12C/2005P010

Change of chemical state of Pb species in fly ash by Mechanochemical treatment

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Introduction

We focused on mechanochemical (MC) treatment as an effective method for detoxification of fly ash containing hazardous compounds such as dioxins and heavy metals. In our study, it was confirmed that MC treatment using CaO as additive degraded dioxins in fly ash and inhibited the elution of heavy metals from fly ash [1]. In order to account for the inhibition effect of heavy metals, the chemical state after the MC treatment must be revealed. It is impossible to determine chemical speciation of heavy metals in fly ash with physical methods such as XRD, XPS because of its low concentration, whereas X-ray adsorption fine structure (XAFS) spectroscopy allows heavy metals speciation in diluted system to be performed [2]. Here, we report the change of chemical state of lead (Pb) species in fly ash by MC treatment, resulting in the inhibition effect, using XAFS analysis.

Experimental

Fly ash (1 g) was mechanochemically treated with CaO (4 g) under atmospheric condition for 4 h, using a planetary ball mill (Pulverizette-7, Fritsch, Germany) with a pair of pots (45 cm^3) in each of which 7 balls (15-mm diameter) were arranged. 1

The treated residue was subjected to X-ray absorption near edge structure (XANES) spectrum analysis by XAFS method using the BL-12C system in order to determine Pb species. In XAFS measurement, Pb speciation was carried out by the 19-element semiconductor detector at the fluorescent mode at the energy range around 13 KeV equivalent to Pb-LIII-absorption edge.

As the reference materials, Pb, $PbCl_2$, PbO, $PbSO_4$, $PbCO_3$, PbS, PbO_2, Pb_3O_4 were measured by Si(111) monochromator at the transmission mode.

Results and Discussion

Compared with XANES spectra of reference materials, spectrum of fly ash is likely in agreement with that of $PbCl_2$ (figure 1). In addition, relative energy position of the edge peak on XANES spectrum of Pb in the fly ash was close to that of $PbCl_2$ (table 1). This indicates that $PbCl_2$ may be the major species of Pb in the fly ash. Whereas, spectra of fly ash treated mechanochemically (1h-MC, 2h-MC and 4h-MC in figure 1) were obviously different from that of fly ash, indicating that chemical state of Pb in fly ash was changed during MC treatment. The treated fly ash showed the similarity in spectrum with Pb_3O_4 in figure 1, and the relative edge energy of the XANES spectra of the fly ashes that were treated for 1 h and 2 h was the same as that of Pb_3O_4 in table 1. These results confirmed the production of Pb_3O_4. This may explain the inhibition of Pb leaching in response to MC treatment since Pb_3O_4 is insoluble in water. However, fly ashes that were treated for 4 h were found to have a relative edge energy that differed from that of Pb_3O_4, which indicates that prolonged MC treatment may have induced a further transformation of Pb_3O_4. This finding is consistent with the changes observed in the first derivative XANES spectra in which the difference was recognized around 13,080 eV (data not shown).

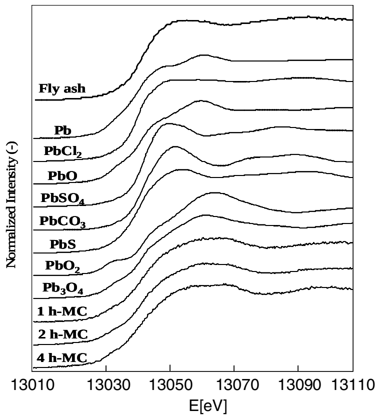

Figure 1 XANES spectra of fly ash, the treated and reference materials.

Table 1 Relative edge energy in the XANES spectra.

Samples	Relative edge energy [eV]
Pb	0
$PbCl_2$	-1.98
PbO	-0.99
$PbSO_4$	-10.89
$PbCO_3$	-8.91
PbS	-6.93
PbO_2	4.95
Pb_3O_4	0.33
Fly ashes	-2.31
1 h-MC	0.33
2 h-MC	0.33
4 h-MC	6.6

References

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