**Chemical State of Boron in Coal Fly Ash Investigated by
Focused-Ion-Beam Time-Of-Flight Secondary Ion Mass Spectrometry
(FIB-TOF-SIMS) and Satellite-Transition Magic Angle Spinning
Nuclear Magnetic Resonance (STMAS-NMR)**

Shun-ichi Hayashi^{a*}, Takafumi Takahashi^a, Koji Kanehashi^a, Naoyoshi Kubota^a, Kaoru Mizuno^b,

Shunsuke Kashiwakura^c, Tetsuo Sakamoto^d and Tetsuya Nagasaka^c

^aNippon Steel Corp., Advanced Technol. Res. Labs., 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan

^bNippon Steel Technoresearch Corp., 20-1 Shintomi, Futtsu, Chiba 293-0011, Japan

^cTohoku University, Graduate School of Environmental Studies, 6-6-20 Aoba, Aramaki, Sendai
980-8579, Japan

^dKogakuin University, Faculty of Engineering, 2665-1 Nakanochō, Hachioji, Tokyo 192-0015,
Japan

TEL: +81-439-80-2248 FAX: +81-439-80-2746 e-mail: hayashi.shunichi@nsc.co.jp

Abstract

The chemical states of boron in coal fly ash, which may control its leaching into the environment,
were investigated by focused ion beam time-of-flight secondary ion mass spectrometry

(FIB-TOF-SIMS) and satellite transition magic-angle-spinning nuclear magnetic resonance (STMAS NMR) spectroscopy. The distribution of boron on the surface and in the interior of micron-sized fly ash particles was directly observed by FIB-TOF-SIMS. Coordination numbers of boron and its bonding with different atoms from particles of bulk samples were investigated by STMAS NMR. Boron in coal fly ash with relatively poor leaching characteristics appears as trigonal BO_3 and coexists with Ca and Fe at the outer layer of every particle and inside CaO-MgO particles. In contrast, boron in coal fly ash with better leaching characteristics appears as CaO- or MgO-trigonal BO_3 and tetragonal BO_4 , and it is distributed only on the outer surface of each ash particle without showing any correlation with a particular element.

Keywords: Coal fly ash, Boron, NMR, TOF-SIMS, Leaching characteristics, Chemical state

1. Introduction

Coal fly ash (CFA) generated as a byproduct of the coal combustion process in electric power plants has a wide range of applications; it can be used in soil amendment and can be used as a building material and a component in cements for civil engineering applications. On the other hand, CFA contains some hazardous elements such as boron, arsenic, selenium, and fluorine that are easily volatilized during coal combustion, and they condense on CFA, rather than on clinker ash (Davison et al., 1974; Klein et al., 1975; Smith et al., 1979; National Academy Press, 1980; Quann et al., 1982; Markowski and Filby, 1985; Boyd, 2002; Sterling and Helble, 2003; Alvarez-Ayuso et al., 2006). As there is a growing concern for environmental and human health risks in modern society, leaching of these elements from CFA has been strictly controlled. Such leaching from CFA-recycled products may also take place.

High concentrations of boron may naturally occur in the soil or in groundwater, or it may be added to the soil from mining, fertilizers, or irrigation water. In addition, various anthropogenic sources of excess boron may increase soil boron to levels toxic for plants and human beings. The most important source of boron is irrigation water; however, other sources include wastes from surface mining, fly ash, and industrial chemicals (Nable et al., 1997). Therefore, the elution of boron from CFA or CFA products is of particular concern.

The toxicity of inorganic pollutants largely depends on their chemical state rather than on their

concentrations, with the less soluble forms being generally regarded as less toxic. In fact, it has been reported that in CFA, the leaching characteristic of boron varies depending on its chemical state (Iwashita et al., 2005). This result suggests that it may be possible to inhibit the leaching of boron by controlling its chemical state. Thus, the analysis of the chemical state of boron in CFA is essential to propose an effective way to restrain the elution of boron to the environment (Kashiwakura et al., 2009).

Conventional analytical techniques such as ICP-AES and ICP-MS evaluate the average concentration of trace elements in bulk samples, but do not provide information on their chemical state. Since the concentration of trace elements in CFAs is generally less than 100 mg kg^{-1} , direct and nondestructive detection for some trace elements such as arsenic and selenium has been conducted by X-ray absorption fine structure (XAFS) with synchrotron radiation (Huggins et al., 2007; Al-Abed et al., 2008). However, the application of XAFS for the detection of boron in CFAs is not straightforward because of boron's light atomic weight. Nuclear magnetic resonance (NMR) can be considered as an alternative method for detecting boron in CFAs because NMR analysis has high sensitivity for ^{11}B , which accounts for 80.1% of boron isotopes. Local forms of boron in raw coals and low temperature ashes have been studied by ^{11}B NMR (Burchill et al., 1990; Kuwabara et al., 2007). Few ^{11}B NMR spectra for CFA have been reported, although ^{29}Si and ^{23}Na NMR spectra have been often acquired to characterize activated CFA (Skavaraa et al., 2007; Criado et al.,

