Coal Combustion and Gasification Products is an international, peer-reviewed on-line journal that provides free access to full-text papers, research communications and supplementary data. Submission details and contact information are available at the web site.

© 2011 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association

Web: www.coalcgp-journal.org

ISSN# 1946-0198

Volume# 2 (2010)

Editor-in-chief: Dr. Jim Hower, University of Kentucky Center for Applied Energy Research

CCGP Journal is collaboratively published by the University of Kentucky Center for Applied Energy Research (UK CAER) and the American Coal Ash Association (ACAA). All rights reserved.

The electronic PDF version of this paper is the official archival record for the CCGP journal.

The PDF version of the paper may be printed, photocopied, and/or archived for educational, personal, and/or non-commercial use. Any attempt to circumvent the PDF security is prohibited. Written prior consent must be obtained to use any portion of the paper’s content in other publications, databases, websites, online archives, or similar uses.

Suggested Citation format for this article:

Fullerenes and Metallofullerenes in Coal-Fired Stoker Fly Ash

Luis F.O. Silva¹, Kátia DaBoit¹, Carmen Serra², Sarah M. Mardon³, James C. Hower⁴

¹ Catarinense Institute of Environmental Research and Human Development – IPADHC, Capivari de Baixo, Santa Catarina, Brazil
² Servicio de Nanotecnología y Análisis de Superficies C.A.C.T.I., Universidade de Vigo, Vigo, Spain
³ Kentucky Department for Natural Resources, Division of Abandoned Mine Lands, 2521 Lawrenceburg Road, Frankfort, KY 40601, USA
⁴ University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511, USA

A B S T R A C T

A suite of high-As, high-C fly ashes from a university-based stoker-fired coal boiler were analyzed by a number of techniques, including high-resolution transmission electron microscopy (HR-TEM), time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), and field-emission scanning electron microscopy (FE-SEM). The sooty carbon is in the form of nano balls with the major fullerenes at C₆₀⁺, C₇₀⁺, and C₈₀⁺, with species at Cᵢ increments from C₅₆⁺ to C₇₈⁺. Arsenic and Hg, among other metals, are found in association with the fullerenes, but, with our techniques, it is not possible to determine if the metals are encapsulated by the fullerenes or attached to the side of the structure. TOF-SIMS studies suggest an association of As with the Al-Si glass; an association of Pb with oxides, sulfates, and carbon; Hg with carbon; Se in elemental form with carbon; and Cr in a variety of forms, including nano carbons, Fe sulfates and oxides, glass, and Cr-oxyhydroxides.

© 2010 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association. All rights reserved.

A R T I C L E  I N F O

Article history: Received 24 September 2010; Received in revised form 1 January 2011; Accepted 14 January 2011

Keywords: fullerene; mercury; arsenic; selenium; coal combustion; fly ash

1. Introduction

The presence of fullerenes has been of great interest since their discovery in natural systems (Kroto et al., 1985), in part because of their characteristic structure, described as a cage by Dunsch et al. (2010) and nicholls et al. (2010), that can retain some potentially hazardous elements (Utsonomiya et al., 2002; Bai et al., 2003; Moses et al., 2003; Hower et al., 2008; Dunsch et al., 2010; Nicholls et al., 2010). Consequently, the questions of natural occurrence of fullerenes may have substantial environmental and human health implications should the future for multi-walled nanotubes (MWNTs) grow as predicted.

The chemical composition of coal-combustion fly ash varies with the chemical composition of the coal being fired and the combustion technology (Wang, 2008). In general, coal-combustion fly ash is comprised of small solid particles, small hollow particles (cenospheres), and thin-walled hollow spheres (plerospheres) containing both cenospheres and solid particles (Goodarzi and Sanei, 2009). Upon combustion in a coal-fired power plant, most volatile elements in coal, such as zinc and arsenic, will be released into the flue gas and subsequently captured by the fly ash, with the concentration of the element on the fly ash increasing as a function of both the decreasing flue gas temperature and the decreasing fly ash particle size at the point of capture (Mardon and Hower, 2004; Hower et al., 2010). In contrast, the capture of mercury, while also highly dependent upon the flue gas temperature, is also a function of the amount and form of fly ash carbon and on the chemistry of the flue gas (summary by Hower et al., 2010). Selenium, to date, has evaded characterization into either of the latter categories (Hower et al., 2009).

