup>, and M.Yomura

Applied Technology Research Center, NKK Corporation, Minamiwatarida 1-1, Kawasaki 210-0855, Japan

1) Engineering Research Center, NKK Corporation., Minamiwatarida 1-1, Kawasaki 210-0855, Japan

2) Kokan Keisoku K.K., Minamiwatarida 1-1, Kawasaki 210-0855, Japan

3) JASRI, Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

Fly ashes and bottom ashes from the municipal solid waste incinerator contain small amount of toxic heavy metal elements such as lead. Recycling these ashes, which is of important from an environmental point of view, requires proper stabilization techniques for these elements. It is very important to clarify the chemical states of these elements not only for estimating the safety of the ashes but also for designing heavy metals stabilization techniques. We have clarified the chemical states of lead (3000 ppm – 9000 ppm) in fly ashes before and after a stabilization treatment by x-ray absorption spectroscopy (XAFS) [1]. However, the typical detection limit of XAFS with a Lytle type detector was estimated to be about 1000 ppm for lead in fly ashes. In this study we have investigated the chemical states of lead (300 ppm – 3000 ppm) in fly ashes and bottom ashes by XAFS with a multi-elements solid-state detector. We have also tried to measure x-ray absorption near edge structure (XANES) spectra for mercury (about 20 ppm) in fly ashes.

Fly ashes and bottom ashes were collected from some incinerators in Japan. The XAFS measurements were carried out at the BL01B1, SPring-8 with a two-crystal Si(311) monochromator, in which Si(311) crystals were used to avoid glitches just at the Pb L<sub>3</sub>-edge from Si(111) crystals. The Pb L<sub>3</sub>-edge and Hg L<sub>3</sub>-edge XAFS spectra were measured in the fluorescence mode using a Ge 19-elements solid-state detector.

Figure 1 shows Pb L<sub>3</sub>-edge XANES spectra for bottom ashes sampled from three different incinerators. The mass concentrations of lead are about 300 ppm, 500 ppm, and 1000 ppm, for ashes 1, 2, and 3, respectively. Pb L<sub>3</sub>-edge Extended-x-ray-absorption-fine-structure (EXAFS) spectra were obtained up to  $k = 8.5 \text{ \AA}^{-1}$  for all samples measured with a dwell time of 20 – 30 sec./point. The Pb L<sub>3</sub>-edge XANES and EXAFS spectra indicate that lead atoms in

measured ashes have a valency of 2+ and are in oxides. Moreover, the Pb L<sub>3</sub>-edge spectra show some differences among the ashes. The detailed study on relationship between local structures of lead atoms and properties of ashes is in progress.

A Hg L<sub>3</sub>-edge XANES spectrum was obtained for mercury of 17 ppm in a fly ash with a dwell time of 18 sec./point. However, it is difficult to identify the chemical states of mercury due to low signal-to-noise ratio. Refinement of the experiments and a longer detection time are needed in order to obtain satisfactory spectra for clarifying the chemical states of mercury.

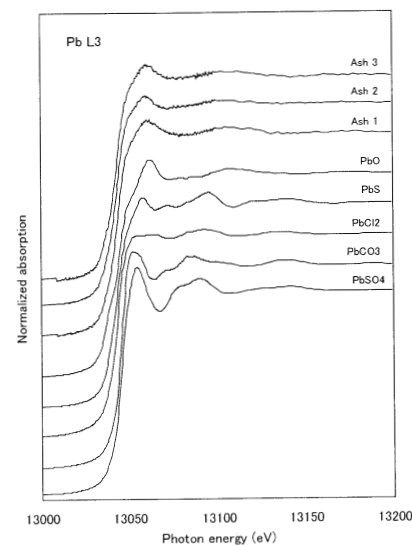


Figure 1 Pb L<sub>3</sub>-edge XANES spectra for bottom ashes and some lead compounds

[1] M.Nagoshi et al., 2000B0580-NX-np.

### The Effect of Ln(Ln = Ce, La) doping on the performance of AlPO<sub>4</sub> Catalysts in CFC's Decomposition

Hiroyasu Nishiguchi\* (5275), Yuichi Ichihashi<sup>#</sup> (3678), Tatsumi Ishihara, Yusaku Takita(5276)

Department of Applied Chemistry, Faculty of Engineering, Oita University

<sup>#</sup> Department of Energy and the Environment, Advanced Institute of Science and Technology

Millions of metric tons of chlorofluorocarbons CFCs produced so far are still being utilized in the form of refrigerants, solvents, etching and cleaning agents in the electronic industry. Since CFCs are chemically stable, those are diffused to the stratosphere and destroy ozone molecules to oxygen molecules. Furthermore, CFCs are significantly responsible for the greenhouse effect. Accordingly, many attempts to decompose CFCs completely are carried out. However, a safe, simple and cheap decomposition method still remains to be developed.

The authors reported that AlPO<sub>4</sub> has high decomposition activity, 100% CO<sub>2</sub> selectivity, and extremely long catalyst life. For example, 0.5 mol% CCl<sub>2</sub>F<sub>2</sub> in the feed gas composed of about 50 mol% water vapor and air, is converted completely at 450°C. After the 1000-h reaction period, X-ray diffraction XRD measurement of the catalyst revealed that AlPO<sub>4</sub> was partly crystallized and a very small amount of AlF<sub>3</sub> was present in the catalyst.

Metal phosphate catalysts were prepared by the precipitation method described below. An aqueous solution composed of stoichiometric amounts of metal nitrate and 85% ortho-phosphoric acid, and an aqueous solution of 10 wt.% ammonium hydroxide were simultaneously dropped into a separate vessel keeping the pH of the mixture as 4.5. The precipitate was well washed by pure water and filtrated. The resulting powder was

pressed, crushed, and sieved into 14–32 mesh granules and finally it was calcined at 1000°C for 5 h in air. The mixed phosphate catalyst was prepared from a mixed solution of Al and Ce nitrates.

Ce K-edge EXAFS spectra for Ce-AlPO<sub>4</sub> were measured at BL01B1 in a transmission mode, the synchrotron radiation was mono-chromatized by a Si(311) monochromator.

Figure 1 shows the Ce K edge XANES of Ce-AlPO<sub>4</sub> at various pretreatment temperatures. Even at low temperature like 120°C, Ce XANES spectrum is very similar to that of CePO<sub>4</sub>. After the catalytic decomposition of CCl<sub>2</sub>F<sub>2</sub>, All XANES spectra did not change at all. These results suggested that the CePO<sub>4</sub> in AlPO<sub>4</sub> matrix tend to crystallize and stable for CFCs decomposition.

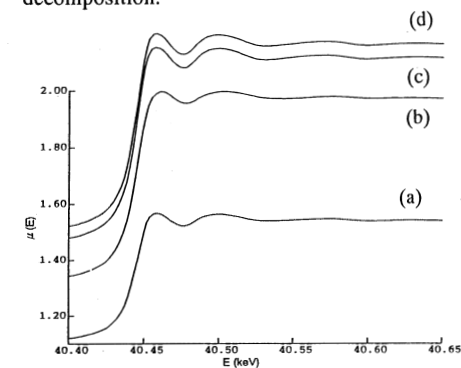


Figure 1. The Ce K edge XANES spectra of Ce-AlPO<sub>4</sub> (a) Ce-AlPO<sub>4</sub> 120°C, (b) Ce-AlPO<sub>4</sub> 800°C, (c) Ce-AlPO<sub>4</sub> 1000°C, (d) CeO<sub>4</sub>