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MECHANISM OF SURFACE ENRICHMENT AND ADHESION
OF COAL COMBUSTION PARTICULATES

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ABSTRACT

During the first three months of the project, the emphasis has been on the following areas:

1. Design of the apparatus and development of the experimental techniques for the controlled adsorption of alkali on potential additives.
2. Development of techniques for the quantitative and qualitative characterization of alkali distribution in small additive particles using Scanning Auger Spectroscopy.

The preliminary experiments of the adsorption of NaCl on bauxite shows a very non-uniform distribution of alkali on the substrate. The chlorine appears to undergo some form of chemical interaction with alumina surface. An optimum set of electron beam parameters are found for which the alkali distribution is stable during Auger Spectroscopy and depth profiling by ion milling.

INTRODUCTION

Alkali compounds are present in raw coals to varying extents, depending largely on the grade of coal. The thermodynamic calculations of Lee and Johnson (1980) suggest that sodium and potassium are vaporized to a great extent in the form of their relatively volatile chlorides. Experience has shown that these alkali chloride vapors contribute significantly to fly ash agglomeration, fouling and corrosion of refractory linings and metal alloys.

One proposed method to reduce the concentration of alkali vapor species in combustors is to add an adsorbent to the coal feed. Several commercially available materials have been screened in our laboratory using a reactor under controlled atmosphere and temperature conditions. One of the most promising additives for alkali capture thus determined is activated bauxite. In order to exploit the maximum potential of bauxite as an adsorbent, it is desirable to know more about the way in which it adsorbs alkali chloride vapors.

Scanning Auger microscopy (SAM) is a powerful technique well suited to provide some insight into the nature of the adsorption process, but several problems must be solved before useful results can be obtained. Since bauxite is composed mostly of alumina, it is a poor conductor of electricity and thus very low beam currents must be used to avoid sample charging during analysis. This necessitates long collection times in order to get data with a reasonable signal-to-noise ratio. Since alkali chlorides are easily damaged by an electron beam, changes in surface structure due to analysis must be considered. Another problem is the high mobility of alkali ions in the presence of an electron beam. This can also result in changes of surface structure.

MATERIALS AND METHODS

Activated bauxite particles (Englehard Porocel, 60-80 mesh) were prepared by heating them in a fluidized bed (nitrogen atmosphere) at 950 degrees C for one hour. NaCl was adsorbed on the bauxite particles with the reactor system shown in Figure 1. Details of the reactor are given elsewhere (Punjak and Shadman, 1986). The NaCl vapor was generated at approximately 798 degrees C from a bed of solid NaCl. UHP nitrogen was used to transport the NaCl vapor to the bauxite bed (0.624 cc, 0.51 g) which was supported by a stainless steel screen. The bauxite bed was maintained at 800 degrees Celsius so that the NaCl vapor in contact with it was slightly under saturated. Adsorption was continued until approximately 23 mg of NaCl was passed through the bauxite bed. After adsorption, the particles were stored in a vacuum desiccator.

The particles were mounted on several 15 mm stainless steel disks with colloidal graphite suspended in isopropanol. The graphite was first painted on a portion of the disk and then the particles were sprinkled on the graphite before it dried. NaCl standards were prepared by putting a few drops of a dilute NaCl solution in a different area on the same disks. The samples were then allowed to dry overnight. Auger data was collected with a Physical Electronics ϕ -600 SAM. All analyses were performed with a 5.0 nA beam at 15.0 KV. This low current was necessary to avoid specimen charging. To check for the presence of sodium and chlorine, a 0-1450 eV kinetic energy survey was collected on several different particles with the electron beam in scan mode (1400X). When a particle with relatively high NaCl peak intensities was found, a more detailed analysis was performed.

Still in scan mode (2000X), a 0-1450 eV survey (Figure 2) was collected on a portion (Figure 4) of one particle (Figure 3) with the system parameters given in Table I. Prior to and just after this survey, as with all following

analyses, two-minute surveys were collected. This was done to check for evidence of surface damage. Next a more detailed survey (parameters given in Table II) was collected with only those kinetic energy windows containing the LVV Cl and $KL_{23}L_{23}$ Na peaks. The normalized N(E) peaks for Na and Cl are shown in Figures 5 and 6, respectively. Maps of all four elements for the same area of Figure 3 were collected with the parameters of Table III and are shown in Figure 7-10.

One of the regions of intense Cl and Na (see Figure 3, region #2) was then scanned (45,000X) with the same parameters given in Table II. The normalized N(E) peaks for the LVV Cl and $KL_{23}L_{23}$ Na from this survey are shown in Figures 11 and 12, respectively. Following the collection of this data, comparison of the short surveys revealed a change in surface structure (Figure 13), so a new region (region #1 of Figure 3) was examined. A depth profile (still at 45,000X) was collected for this area by alternating survey collection with surface sputtering. A 2 KV, 12 A/sec argon ion beam was used for sputtering. This data is shown in Figure 14.