In this study, we are conducting a detailed study of the fine structure and the associated chemistry of carbons in the baghouse-collected fly ash from a coal-fired stoker steam plant. The petrology and bulk chemistry of the fly ashes had been previously discussed by Mardon et al. (2008).

Corresponding author: Tel.: 1-859-257-0261. E-mail: hower@caer.uky.edu

doi: 10.4177/CCGP-D-10-00007.1
© 2010 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association. All rights reserved.
Fig. 1. Examples of the most abundant glassy aluminosilicate spherical particles (FE-SEM and HR-TEM images).
2. Methods

2.1 Sample Collection

Selected fly ashes were collected from the baghouse hoppers of a university-based coal-fired stoker boiler (Mardon et al., 2008). The coal source was a medium-S, Pennsylvanian-age, eastern Kentucky high volatile A bituminous coal. The whole fly ash, sample 93261, and fractions wet screened at 100, 200, 325, and 500 mesh were available for this study.

2.2 X-Ray Diffraction

The mineral composition of coal fly ashes (CFA) was determined using a Siemens model D5005 X-ray diffraction. The samples were ground by hand in a ceramic mortar and pestle, dry mounted in aluminum holders, and scanned at 8–60° with Cu K-α radiation.

2.3 Electron Beam Methods

Electron beam methods included Field Emission Scanning Electron Microscope (FE-SEM) with energy-dispersive X-ray spectrometer (EDS) capabilities and high-resolution transmission electron microscope (HR-TEM) with SAED (selected area electron diffraction) or MBD (microbeam diffraction), and scanning transmission electron microscopy (STEM). Time of flight secondary ion mass spectrometry (TOF-SIMS) and Fast Fourier transformation (FFT) were used to investigate the elemental and molecular structure of the samples. Surface composition was determined by X-ray photoelectron spectroscopy (XPS). Procedures for the electron beam methods are outlined in Appendix A.

2.4 Mineral Extractions

As-received coal fly ashes (CFAs) were also analysed via XRD, FE-SEM, and HR-TEM. For appropriate geochemical interpretation, it is crucial to combine the application of XRD, FE-SEM, and HR-TEM mineralogical analyses of CFAs with sequential extraction (SE). This provides an improved understanding of the retention behavior of mobile elements by specific carbonaceous particles, primary minerals, and secondary soluble minerals. A brief explanation of the selected experimental conditions and of the expected information offered by each step of the sequential extraction are presented in Appendix A.

3. Results and Discussion

Coal-derived fly ash is primarily comprised of <10-nm- to >100-μm-diameter glassy aluminosilicate spheres (Figure 1). The combustion temperature of the coal was in excess of 1300 °C, slightly lower than pulverized-coal combustion boilers. In the present work, we detected different structures of metal-agglomerate-bearing carbons, including carbon fibers, graphitic particles, fullerenes, MWNTs, and amorphous carbon.

3.1 Petrology and X-Ray Diffraction Mineralogy

Details of the petrology of baghouse fly ash sample 93261 and the wet-screened size fractions from the ash were published by Mardon et al. (2008). As in most fly ashes, glass and amorphous carbon comprise the non-crystalline portion of the sample, with glass comprising the majority of the fly ash. X-ray diffraction revealed the presence of a number of mineral phases, including quartz, mullite, maghemite (spinel in Hower et al.’s (1995) nomenclature), magnesioferrite, wollastonite, microcline, and albite, not all detected in each fraction. The latter three minerals, in particular, were rarer than the other minerals.

3.2 Electron Beam Results

HR-TEM/EDS/SAED/MBD and Fast Fourier transformation (FFT) images show nano particles, some containing hazardous
Fig. 3. Left top - HR-TEM image of CNTs encapsulating fullerenes and Hg; Right top – Basic nanotube structure; Below - Illustration of our ideas related to formation and metals interaction in CNTs and fullerenes. Nanotubes can encase a C_{60} sphere which, in turn, can be associated with trace metals. On the right, two possible mechanisms for trace element association are illustrated. At the scale of this study, it is not possible to resolve the nature of the association.
elements (Figures 2–5). Most carbon species were found as 10–
200nm carbon nano balls (Figure 2A and 2B), corresponding to
soot or black carbon with concentrically stacked graphitic layers
(as also noted by Chen et al., 2006; Nejar et al., 2007). The fractal-
arranged aggregates vary in size and exhibit a microtexture
consisting of roughly concentrically stacked graphitic layers
(Figure 2B). This is a form of amorphous carbon that gives fly ash
characteristics of a dark and wet powder and is a major
component of smoke from the combustion of carbon-rich organic
fuels in the absence of sufficient oxygen (Chen et al., 2006). Many
hazardous-element/carbon-particle aggregates (containing, for
example, Br, Mo, Se; Figure 2A) form via a vaporization–
condensation mechanism during coal combustion and the cooling
of the flue gas and fly ash in the pollution-control devices. Their
presence in coal fly ash samples and the carbon content detected
by ultimate analysis and HR-TEM/EDS suggests incomplete coal
combustion.