2008). Most recently, some authors have succeeded in obtaining high-resolution ^{11}B satellite transition magic angle spinning (STMAS) NMR spectra from two types of CFA samples (Takahashi et al., 2009a; Takahashi et al., 2009b). It has been proven by STMAS NMR that boron in the two CFA samples certainly differed in its chemical state. It is worth noting that NMR spectroscopy extracts the chemical state information of many CFA particles, not just of a single particle.

In fact, the chemical composition of CFA particles is heterogeneous rather than homogeneous (Yamashita et al., 2000; Goodarzi, 2006; Kutchko and Kim, 2006), indicating that each particle consists of different kinds of compounds. Furthermore, the chemical composition differs between the outer layer and interior of a single particle according to the heat history of its formation (Kashiwakura et al., 2010). Occasionally, hollowed particles are observed in an actual CFA and are found to consist of several kinds of gangue mineral. In this study, prototype focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) is first applied for the direct observation of boron in CFA. This technique provides information on the elemental distributions not only at the surface but also in the interior of a CFA particle. This approach is suitable for examining the correlation of boron and other elements in a CFA particle (Sakamoto et al., 2003). SIMS is one of the most highly sensitive surface analytical tools. Thus far, however, lateral imaging has never been performed because active primary ion beams, e.g., O_2^+ , Cs^+ , etc., could not be focused down to several tens of nanometer. Our prototype FIB-TOF-SIMS apparatus was

demonstrated to have a lateral resolution of 40 nm (Sakamoto et al., 2008; Sakamoto and Yamaguchi, 2008). In this study, particles of CFAs as small as 5–10 nm in diameter were analyzed. Lateral resolution on this scale allows the demonstration of element heterogeneity within an individual fly ash particle. Based on the results of solid state NMR and FIB-TOF-SIMS experiments, the chemical state of boron in the CFAs is clearly identified. Finally, the relationship between the leaching characteristic of boron and its chemical structure is discussed.

2. Materials and methods

Two types of CFA samples, N-CFA and F-CFA, obtained from coal-fired plants in Japan, were used as typical examples of CFA for the FIB-TOF-SIMS and solid-state NMR experiments. Their chemical compositions are summarized in Table 1, showing that the sum of silica (SiO_2) and alumina (Al_2O_3) accounts for more than 80 wt% in both samples.

The boron concentrations are found to be 540 and 1050 ppm by weight for N-CFA and F-CFA, respectively (Table 1). The two CFAs have different boron leaching characteristics: less than 17% (boron) was eluted to water in N-CFA, while approximately 50% was eluted to water in F-CFA. The testing method is based on the official Japanese leaching test method, “Notification #46” in Japan (Notification #46, 2001). The procedure is as follows. Specimens are air-dried and crushed to a particle size less than 2 mm. Crushed specimens of 50 g are mixed with 500 mL of

ion-exchanged water whose pH is adjusted in the range of 5.8 to 6.3 by addition of HCl. The solution is then shaken for 6 h, and the filtrate then undergoes chemical analysis. In this research, the concentration of boron was measured by inductively coupled plasma atomic emission spectrometry (ICPS8100, Shimadzu).

^{11}B MAS and STMAS NMR spectra were acquired using a 16.4 T narrow bore magnet (JEOL-ECA700) equipped with a home-built STMAS probe. The detailed experimental conditions were described elsewhere (Takahashi et al., 2009a; Takahashi et al., 2009b). Several standard samples of borates containing potassium $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, calcium $\text{Ca}_2\text{B}_2\text{O}_5/\text{Ca}_3\text{B}_2\text{O}_6$, aluminum $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 1.5\text{H}_2\text{O}$, sodium $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7$ (anhydrate), and magnesium $\text{Mg}_2\text{B}_2\text{O}_5/\text{Mg}_3\text{B}_2\text{O}_6$ were used in order to assign the STMAS NMR peaks.

A TOF-SIMS instrument was also originally designed and developed. The details have been described elsewhere by one of the authors (Sakamoto et al., 2008, Sakamoto and Yamaguchi, 2008). The apparatus consists of a Ga-FIB column, an electron beam column, and a Time-of-Flight mass spectrometer. A TOF-SIMS with a function of micro-cross sectioning by a FIB source was applied to evaluate the CFA particles. Each particle was also cross-sectioned by a FIB in a shave-off mode after TOF-SIMS analysis of the surface only, and rotated on a sample holder by 180 degrees, as shown in Fig. 1. This feature enabled us to obtain SIMS elemental images not only of the outer surface but also of the interior. As a result, small amounts of boron and some matrix

elements could be observed separately on the particle surface and inside it using our instruments.

