Approach for estimation of the minor crystalline phases in fly ash by correlation analysis of elemental compositions using X-ray fluorescence spectrometry

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X-ray diffraction (XRD) is applied for the crystalline phase analysis of many materials. While major crystalline phases can be identified and quantified using XRD, the analysis of minor crystalline phases containing heavy metals is difficult due to the insufficient sensitivity of XRD. Minor crystalline phases are generally analyzed using X-ray absorption fine structure (XAFS)[1)] and X-ray photoelectron spectroscopy (XPS)[2)]. However, a high brightness X-ray source, such as a synchrotron radiation facility, is required for XAFS, and only surface information is obtained using XPS. Moreover, the elution characteristics of heavy metals depend on a variety of experimental conditions, such as the solution pH, and can also be associated with their crystal morphology. Therefore, a general method for the analysis of minor crystalline phases containing heavy elements is needed to comprehensively determine the elution characteristics. Herein, we estimated the minor crystalline phases of the heavy elements in a fly ash sample collected monthly at a municipal solid waste incinerator for one year[3)]. The estimation of the crystal morphology of the heavy elements will be useful in understanding the heavy element elution characteristics of the ash for recycling processes, and the management or control of ash landfilling sites.

The six heavy metals in the fly ash, which are Cr, Ni, Cu, Zn, Br and Pb, were quantified by an X-ray fluorescence spectrometer using the powder briquette method. The fly ash, collected throughout the year, consisted mainly of SiO_2, Cl, and CaO, and contained several thousand ppm (μg/g) of Zn, Br, and Pb. Also, six crystalline phases, namely anhydrite ($CaSO_4$), calcite ($CaCO_3$), gehlenite ($Ca_2Al_2SiO_7$), halite (NaCl), quartz (α-SiO_2), and sylvite (KCl), were identified on the diffraction pattern. The crystalline phases of the major elements in the ash sample were identified using XRD; however, identification of the crystalline phases of minor elements, including heavy elements, was difficult due to their lower levels. Therefore, the relationships among the concentrations of different elements were used to estimate the crystal morphology of the heavy elements. Analysis of the samples revealed strong correlations among the concentrations of the major elements. High correlation values were observed, for example, between Na_2O and Cl (R=0.9000), K_2O and Cl (R=0.9092), and SiO_2 and Al_2O_3 (R=0.9601) in the fly ash, as these elements were present in the same crystalline phases, namely halite, sylvite, and gehlenite. High correlation values of $R > 0.75$ were also found among the heavy metal elements, and between heavy metals and other elements in the fly ash, namely between Ni and K_2O (R=0.7710), Ni and Cr (R=0.7512), Cu and Cl (R=0.7901), Cu and K_2O (R=0.7677), Cu and CaO (R=0.7523), Br and Cl (R=0.8067), Br and K_2O (R=0.8062), Br and CaO (R=0.7661), Pb and MgO (R=0.8403), and Pb and Cl (R=0.7732). The results indicated that a fraction of the Cu and Pb in the fly ash formed chloride compounds such as $CuCl_2$ and $PbCl_2$, as these elements showed strong correlations with Cl. Copper also formed compounds with CaO, such as Ca_2CuO_3, Ni and Cu formed compounds with K_2O, that is, K_2NiO_3 and KCuO, and Pb formed $PbMg(CO_3)$ with MgO.

References

1) M. Takaoka, T. Yamamoto, T. Tanaka, N. Takeda, K. Oshita, and T. Uraga, *Physica Scripta*, **T115**, 943-945, 2005.
2) A. Ohki, T. Nakajima, Y. Sakaguchi, A. Iwashina, and H. Takanashi, *J. Hazard. Mater.*, **119**, 213-217, 2005.
3) A. Ohbuchi, Y. Koike, T. Nakamura, *Analytical Sciences* (in press).