Other carbon structures were observed and characterized as
onion-structured or related concentric, multishell carbon nano-
pyhedra (Murr et al., 2005), reminiscent of high-temperature
treatments of soot catalyzed by metals that transform the typical
amorphous soot aggregates to more regular fullerenes (Cobo et al.,
2009). In this process, the precursor fragments are curved around
the metal catalyst, but flat-sheet fragments also form an aggregate
into nanospherules or spherule aggregates.

HR-TEM analysis provides evidence of weak metal/support
interactions, with carbon nanotube (CNTs) tip growth visible
(Figure 3). CNT tip-growth is suggested to occur when a low-
strength interaction exists between the metal and the support.
Similar environments were discussed by several studies (Baker,
1989; Kuznetsov et al., 2003; Du et al. 2007; Hower et al. 2008).
While suggested as a possible model, it cannot be known at this
scale of analysis whether the metals are bound within the fullerene
balls or bound to the side of the structures.

The encapsulation of potentially hazardous elements such as As,
Cd, Co, Cr, Hg, and Ni inside MWNTs are of considerable
importance in environmental science. A large number of nanotube
ends are visible in the coal fly ashes (particularly after Step 4 from
Appendix A), including both terminations at hazardous metal
particles and metallofullerenes, offering an opportunity to examine
dimensionally confined systems. Encapsulated hazardous ele-
ments (e.g. Hg, Figure 3) are also likely to contribute to element
retention in power plant fly ashes, resisting degradation due to
their surrounding protective carbon shells (Sun et al., 2002). Studies have been made of the encapsulation of iron-group metals
within the carbon shells, with fewer investigations of the transition
metals (Byeon and Kim, 2010). In the carbon-encapsulated-
hazardous-element nanoparticles (CEHENs) studied here, several
nanometer-thick carbon shells provide chemical stability and
protection from the agglomerates of element nanoparticles (e.g
Figure 4), while the nanosized core metal particles can provide
specific functions that are unavailable in bulk form.

3.3 TOF-SIMS Characterization of Fullerenes

Positive-ion TOF-SIMS analysis, maintaining a primary ion dose
less than $10^{12}$ ions/cm$^2$ to ensure the static SIMS conditions, results
in minimum surface destruction. The positive spectrum was
calibrated to H$^+$, H$_2^+$, H$_3^+$, C$^+$, CH$^+$, CH$_2^+$, CH$_3^+$, C$_2$H$_3^+$, C$_3$H$_5^+$,
C$_4$H$_7^+$, C$_5$H$_9^+$ and C$_6$H$_{11}^+$. The negative TOF-SIMS spectrum was
not considered in this study due its minimal information content
and the absence of molecular fullerene peaks.

The TOF-SIMS peaks between the mass 650 amu and 970 amu,
the region where fullerene ions should appear, is shown on
Fig. 5. (A) As-bearing jarosite following water extraction (fly ash100×500): STEM image and mapping to As (in red) and Fe (in green); (B) Jarosite crystals contain mixed As-O-Pb amorphous; (C) As-bearing carbonaceous material; (D) Spherical Al-Si-Pb particle and carbonaceous matrix with Pb-oxide nanoparticle.
Figure 6. In this region, we have detected the fullerene peaks corresponding to C$_{60}^+$ at 720 amu, C$_{70}^+$ at 840 amu, and C$_{80}^+$ at 960 amu but we have also detected intermediate fragments which correspond to the consecutive loss of two units of carbon (C$_2$ loss) from each of the principal fullerene molecules. Therefore, from C$_{60}^+$ and due to carbon depletion phenomena, we have detected C$_{58}^+$ and C$_{56}^+$. From C$_{70}^+$ we have also detected C$_{68}^+$, C$_{66}^+$, C$_{64}^+$, and C$_{62}^+$ and from C$_{80}^+$ we have detected C$_{78}^+$, C$_{76}^+$, C$_{74}^+$, and C$_{72}^+$. This phenomenon of loss or depletion of two carbons in fullerenes has been reported by Foltin et al. (1993) and Kato et al. (2008).