The elemental mapping could be obtained for a CFA particle with an average diameter of 5–10 μm .

3. Results

There is not much difference in the crystalline phases between F-CFA and N-CFA from XRD patterns. Sharp peaks of quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) are observed as the major crystalline phases. These two compounds account for most of the peaks. There is some distortion of the baseline in both samples, which indicates the presence of amorphous phases (Kashiwakura et al., 2009).

The ^{11}B MAS spectra of both (A) F-CFA and (B) N-CFA in Fig. 2 show peaks around 0 and 17 ppm that correspond to a four-coordinate (tetrahedral BO_4) and a three-coordinate (trigonal BO_3) boron oxide, respectively (Turner et al., 1983). These spectra clearly show that trigonal BO_3 is the dominant chemical state of boron in N-CFA, while both trigonal BO_3 and tetrahedral BO_4 are present in F-CFA. Furthermore, there are strong spinning side bands in the ^{11}B MAS spectra of N-CFA. As described elsewhere (Takahashi et al., 2009b), this observation implies that the boron and iron atoms in N-CFA are positioned at close range. The sidebands appear for the trigonal BO_3 , but not for tetrahedral BO_4 . Hence, we can infer that iron is close to the trigonal BO_3 .

To clarify the differences in the chemical state of boron, ^{11}B STMAS NMR spectra were

acquired. Figure 3 shows ^{11}B STMAS spectra for (A) F-CFA and (B) N-CFA with those of some borates. In the STMAS spectra, the projection on the isotropic axis provides a spectrum that is free from second-order quadrupolar interaction, whereas the projection on the MAS axis provides a spectrum that corresponds to the MAS spectrum (Amoureux et al., 2002). In the ^{11}B STMAS spectra of N-CFA, the trigonal BO_3 is observed predominantly, while in those of F-CFA, both trigonal BO_3 and tetragonal BO_4 are observed.

As seen from the contour plots of both samples, the center of gravity of the trigonal- BO_3 sites is positioned at the middle of the region for $\text{Ca}_2\text{B}_2\text{O}_5$ and $\text{Ca}_3\text{B}_2\text{O}_6$ and for $\text{Mg}_2\text{B}_2\text{O}_5$ and $\text{Mg}_3\text{B}_2\text{O}_6$. It cannot be denied that B_2O_3 is a dominant borate in F-CFA particles; however, the existence of boron as calcium or magnesium-bearing borate was also indicated in a series of our studies (Kashiwakura et al., 2009, Kashiwakura et al., 2010). However, the chemical state could not be assigned to either calcium borate or magnesium borate from the ^{11}B NMR spectra, because of their isomorphous crystal structures and similar surroundings around boron atoms. Therefore, elemental mapping of CFA particles was conducted by FIB-TOF-SIMS for the direct observation of elements that show strong correlation with the distribution of boron. SIMS is the most promising technique for detecting light elements such as boron, utilizing its high sensitivity and high lateral resolution.

Figure 4 shows the SIMS images of the major elements of F-CFA particles (A) and N-CFA particles (B). In N-CFA, there are two types of particles, which have clearly different

compositions. One is an $\text{Al}_2\text{O}_3\text{-SiO}_2$ particle, and the other is a CaO-MgO particle (Yamashita et al., 2000). In contrast, such phase separation as in N-CFA cannot be observed in F-CFA. Most particles comprise Al, Si, Mg, and Ca as the matrix elements, although each particle has a different composition.

Figure 5 shows the boron SIMS images with those of Si, Al, Mg, and Ca for N-CFA and F-CFA. In spite of such a small amount of boron in the CFA particles, direct monitoring was successfully conducted by using our prototype FIB-TOF-SIMS. The distribution patterns of boron in these two CFAs are certainly different. In N-CFA, boron is selectively concentrated in the CaO-MgO particles, and not found in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ particles. On the other hand, in F-CFA, boron is not concentrated in specific particles but distributed on every particle's surface. Hence, the distribution of boron in F-CFA does not show a strong correlation with that of any type of matrix elements.

Figure 6 shows the cross sections of elemental SIMS images and a scanning ion microscope image in N-CFA. As shown in Fig. 6, calcium and magnesium are distributed complementally, i.e., in a sea-island structure, and boron is strongly concentrated in the CaO phase, and not in the MgO phase. Furthermore, the FIB-TOF-SIMS analysis has proved our estimation (Takahashi et al., 2009b) that boron and iron in N-CFA are positioned at close range.