The NaCl standard was analyzed using the same beam conditions (15.0 KV, 5.0 nA) with a 2000X scan area. The region of the standard chosen was where the NaCl had dried to thin, crystalline crust. The surface was sputtered until a brief survey indicated no carbon was present. Then a 0-1100 eV survey (Figure 2) was collected using the system parameters given in Table I. A more detailed survey of the LVV Cl and $KL_{23}L_{23}$ Na peaks was then collected and displayed in N(E) form (Figures 5,11 and 6,12, respectively) with the system parameters of Table II.

RESULTS

A comparison of the pre- and post-analysis two-minute surveys in all

cases, except the analyses at 45,000X, showed virtually no change in peak shape or height. By contrast, the analyses at 45,000X resulted in a reduction of the Na and Cl peak intensities with a corresponding increase in the oxygen and aluminum peak intensities.

It can be seen in Figure 5 that the LVV Cl peak for the NaCl adsorbed on bauxite (2000X) is shifted to a slightly higher energy and is broader than the corresponding peak for the standard. Figure 11 (NaCl adsorbed on bauxite, 45,000X), however, shows little energy shift between the standard and the sample, but the peak of the latter is still broader. The corresponding $KL_{23}L_{23}$ Na peaks (Figures 6 and 12) show no appreciable difference in peak energy and shape.

The distribution of Na and Cl is very non-uniform from particle-to-particle and on the surface of an individual particle, as evidenced by the elemental mappings (Figures 7-10). The maps do reveal, however, that a strong correlation exists between the presence of sodium and chlorine and a corresponding absence of aluminum and oxygen.

The depth profile, given as peak-to-peak heights as a function of sputter time in Figure 14, shows a sharp decline in Na and Cl during the first few seconds of sputtering (roughly 50 Å) followed by a more gradual decline. A corresponding increase in the aluminum and oxygen intensities was also observed.

DISCUSSION

The pre- and post-analysis surveys suggest little or no change in surface chemistry took place during data collection for the 200X analyses. By contrast, the 45,000X survey caused a significant change. Since the Na and Cl peak intensities declined, both were probably vaporized or driven into the

solid by the electron beam. In either case, only qualitative conclusions can be drawn from the data collected at 45,000X.

Based on the difference in peak shape and energy between the standard and sample for the LVV Cl peak, it appears that the chlorine may be interacting chemically with the alumina surface. In general, the increasing electronegativity of a bond results in a peak shift to lower energies (Briggs and Seak, 1983). This is consistent with the present findings since the NaCl bond is more electronegative than a Cl-O or Cl-Al bond. It must be kept in mind, however, that this could be an average effect; that is, chlorine is both in the form of NaCl and some species chemically bound to aluminum or oxygen. This could explain why the sample's Cl peak is broader than the standard's Cl peak and that the Cl peak for the 45,000X survey is not shifted as low in energy as the peak collected at 2000X. Since no appreciable difference in peak shape and energy is observed for the Na peak, the Na may be associated exclusively with NaCl.

The highly non-uniform distribution of Na and Cl could be due to the presence of isolated active centers on the bauxite. The particle-to-particle non-uniformity could also be explained by some limitation of the reactor used for adsorption. Despite its non-uniformity, the occurrence Na with Cl suggests it is still predominantly in the form of NaCl or, if it chemically interacts with the surface, the Na and Cl adsorbed species are highly non-mobile under the conditions at which they were absorbed. The low aluminum and oxygen intensities in the areas of high Na and Cl suggest that the peak intensities are genuine and not strictly associated with topography.

The depth profile results suggest that the Na and Cl are confined to the near surface region (top several atomic layers). The reason for the gradual decline in Na and Cl peak intensities after the initial rapid decline is not

clear. Since the bauxite surface has a lot of topography and microporous structure, it is possible that primary beam electrons are emerging from the surface (in a pore, for instance) and excite atoms as they enter the solid a second time. Another explanation is that some of the Na and Cl is being driven deeper into the surface during analysis/sputtering and consequently gets detected at long sputter times.

REFERENCES

Briggs, D. and Seah, M.P. (1983) Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy. John Wiley and Sons, New York, p. 193.

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TABLE I
SYSTEM PARAMETERS FOR
THE 2000X SURVEYS

Number of cycles:	49
Data acquisition time:	60.43 min
Volts/step:	1.00
Time/step:	50 msec
Beam voltage:	15.0 kV
Beam current:	5.0 nA

TABLE II
SYSTEM PARAMETERS FOR
THE 2000X AND 45,000X
DETAILED (REGION) SURVEYS

Number of cycles	2
Data acquisition time:	14.29 min
Volts/step:	0.50
Time/step:	50 msec
Number of sweeps:	50
Beam voltage:	15.0 kV
Beam current:	5.0 nA

TABLE III
SYSTEM PARAMETERS FOR
THE 2000X ELEMENTAL MAPS

Number of lines:	100
Number of sweeps:	2
Points/line:	100
Time/point:	50 msec
Beam voltage:	15.0 kV
Beam current:	5.0 nA

FIGURE LEGENDS

Figure 1: Reactor system for NaCl adsorption on bauxite: (a) Overall system schematic and (b) Reactor details.

