**INVESTIGATION OF FLY ASH AND ACTIVATED
CARBON OBTAINED FROM PULVERIZED COAL BOILERS**

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ABSTRACT

One of the techniques for Hg capture in coal-fired boilers involves injection of activated carbon (AC) into the boiler downstream of the air preheater. Hg is adsorbed onto the AC particles and fly ash, which are then both removed in an electrostatic precipitator or baghouse.

This project addresses the issues of Hg on activated carbon and on fly ash from a materials re-use point of view. It also addresses the possible connection between SCR reactors, fly ash properties and Hg capture. The project is determining the feasibility of separating AC from fly ash in a fluidized bed and of regenerating the separated AC by heating the AC to elevated temperatures in a fluidized bed. The temperatures needed to drive off the Hg from the ash in a fluidized bed are also being determined. Finally, samples of fly ash from power plants with SCR reactors for NO_x control, are being analyzed to determine the effect of SCR on the ash. These analyses will also determine the properties of ash which are important for Hg capture.

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INTRODUCTION

One of the techniques for Hg capture in coal-fired boilers involves injection of activated carbon (AC) into the boiler downstream of the air preheater. Hg is adsorbed onto the AC particles and onto the fly ash, which are then both removed in an electrostatic precipitator or baghouse. While field trials with AC injection have demonstrated the ability to remove significant fractions of the Hg at some units, there are also problems in using AC for Hg capture. Activated carbon is relatively expensive, leading to very high projected costs for Hg capture (Ref. 1, 2). The AC can increase opacity at units with electrostatic precipitators, due to increased particulate loading and the low resistivity of AC particles. The feed rates of AC required to control Hg can also result in significant increases in the carbon content of the ash. However, fly ash used in concrete must have carbon contents of 4% or less in order that the concrete have acceptable mechanical properties. This has raised concerns that widespread use of AC for Hg capture will eliminate concrete as a viable market for re-use of ash, thereby greatly reducing the percentage of coal ash which can be re-used.

Laudal et al. (Ref. 3) reported data from field tests at 4 boilers equipped with SCR reactors in which Hg emissions were measured with and without the SCR reactors in operation. The results showed that in 3 of the 4 cases, the SCR reactors caused a reduction in gas phase emissions of Hg, but the actual cause of the reduction needs to be determined.

This project addresses the issues of Hg on activated carbon and on fly ash from a materials re-use point of view. It also addresses the possible connection between SCR reactors, fly ash characteristics and Hg capture. The project is determining the feasibility of separating AC from fly ash in a fluidized bed and of regenerating the separated AC by heating the AC to elevated temperatures in a fluidized bed. The project is also determining the temperatures needed to drive off the Hg from the ash in a fluidized bed. Finally, samples of fly ash from power plants with SCR reactors for NO_x control are being analyzed to determine the effects of SCR on the ash.

Objectives

The objectives of this project are as follows:

- Determine the potential for separation of AC from fly ash in a bubbling fluidized bed
- Determine the temperatures needed to remove Hg from spent AC in a bubbling fluidized bed, thereby creating the possibility of recycling regenerated AC back to the boiler
- Determine the temperatures needed to remove Hg from fly ash in a bubbling fluidized bed
- Determine which components of fly ash are important for Hg capture
- Determine if SCR reactors affect fly ash chemistry in relation to Hg capture

EXECUTIVE SUMMARY

One of the techniques for Hg capture in coal-fired boilers involves injection of activated carbon (AC) into the boiler downstream of the air preheater. Hg is adsorbed onto the AC particles and fly ash, which are then both removed in an electrostatic precipitator or baghouse.

This project addresses the issues of Hg on activated carbon and on fly ash from a materials re-use point of view. It also addresses the possible connection between SCR reactors, fly ash properties and Hg capture. The project is determining the feasibility of separating AC from fly ash in a fluidized bed and of regenerating the separated AC by heating the AC to elevated temperatures in a fluidized bed. The temperatures needed to drive off the Hg from the ash in a fluidized bed are also being determined. Finally, samples of fly ash from power plants with SCR reactors for NO_x control, are being analyzed to determine the effect of SCR on the ash. These analyses will also determine the properties of ash which are important for Hg capture.

Progress made during the last year is described in the following paragraphs:

Task 1 experiments were performed with a mixture of activated carbon and fly ash to determine to what extent the activated carbon and naturally occurring carbon can be separated from the remainder of the mixture in a fluidized bed. The data show segregation is very sensitive to superficial gas velocity, with the strongest segregation occurring at superficial velocities of 0.7 to 0.8 cm/s. At these conditions, the carbon content at the top of the bed was approximately 27% and it was less than 17% in the bottom layer. Very little or no carbon segregation occurred at velocities much lower or higher than 0.7 to 0.8 cm/s. Samples of AC/Ash obtained from each layer of the bed during the tests at 0.6, 0.7 and 0.8 cm/s were analyzed for Hg content using the LECO Hg Analyzer. These results show a strong dependence of Hg capture on particle carbon content, with the Hg content approaching a value close to zero as LOI approaches zero.