3.4 Volatile Element Behavior

Hazardous-element-bearing anthropogenic nanoparticles and secondary nanominerals are attracting attention due to their unique role as agents of elemental transport and their enhanced reactivity in thermal systems (Hochella et al., 2008; Hower et al., 2008; Graham et al., 2008; Silva et al., 2009; Silva and DaBoit, 2010). The behavior of nanoparticles and nanominerals in anthropogenic systems within coal-fired power plants is still not well understood due to a lack of experimental evidence about their physical-chemical properties. While a decrease in particle size to the nanoscale level can promote phase instability due to the increase in surface energy (Reich et al., 2006), information is needed on how nanoscale effects influence the occurrence of nanoparticles at high-temperature conditions.

In general, the combustion of coal results in a redistribution of the solid byproducts into approximately 20–25% bottom ash, 75–80% fly ash (Stultz and Kitto, 2005), and <0.5% fine particles emitted from the stack (Goodarzi, 2006; Goodarzi et al., 2008). In oxidizing environments in coal-fired power plants, metals tend to be converted into (or trapped by) less-volatile compounds, such as oxides, sulfates, amorphous aluminosilicates, and carbonaceous phases. The volatile trace element behavior of As, Hg, Se, Pb, and Cr were observed mainly in individual particles (usually occurring as individual <100 nm-size particles) and will be discussed below with respect to their fate in the environment and impact on health.

3.4.1 Arsenic

Arsenic exposure in humans is associated with increased risks of leukemia and skin, lung, liver, breast, bladder, and bone cancers (Lyman et al., 1985), and is the result of chronic ingestion or chronic inhalation. The dose-response curve is dependent on location, sources, and population susceptibility and/or tolerance (Fergusson, 1990; Ding et al., 2001; Mandal and Suzuki, 2002). Coal-fired power plants are a significant anthropogenic source of fine- and nano-As particles (Figures 4, 5 and 7), and power station emissions have received considerable attention as they are
associated with a number of types of fine-particle pollution which may contribute to health effects. However, As-CFA interactions are complex.

HR-TEM and FE-SEM investigations demonstrate that As-CFA is associated with amorphous nanoparticles (Figure 4), sulfates (e.g. jarosite, Figure 5), CEHENs-bearing fullerenes, Fe, and Al-oxide deposits on the particles of CFA. However, it was difficult to estimate the total number of nanoparticles due to their short lifetime under the HR-TEM and FE-SEM beam, particularly for hydrated sulfate and nitrate salts species. The combination of FE-SEM/EDS, STEM/EDS, hazardous/volatile elements mapping, and HR-TEM/SAED/FFT was important in investigations of nanoparticles and nanominerals in CFAs samples (e.g. Figure 5A of As-bearing jarosite). In addition, the high resolution spectrum of As$^{3d}$ obtained by XPS showed the presence of As at the sample surface. The position in binding energy of the peak As$^{3d_{5/2}}$ at 45.85 eV can be attributed to As$_2$O$_5$ - As(V) (Figure 7).

The surface chemical maps obtained by TOF-SIMS corresponding to As and Al distribution are shown in Figure 8. The aluminum distribution is ubiquitous across the surface, but is most intensive in the center of the image. The arsenic (AsO) signal is detected in much lower intensity than the Al but its distribution shows concordance with the Al distribution, suggesting that the As detected is on the surface of the Al-Si glassy fly ash particles.

### 3.4.2 Lead

Human exposure to Pb occurs through various intermediate routes, but there are four main pathways of Pb from the environment to humans: inhaled aerosol particles, dusts, food, and drinking water (US EPA, 2008). High concentrations of Pb cause serious problems in the central nervous system, peripheral nervous system, and the vascular system of humans (Mejia et al., 1997). Both PbO and Pb-arsenate are listed in the Hazardous Substance Data Bank (NLM, 2008). In addition, Pb sulfate is listed in the Toxicology Data Network (NLM, 2008). In general, Pb sulfate appears to be more toxic than elemental Pb upon ingestion; overall, Pb compounds are more toxic when inhaled than when administered via other routes.

