V. 6. PIXE Analysis of Individual Particles in Coal Fly Ash

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Introduction

Coal is the largest source of energy for the generation of electricity. Consumption of coal is increasing as an alternative for petroleum, since the depletion of petroleum has become world wide problem1). Coal is pulverized and then combusted in a furnace with a boiler for electricity generation in coal-fired power plants. During the process, waste products such as coal ash residue and flue gas desulfurization sludge are produced. There are two types of coal ash residues, the first is fly ash generated from the boiler, and the second is clinker ash that falls to the bottom of the boiler furnace. The proportion of fly ash is about 80 to 85% of coal ash residues. Although coal ash is partly reused as cement admixture and concrete aggregate, the residuals are disposed as an industrial waste2). Coal fly ash contains mercury, arsenic, and other toxic heavy metals, which leads to a concern about the possibility of leakage into environment. While extraction tests of coal fly ash show that coal fly ash is environmentally safe under natural pH condition, some metals are soluble under aggressive pH conditions3). Therefore, it could adversely affect humans, animals, plants and living environment. However, it is difficult to investigate a direct correlation between pH of coal fly ash and leakage of elements. The assessment of leakage of toxic elements into the environment and the effect on human beings and animals strongly depend on their spatial distribution in the particles and on their chemical form as well as elemental concentrations3,4). Therefore, the physicochemical conditions of the coal fly ash should be investigated. For this purpose, analysis of individual fly ash particle by using microbeam analysis will provide valuable information in this field5). In this study, we analyzed coal fly ash from coal-fired power plants with 1 μm spatial resolution by using the simultaneous micro-PIXE/RBS/off-axis STIM system at Tohoku University. The combination of PIXE, RBS and off-axis STIM methods enabled simultaneous analysis of hydrogen to metal elements and revealed the chemical composition of these particles.

Experimental

Sample preparation

In order to analyze all elements contained in fly ash particles with spatial resolution of 1 μm, it is necessary to attach them on a thin polymer film without using any adhesive. Chemical treatment should not be done because chemical form might change. For this purpose we used an impactor which was developed in aerosol study6). Fly ash particles were suspended in a box and were sampled at a flow rate of 1.3 l/min for one hour. The effective 50% cutoff diameter is estimated as ca 2 μm. Fly ash particles were impacted on a 2 μm Mylar ($H_8C_{10}O_4$) film or a 4 μm Prolene (H_6C_3) film. Although particle size of coal fly ash particles ranges from 3 to 20 μm, those of collected particle were 3 to 5 μm in diameter. It was an effect of upper cut-off of the impactor. In order to analyze bigger particles than 5 μm, fly ash particles were put on the Mylar film and were attached by electrostatic force. Number of particles on the film was low, bigger particles than 5 μm could be collected. We analyzed six samples generated in coal-fired power plants in Japan.

Analysis

We performed individual particle analysis of the coal fly ash with a microbeam system at Tohoku University. Technical details of the system were presented in previous publication7,8). Simultaneous PIXE/RBS/off-axis STIM analysis was conducted with the proton beam energy of 3 MeV, beam spot size of 1×1 μm^2 and beam currents of 50 to 100 pA. The beam scanning area was 10×10 to 100×100 μm^2.

Quantitative PIXE analyses were performed by using GeoPIXEII software9). After generating the elemental maps, individual particles were selected from these maps and corresponding PIXE, RBS, and off-axis STIM spectra were extracted. The elemental concentrations for elements heavier than carbon were then deduced from the fit of the extracted PIXE spectra. For quantitative analysis, yield correction of X-rays was performed for each particle considering the particle size, shape, the changes in X-ray production cross section and self absorption of X-rays. However, the effect of shape is small even for light elements and is negligible for heavy elements, in particle sizes (<5 μm)[5,10]. In this study, no shape correction did not apply and the changes in X-ray cross section and self absorption effects were considered assuming a flat homogeneous slab. Concentrations of carbon, oxygen, and hydrogen were derived from peak yields of extracted RBS and STIM spectra, which were calibrated by measuring the peak yields from Mylar films of known thickness. Quantitative analysis of hydrogen was carried out by analyzing the extracted off-axis STIM spectra.

Results and Discussion

We analyzed about 80 coal fly ash particles obtained from six coal-fired power plants in Japan and obtained elemental concentrations and elemental distribution images. The coal fly ash particles are mainly composed of O, Si and Al. Sum of the masses of O, Si and Al in each of the particles is 80-95% of the total mass. Figure 1 shows the correlation between number of oxygen atoms and that of metals for the particles. In this analysis, particles collected on the Mylar film and which were bigger than 5 μm were excluded from the analysis. The results on 50 particles are shown in the graph. Number of oxygen atoms increases with that of metals. Atomic ratio is around 2. It is apparent that these particles exist as dioxide. The particles also contain Ca, Ti, Fe, Na, Mg and K. Hydrogen and carbon are not observed in these particles, which implies that coal is completely burned and carbon dioxide and water vapor is dissipated.

Examples of elemental distribution images are shown in Fig. 2 (a), (b) and (c). The oxygen image in Fig. 2 is obtained by RBS. As mentioned previously, Oxygen, silicon and aluminum show similar distributions. As for trace elements, the content of each element is quite different in each particle. Forty percent of the particles contain V and Zn. All of the particles from one of the power plants contain V and Zn. Five to ten percent of these particles contains Sr, Cu, Ni, Mn and Cr. A few particles contain arsenic. These elements distribute homogeneously as shown in Fig. 3 (a) and (b). One exception is shown in Fig. 3 (c). Since the size of the particle is around 20 μm, the yield map of Al and Si is strongly influenced by self absorption, and X-ray intensity of right side is low. While silicon distributes uniformly, Al, Ca, Fe, Zn, As and Zr are distributed on the surface of the particles. It is reported that the elements having boiling points lower than the combustion temperature of the furnace in the power plant condense on the surface of the particle at the low temperature following combustion[4].