4. Discussion

In light of these results, the relationship between the chemical state of boron and its leaching behavior can now be discussed. Boron in F-CFA occurs as trigonal BO_3 and tetragonal BO_4 with various compositions, and is distributed on the outer surface of $\text{SiO}_2\text{-Al}_2\text{O}_3$ particles as a thin coating. According to the results of STMAS, boron exists at the surface as $\text{Ca}(\text{or Mg})_2\text{B}_2\text{O}_5$ and/or $\text{Ca}(\text{or Mg})_3\text{B}_2\text{O}_6$. In this case, the boron-bearing compound easily dissolves when it is exposed to water. As a result, boron is preferentially and quickly eluted into aqueous systems to yield a high leaching characteristic. In contrast, boron in N-CFA occurs as trigonal BO_3 with compositions of $\text{Ca}_2\text{B}_2\text{O}_5$ and $\text{Ca}_3\text{B}_2\text{O}_6$, and is distributed not only on the surface, but also in the interior of CaO-MgO particles.

Kashiwakura et al. (2010) reported that alkali earth borates, mainly calcium borates, absorbed at the surface of alumino-silicate particles and in calcia-magnesia ones are completely eluted in a hydrochloric acid aqueous solution of low pH in the range of 2.2 to 3.5. This means that the calcia-magnesia particles would be eluted in such pH ranges.

On the other hand, calcia-magnesia particles still remain after leaching tests in pH ranges of 5.8 to 6.2 according to the official method named “Notification #46” in Japan. As a result, the elution of boron in N-CFA is suppressed to less than 17%.

The origin of the difference in the chemical state of boron remains unclear. It may depend

strongly on the heating and cooling history during the coal combustion process and the chemical state of boron in the original coal. However, the boron-bearing compounds in F-CFA would be produced after the formation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ particles, whereas those in N-CFA would be produced in the very early stages of ash particle formation. Thus, the chemical state of boron might be determined by its initial occurrence mode or by the conditions of coal combustion.

5. Conclusions

The chemical state of boron in two types of CFA samples, which have different leaching behaviors, has been investigated by STMAS NMR and FIB-TOF-SIMS. The coordination number of boron was identified by ^{11}B STMAS NMR. Different distributions of boron in the CFAs are observed by FIB-TOF-SIMS imaging. In N-CFA, boron mainly appears as trigonal- BO_3 and preferentially concentrates in the CaO-MgO particles, especially in the CaO phase. In leaching tests, only the alkali earth borates, mainly calcium borates, which are distributed on the surface of the particles, dissolve in pH ranges of 5.8–6.2, while the borates that exist inside the calcia-magnesia particles remain after leaching.

On the other hand, in F-CFA, boron appears as trigonal (BO_3) and tetragonal (BO_4) oxides distributed on the outer surface of $\text{SiO}_2\text{-Al}_2\text{O}_3$ particles. Alkali earth borates absorbed at the surface of alumino-silicate particles are almost entirely eluted into water in an identical leaching test.

A combination of chemical state analysis with the aid of STMAS NMR and sub-micrometer elemental imaging by FIB-TOF-SIMS shows the definite relationship between the chemical state of boron in CFA and its leaching behavior. Hence, information regarding the chemical state of boron is useful for optimizing the combustion process, selecting the best coals for use in combustion at the electric power plant, and proposing a novel pretreatment process for CFAs to reduce the elution of hazardous elements.

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Table 1. Chemical compositions of the major elements and trace element (boron) for F-CFA and N-CFA.

Constituents (wt%)	F-CFA	N-CFA
SiO ₂	63.1	56.1
Al ₂ O ₃	20.5	31.6
Fe ₂ O ₃	3.99	3.66
CaO	5.84	3.99
MgO	1.37	0.95
B (ppm)	1050	540

Figure captions

Figure 1. XRD patterns of (A) F-CFA and (B) N-CFA.

●: SiO₂ ▲: Mullite

Figure 2. ¹¹B MAS spectra for (A) F-CFA and (B) N-CFA. An asterisk (*) indicates the spinning side band.

Figure 3. ¹¹B STMAS spectra for (A) F-CFA and (B) N-CFA.

Figure 4. Elemental (Si, Al, Mg and Ca) SIMS images of (A) F-CFA particles and (B) N-CFA ones.

Figure 5. B, Al and Ca SIMS images of (A) F-CFA particles and (B) N-CFA ones.

Figure 6. Cross sectional elemental SIMS images and SIM (Scanning Ion Microscope) image in N-CFA.

(a) Measurement of surface of particles

(b) Shave-off mode

(c) Measurement of cross-sectioned area of particles

180 degree rotation

FIG.1 Hayashi

FIG.2 Hayashi

FIG3. Hayashi

(A)

(B)

FIG.4 Hayashi

(A)

(B)

FIG.5 Hayashi

FIG.6 Hayashi