In the present study, the Pb phases identified by FE-SEM, HR-TEM, EDS, FFT, SAED, and MBD include Pb-oxide [e.g. massicot (PbO), Figure 5D], Pb-sulfate (e.g. anglesite as isolated particles ~50–300nm in length), Pb encapsulated in carbonaceous matter (e.g. Figure 5D), abundant amorphous minerals, and a Pb-As phase in the respirable particle matter category. Our results emphasize the need for detailed single-nanoparticle characterization of anthropogenic nanoparticle and secondary nanominerals emitted from coal-fired power stations.

![Fig. 8](image1.png) TOF-SIMS image of overlapping Al and AsO (in blue) showing the concordance between both signals.

![Fig. 9](image2.png) XPS spectra of the binding energy of Pb at the fly ash surface.
The high resolution spectrum of Pb 4f obtained by XPS showed the presence of Pb at the sample surface (Figure 9). The position in binding energy of the Pb4f\textsubscript{7/2} at 139.9 eV can be attributed to PbSO\textsubscript{4} \textsuperscript{2-} - Pb (II), in excellent concordance with anglesite phase detected by FE-SEM, HR-TEM. TOF-SIMS results also demonstrate the presence of Pb in the fly ash samples. Lead was detected in elemental form in conformity with the expected isotopic distribution for this element (Figure 10).

### 3.4.3 Mercury and Selenium

Coal power plants are the largest point sources of Hg release to the atmosphere. The high Hg and Se concentration in the CFA...
The relationship between carbon nanoparticles, Se (Figure 2A), and Hg (e.g. Figure 3) suggests that there were other (metallofullerene, elemental metals, and metal-bearing organic compounds) factors involved in the relationship between carbon nanoparticles and these elements. FE-SEM/EDS and HR-TEM/EDS results indicate that the carbon (e.g. fullerene, amorphous carbon, and MWNTs) in CFA is responsible for capturing some of the Hg and Se, suggesting higher carbon content would yield a higher Hg and, perhaps, Se content in the CFA. The relationship between fly ash carbon and Hg capture is well established for pulverized-fuel (pf) fly ashes, in general (Hower et al., 2010), and for fullerenes in pf ashes (Hower et al., 2008). For the stoker fly ash, a possible explanation for this might be that the lower combustion temperature in the boiler (compared to pulverized fuel boilers) may benefit Hg and Se condensation/absorption on, and inclusion within, the nanocarbon particles, thus influencing element trace capture and/or encapsulation.

Fig. 12. XPS spectra of the binding energy of Cr at the fly ash surface.

Fig. 13. A/ TOF-SIMS images of Al, Fe, and Cr distribution on fly ash. B/ Overlap of Al and Fe TOF-SIMS images. C/ Overlap of Al and Cr TOF-SIMS images.
Despite the low Se-concentrations detected by EDS, nanoparticles of amorphous elemental Se have been observed in the CFA by SAED, MBD, and FFT. In general, in our FE-SEM and HR-TEM images, Se appears in dark, rounded nanoparticles (e.g. Figure 2A and Figure 4). EDS spectra of Se-rich regions do not display an oxygen peak. In general, these particles consist of Se (93.8 wt%), with minor Al (2.2 wt%), Si (2.7 wt%), and S (1.3 wt%). Based on these observations and the Se reaction path, it is reasonable to speculate that the Se-particles observed in our CFA consist of elemental Se encapsulated by carbonaceous nanoparticles.

3.4.4 Chromium

In the present study, the Cr phases identified by FE-SEM, HR-TEM, EDS, FFT, SAED, and MBD include Cr-oxide (e.g. chromite); Cr encapsulated in carbonaceous matter containing amorphous Al-Si (e.g. Figure 11); absorbed in Fe-sulfates (e.g. schwertmannite, paracoquimbite, and jarosite) and/or Fe-oxides (e.g. hematite and magnetite); in association with aluminosilicate phases (such as glass); and poorly crystallized chromium oxyhydroxide (CrOOH). The high resolution XPS spectrum of Cr2p shows the presence of a very low intensity Cr signal at the sample surface (Figure 12). The position in binding energy of the Cr2p3/2 is around 576.7 eV, which is normally attributed to chromium oxide Cr(III). TOF-SIMS illustrates the coincidence of Al-, Fe-, and Cr-bearing areas (Figure 13), which would suggest a spinel association, but does not provide added clues to the dominance of any single Cr association.