Conclusions

Coal fly ash particles contain mercury, arsenic, and other toxic heavy metals, which might lead to leakage into environment. The spatial distribution and chemical form as well as elemental concentrations of the trace elements are important factor in the assessment of leakage into the environment. In this study, we analyzed coal fly ash from coal-fired power plants with 1 μm spatial resolution by using the microbeam analysis system at Tohoku University. Fly ash particles were attached on the Prolene film using impactor. Particle size range collected by the impactor was 3-5 μm in diameter which was smaller than that of fly ash particle. Bigger particles were attached on the Mylar film by electrostatic force. We analyzed about 80 coal fly ash particles obtained from six coal-fired power plants in Japan. The coal ash particles are mainly composed of O, Si and Al and estimated as dioxide. The particles also contain Ca, Ti, Fe, Na, Mg and K. As for trace elements, V, Zn, Sr, Cu, Ni, Mn, Cr and As are contained. Correlation between these elements is not seen. These elements distribute homogeneously. As an exception, Al, Ca, Fe, Zn, As and Zr are distribute on the surface of the particles which might be related to the combustion process. Microbeam analysis of individual fly ash particle will provide valuable information in this field.

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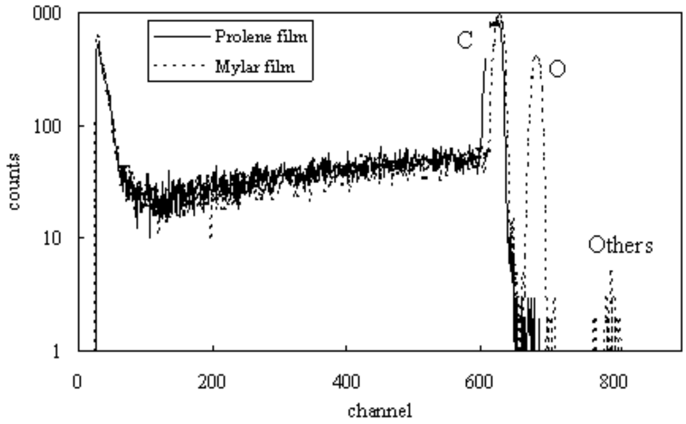

Figure 1.   Correlation between Oxygen and sum of Al, Si, Ca, Ti and Fe.

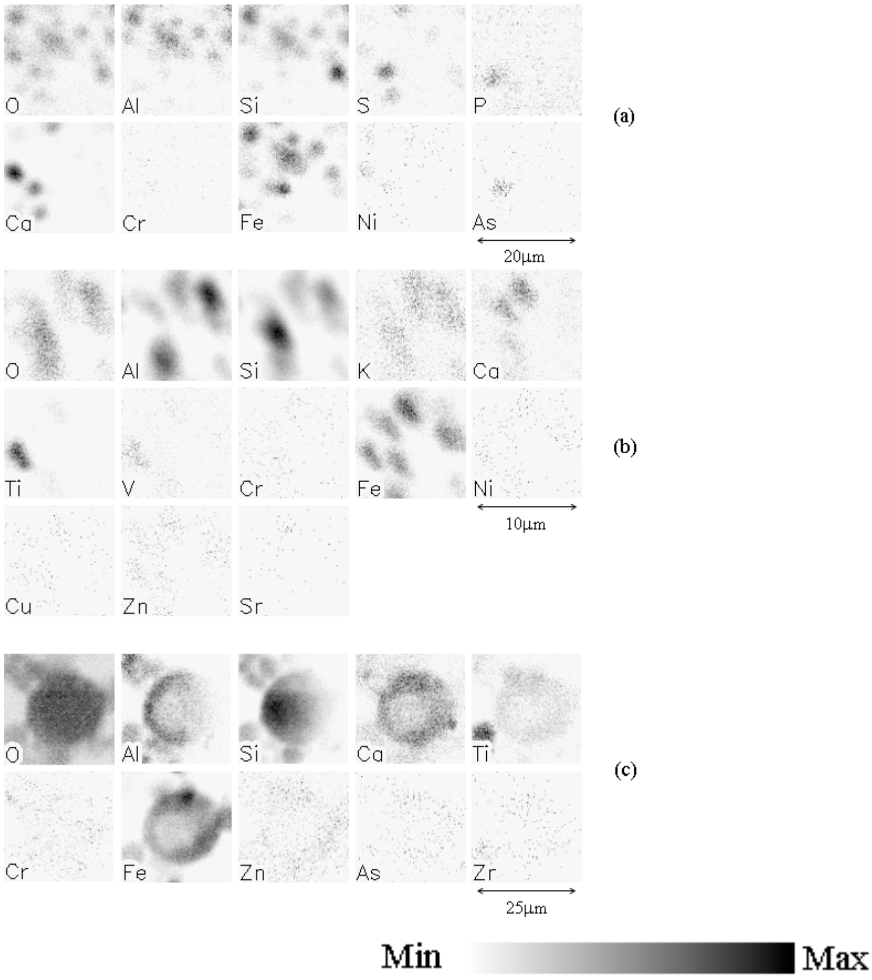

Figure 2.   Elemental distribution maps of the fly ash particles.