Figure 2: Auger spectrum (2000X scan) of: (a) NaCl on bauxite of the region corresponding to the secondary electron image of Figure 4 and (b) NaCl standard.

Figure 3: Bauxite particle with adsorbed NaCl. Inset is the area photographed in Figure 4.

Figure 4: Region of bauxite particle in Figure 3 with adsorbed NaCl. Boxed region #1 is the area depth profiled (Fig. 14). Boxed region #2 is the area surveyed in detail at 45,000X (Fig. 11 and 12).

Figure 5: LVV chlorine peak for: (a) bauxite (2000X, Fig. 3) and (b) NaCl standard (2000x).

Figure 6: $KL_{23}L_{23}$ sodium peak for: (a) bauxite (2000X, Fig. 3) and (b) NaCl standard (2000X).

Figure 7: LVV chlorine Auger map of Figure 3. Brighter regions correspond to higher Cl peak intensities.

Figure 8: $KL_{23}L_{23}$ sodium Auger map of Figure 3. Brighter regions correspond to higher Na peak intensities.

Figure 9: $KL_{23}L_{23}$ oxygen Auger map of Figure 3. Brighter regions correspond to higher oxygen peak intensities.

Figure 10: $KL_{23}L_{23}$ aluminum Auger map of Figure 3. Brighter regions correspond to higher aluminum peak intensities.

Figure 11: LVV chlorine peak for: (a) bauxite (45,000X, region #2, Fig. 4) and (b) NaCl standard (2000X).

Figure 12: $KL_{23}L_{23}$ sodium peak for: (a) bauxite (45,000X, region #2, Fig. 4) and (b) NaCl standard (2000X).

Figure 13: Comparison of short surveys before (a) and after (b) detailed surveys of Figures 11 and 12. Note surface damage as revealed by reduction of Na and Cl peaks and increase of oxygen and aluminum peaks.

Figure 14: Depth profile of region #1 in Figure 4 (45,000X scan).

FIGURE 1

Reactor system for NaCl adsorption on bauxite: (a) Overall system schematic and (b) Reactor details

(a)

(b)

FIGURE 2

Auger spectra (2000X scan) of: (a) NaCl on bauxite of the region corresponding to the secondary electron image of Figure 4 and (b) NaCl standard

FIGURE 3

Bauxite particle with adsorbed NaCl. Inset is the area photographed in Figure 4. Beam voltage: 3.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

FIGURE 4

Region of bauxite particle in Figure 3 with adsorbed NaCl. Boxed region #1 is the area depth profiled (Fig. 14). Boxed region #2 is the area surveyed in detail at 45,000X (Fig. 11 and 12). Beam voltage: 15.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

(a)

(b)

FIGURE 5

LVV chlorine peak for: (a) bauxite (2000X, Fig. 3) and
(b) NaCl standard (2000X)

(a)

(b)

FIGURE 6

KL₂₃L₂₃ sodium peak for: (a) bauxite (2000X, Fig. 3) and
(b) NaCl standard (2000X)

FIGURE 7

LVV chlorine Auger map of Figure 3. Brighter regions correspond to higher chlorine intensities. Beam voltage: 15.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

FIGURE 8

KL₂₃L₂₃ sodium Auger map of Figure 3. Brighter regions correspond to higher sodium intensities. Beam voltage: 15.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

FIGURE 9

KL₂₃L₂₃ oxygen Auger map of Figure 3. Brighter regions correspond to higher oxygen intensities. Beam voltage: 15.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

FIGURE 10

KL₂₃L₂₃ aluminum Auger map of Figure 3. Brighter regions correspond to higher aluminum intensities. Beam voltage: 15.0 kV. Beam current: 5.0 nA. Tilt: 45 degrees. Aperture: 4 mils.

(a)

(b)

FIGURE 11

LVV chlorine peak for: (a) bauxite (45,000X, region #2, Fig. 4) and (b) NaCl standard (2000X)

(a)

(b)

FIGURE 12

$KL_{23}L_{23}$ sodium peak for: (a) bauxite (45,000X, region #2, Fig. 4) and (b) NaCl standard (2000X)

(a)

(b)

FIGURE 13

Comparison of short surveys before (a) and after (b) detailed surveys of Figures 11 and 12. Note surface damage as revealed by reduction of Na and Cl peaks and increase of oxygen and aluminum peaks.

FIGURE 14

Depth profile of region #1 in Figure 4 (45,000X scan)

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