4. Summary

Fly ashes collected from the baghouse of a university-based coal-fired stoker boiler were analyzed by XRD and a number of electron beam techniques, including HR-TEM, TOF-SIMS, XPS, and FE-SEM.

The fly ashes, derived from an eastern Kentucky high volatile A bituminous coal, were dominated by an Al-Si glass and fine carbon. XRD results showed that the mineral phases included quartz, mullite, maghemite, and magnesioferrite; with lesser amounts of wollastonite, microcline, and albite in some of the samples.

The original ash, as discussed by Mardon et al. (2008), had significant concentrations of some trace elements, including As and Hg. Some of the sooty carbon is in the form of nano-carbon balls. TOF-SIMS peaks between 650–970 amu show the major fullerenes at C_{60}^+, C_{70}^+, and C_{80}^+ and species from C_{56}^+ to C_{78}^+ reflecting C_2 loss from the major species. HR-TEM indicated the association of metal, including As and Hg, associations with fullerenes and multi-walled nanotubes. At the level of resolution available with HR-TEM, it is not possible to determine if the metals are bound within the fullerene balls or to the side of the structure. In either case, the association with the carbons contributes to the retention of trace metals in fly ashes.

TOF-SIMS analysis indicated a correspondence between the location of As and Al on the surface, indicating some As association with the Al-Si glass component of the fly ash. Lead phases included oxides, sulfates, and Pb associated with the carbon. As anticipated, mercury was noted to be in association with carbon. Selenium, although in low concentrations, appears to be present in elemental form in association with the nano carbons. Chromium is encapsulated by nano carbons, adsorbed in Fe-sulfates or Fe-oxides, in association with glass, and in the form of Cr-oxyhydroxide. While there is some indication of an association of Cr with spinel minerals, TOF-SIMS did not provide an indication of a dominant Cr association.

Acknowledgements

The work performed by the group from Brazil (FE-SEM, HR-TEM, XRD, and mineral extractions) was carried out with support from the Catarinense Institute of Environmental Research and Human Development – IPADHC.

References

Fergusson, J. E., 1990. The heavy elements, chemistry, environmental impact and health effects; Pergamon, NY.

Human Development – IPADHC.


Appendix A

A.1 Field Emission Scanning Electron Microscope (FE-SEM) and High-Resolution Transmission Electron Microscope (HR-TEM) Procedures

Field Emission Scanning Electron Microscope (FE-SEM) and high-resolution transmission electron microscope (HR-TEM) allow the direct (real space) visualization of nanominerals and ultra-fine particles. In this investigation morphology, structure, and chemical composition of ultrafine particles and minerals were investigated using a FE-SEM Zeiss Model ULTRA plus with charge compensation for all applications on conductive as well as non-conductive samples and a 200-keV JEOL-1010F HR-TEM equipped with an Oxford energy dispersive X-ray detector, and a scanning (STEM) unit (Silva and DaBoit 2010). The FE-SEM was equipped with an energy-dispersive X-ray spectrometer (EDS) and the mineral identifications were made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes (Silva et al., 2009a, b). Geometrical aberrations were measured by HR-TEM and controlled to provide less than a π/4 phase shift of the incoming electron wave over the probe-defining aperture of 14.5 mrad (Silva et al., 2010c). The scanning acquisition was synchronized to the AC electrical power to minimize 60-Hz noise, and a pixel dwell time of 32 μs was chosen. EDS spectra were recorded in FE-SEM and HR-TEM images mode and then quantified using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into atomic or weight percentages. Electron diffraction patterns of the crystalline phases were recorded in SAED (selected area electron diffraction) or MBM (microbeam diffraction) mode, and the d spacings were compared to the International Center for Diffraction Data (ICDD, 2010) inorganic compound powder diffraction file (PDF) database to identify the crystalline phases. Hexane, acetone, dichloromethane, and methanol suspensions were utilized to prevent possible mineralogical changes in individual solvents. The suspension was pipetted onto lacy carbon films supported by Cu grids (200 mesh) and left to evaporate before inserting the sample into the FE-SEM and HR-TEM. This method may have led to agglomeration but is a widely used standard procedure for most minerals, including metal sulphates (Giere et al., 2006; Silva et al., 2010b, c). Before FE-SEM and STEM analysis, the HR-TEM specimen holder was cleaned with an Advanced Plasma System-APS (Gatan Model 950) to minimize contamination. A drift correction system was used for the STEM-EDS mapping.

A.2 X-Ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) Procedures

Detailed information on both the surface and internal structures of CFA micro and nanoparticles, plays an important role in the development of new analytical techniques for toxic compounds on and beneath the surface (Sakamoto et al., 2003; Silva et al., 2009a). However, conventional analytical techniques such as XRD, FE-SEM, HR-TEM, ICP-AES and ICP-MS evaluate the morphology and average concentration of trace elements in bulk samples, but do not provide information on their chemical state or molecular structure at the outermost surface where many chemical changes occurs. Therefore we have employed surface sensitive techniques to afford the chemical analysis of the surface.

Time of flight secondary ion mass spectrometry (TOF-SIMS IV instrument from Ion-Tof GmbH) was applied to investigate the elemental and molecular structure of the samples giving the possibility of a better understanding of the chemical composition, localization and relative quantity of the different present species at the surface. The secondary ions collected and represented at the TOF-SIMS experiment, the sample was bombarded with a pulsed Bismuth ion beam. The secondary ions generated were
extracted with a 10 KV voltage and their time of flight from the sample to the detector was measured in a reflection mass spectrometer. Typical analysis conditions for this work were: (1) 25 keV pulsed Bi\textsuperscript{182} beam at 45° incidence, rastered over 200×200 μm\textsuperscript{2} for spectroscopy and 464×464 μm\textsuperscript{2}; for mapping (2) Low energy Flood Gun was applied compensate the surface charge during the experiments. As a result, the surface excitation by particle bombardment leads to the emission of secondary ions characteristic of the chemical composition in the uppermost monolayer. For each type of molecule, secondary ion emission results in a characteristic set of ionized molecular fragments with well-defined mass spectra. These secondary ions are analyzed with respect to their mass to charge ratio. In a time-of-flight (TOF) mass spectrometer the separation is based on the fact that ions of the same energy that have different masses have different flight times towards the detector.

The chemical maps produced by TOF-SIMS represent the ions that reached the detector rather than the ions that were present on the surface, and each solid has its own characteristic ability to release ions, so intensities cannot be used to derive absolute surface concentrations. However, chemical maps are very good at indicating relative surface concentration and its change as a function of sample treatment or time. This technique provides information on the elemental distributions not only at the surface but also in the interior of a CFA particle (Hayashi et al., 2010).

In the case of coal fly ash, the presence of a wide range of organic and inorganic compounds was determined. In general terms the composition of this kind of samples is very complex, and we have detected light elements, heavy metals, and hydrocarbons. In general terms, we will emphasize the regions of the spectrum that have the maximum interest: polluting heavy metals and fullerenes.

For high resolution chemical state investigation we have applied XPS which provides information about surface composition with spatial resolution of a millimeter or less, with information depth limited to 10 nanometers. This allows the possibility to investigate the average chemical nature of the solid. Chemical identity, bonding structure, and reox state can be determined. XPS analysis of the CFA samples was performed using a Thermo Scientific K-Alpha ESCA instrument equipped with aluminum Ka\textsubscript{1,2} monochromatized radiation at 1486.6 eV X-ray source. Due the non conductor nature of samples it was necessary to use an electron flood gun to minimize surface charging. Neutralization of the surface charge was performed by using both a low energy flood gun (electrons in the range 0 to 14 eV) and a low energy Argon ions gun. The XPS spectra for CFA were obtained using X-ray photoelectron spectrometer with a monochromatized Al K\textalpha\ (1486.6 eV) source. The pressure in the analytical chamber was below 10-9 mbar. The survey and narrow scans were recorded with pass energy of 100 and 20 eV, respectively. In order to obtain oxidation status of surface contaminants, narrow scan spectra of the C 1s, Cr 2p, S 2p, O 1s, As 3d, and Pb 4f were acquired. Due to the nature of the sample, it would be expected that charge effects could occur, resulting in the shifting of spectra. To prevent problems we have used a dual beam (electrons and Argon ions) to compensate the surface charge. To calibrate in binding energies, the peak at the lower binding energy in the C1s spectrum was fixed at 285 eV and was used as a binding energy reference. The narrow scan spectra were fitted using an Avantage fitting program with Gaussian Lorentzian function through background-subtraction corrections using a Shirley-type optimization. The atomic concentrations were determined from the XPS peak areas using the Shirley background subtraction technique and the Scofield sensitivity factors. The High Resolution spectra were recorded, acquiring several scans (40 scans) in order to improve the signal/noise ratio, for the minor elements including Cr, Pb, and As.

Sample preparation for TOF-SIMS and XPS examination: Special preparation of the sample was done to prevent – in both instruments- that any particle can be accidentally detached from the sample holder inside the analysis chamber. The sample preparation consists only of a process for powders compaction (molded), which was done using a pneumatic press and by obtaining tablets.

A.3 Sequential Extraction Procedures

1) For the water-soluble fraction, a 1-mg CFAs sample (five replicates) was mixed with Millipore-system water (1mL) with electric conductivity of0.1–0.5\textmu S/cm. Samples were shaken in the dark for 4 h, then centrifuged (3000 rpm, 10 min) and filtered (< 22 μm). This extraction dissolves salts (e.g. epsomite, albite, and pickeringite), jarosite, alunogen, gypsum (partially soluble in water), and other minerals soluble in water. For the secondary sulfates and salts formed in CFAs environments, such an initial water-extraction step is essential for a complete understanding of materials involved. The solid fraction was cold dried, suspended in acetone, pipetted on to separated lacy carbon films supported by Cu grids, and left to evaporate before inserting the sample into the FE-SEM and HR-TEM. The liquid fraction was air dried/crystallized before inserting the sample into the XRD, and FE-SEM.

2) Exchangeable fraction, 1M NH\textsubscript{4}-acetate pH 4.5, samples were shaken in the dark for 2 hours at room temperature, then centrifuged (3000 rpm, 10 min) and filtered (<22 μm). This extraction dissolves vermiculite-type mixed-layer, absorbed, and exchangeable ions (Dold, 2003).

3) For poorly ordered Fe and Al oxyhydroxides/sulphates (Gagliano et al., 2004; Regenspurg et al., 2004), a 1-mg mineral sample (five replicates) was mixed with ammonium oxalate (1mL) reagent (28 g/L ammonium oxalate + 15 g/L oxalic acid solution, pH ~ 2.7). The samples were then shaken in the dark for 4 hours, centrifuged (3000 rpm, 10 min) and filtered (<22 μm) (Peretyazhko et al., 2009). This extraction dissolves poorly-crystalline Fe (III) oxides (e.g. ferrihydrite, schwertmannite) in preference to more insoluble crystalline Fe (III) oxides (e.g. goethite, hematite) (Cornell and Schwertmann, 2003; Silva and Da Boit, 2010). More than 85% of the total iron was released in this step. The solid fraction was cold dried before inserting the sample into the Raman, XRD, FE-SEM, and HR-TEM.

4) Highly ordered Fe\textsuperscript{III} hydroxides and oxides (hematite and goethite) were partially dissolved by acid ammonium oxalate (Kumpulainen et al., 2007) using a SE step described by Dold (2003). As in step 2, the extractant used was 0.2 M NH\textsubscript{4}-oxalate for 2h, but in this case the samples in batch system were exposed to light and heated to 80 °C in a water bath. The solid fraction was cold dried, suspended in toluene, pipetted onto separated lacy carbon films supported by Cu grids, and left to evaporate before inserting the sample into the FE-SEM and HR-TEM. The liquid fraction was air dried/
crystallized before inserting the sample into the XRD and FE-SEM.

5) For organic matter (after steps 1–4) a 0.1-mg resultant CFAs sample (five replicates) was mixed with 1 mL of dimethyl sulfoxide (DMSO) reagent. The samples were shaken in the dark for 12 hours, then centrifuged and filtered (< 22 µm). This extraction dissolves organic anions absorbed on Al-OH/Fe-OH surface of minerals, due to electrostatic interactions, and can lead to increased repulsion between uniformly and negative charged particles;

6) Residual organic and secondary metal-sulfides were mixed with 35% H2O2 heat in water batch for 1 hour, then centrifuged and filtered (< 22 µm). This extraction dissolves sulfides (chalcopyrite, cinnabar, galena, pyrite, sphalerite, stibnite, and tennantite-tetrahedrite). The solid fraction was hot dried (100 °C), suspended in toluene, and pipetted onto lacy carbon films supported by Cu grids (400 mesh). Before FE-SEM analysis, the HR-TEM specimen holder was cleaned with an APS to minimize contamination.

References