Task 2 experiments were performed with the AC/ash mixture in a heated fluidized bed to determine the temperature at which Hg is driven off. The data from each test show a relatively constant Hg concentration until a temperature of approximately 320 to 380°C was reached, after which the Hg concentration decreased rapidly with temperature. The Hg concentration approached zero at temperatures close to 500°C.

One activated carbon/ fly ash mixture has been tested, so far, in Tasks 1 and 2. This mixture was obtained from a Hg- capture field trial at a utility boiler. The extent of the ability to separate carbon from non-carbonaceous ash constituents in a fluidized bed will vary from boiler to boiler due to differences in particle size and density distributions. We also suspect the Hg desorption temperature varies with the physical and chemical characteristics of the AC/ash mixture. As additional Hg-capture field trials are carried out and we are able to obtain additional suitable AC/ash samples, we plan to perform more experiments on carbon separation and Hg desorption.

During this last year, considerable effort went into using Scanning Electron Microscopy and Transmission Electron Microscopy to study the physical and chemical characteristics of the AC/ ash mixture used for the Task 1 and 2 experiments. Five distinct morphologies have been identified: large (30-100 μm), irregularly-shaped carbon particles, 0.1 to 20 μm spherical alumino-silicate particles, 50-100 μm hollow carbon particles with porous walls, fine 50-200 nm amorphous carbon particles, and large 20-50 μm angular activated carbon particles. With this background, we will now be able to carry out a semi-quantitative evaluation of how the various components redistribute during the fluidized bed separation experiments.

We've also been searching for Hg in the ash and AC, but the Hg concentrations are too small to detect by either TEM or XPS analyses. We plan to artificially dope samples of ash with Hg to high enough levels to make it possible to detect the presence of Hg. If we are successful in doing this, we hope to be able to determine the nature of the carbon particle to which Hg attaches and the type of Hg compound which is captured.

We have obtained preliminary results from XPS analyses on the effects of an SCR reactor on fly ash surface chemistry. The data show differences in Cl, S and Fe, but further analyses are needed to reach firm conclusions. It is planned to carry out these analyses in the next several months.

EXPERIMENTAL

This project is, predominately, an experimental study, involving experiments in fluidized beds and laboratory analyses of activated carbon and fly ash by electron microscopy methods and other analytical techniques.

Task 1: Separation of Activated Carbon and Fly Ash in a Fluidized Bed. Because of the strong solid phase mixing and gas-solids interactions which occur in a bubbling fluidized bed operated at gas velocities well above minimum fluidization, fluidized beds are in widespread use in industry for applications such as heat exchangers, combustors, gasifiers, chemical reactors, and solids dryers. However, at superficial gas velocities just slightly above minimum bubbling, the solids do not mix well, and as a result particle segregation occurs in the vertical direction, with the more dense particles settling downward towards the distributor and the lowest density particles moving towards the free surface of the bed (Ref. 4 and 5).

The activated carbon used in Hg capture field trials sponsored by EPRI and DOE has approximately the same mean particle size as fly ash (15 to 20 μm mass mean diameter), but has a particle density significantly less than that of ash due to the high porosity of activated carbon. This difference in particle density may make it possible to separate the bulk of the spent activated carbon from the fly ash in a fluidized bed, and the first group of experiments will determine the bed operating conditions needed to accomplish this.

Previous research by the Principal Investigator on the behavior of fly ash in bubbling fluidized beds showed that, under normal circumstances, fly ash can be difficult to fluidize. The very small particle size leads to significant attractive (Van der Waal) forces between particles which can make the ash cohesive. Fly ash falls into the category of Geldart type C powders, which exhibit gas channeling and spouting, instead of bubbling (Ref. 6). However, previous research has shown that cohesive powders can be made to bubble in a gas fluidized bed with the assistance of high intensity sound (Ref. 7 and 8). Figure 1.1 shows a gas fluidized bed with a loudspeaker positioned

above the free surface of the bed. The high intensity sound waves agitate the bed material, disrupt the inter-particle forces, and make it possible to obtain stable bubbling. Figure 1.2 shows the effect of sound pressure level (SPL) in the bed on minimum

Figure 1.1: Laboratory Batch Fluidized Bed.

Figure 1.2: Variation of Minimum Bubbling Velocity with Sound Pressure Level.

bubbling velocity for three cohesive powders, including fly ash (Ref. 9). The background SPL in the laboratory is ~ 85 dB. The data show the powders could not be made to fluidize unless the SPL exceeded 120 to 133 dB. At higher values of SPL, the minimum bubbling velocity decreased with increasing SPL.

All of the fluidized bed experiments being performed in this project are being carried out with acoustic excitation of the bed material. The activated carbon separation experiments are being performed with spent mixtures of AC and fly ash generated during field trials at pulverized coal power plants involving Hg capture using injected AC.

The first set of experiments is being performed in a 15 cm diameter batch fluidized bed operating with room temperature air as the fluidizing gas. The bed has a porous plate distributor, is equipped with a loudspeaker above the freeboard, is instrumented with a rotameter to measure air flow rate and a microphone to measure sound pressure level in the bed. The laboratory setup is similar to that illustrated in Figure 1.1.

Each experiment is performed by first loading the material into the bed vessel, turning on the sound and air flow, fluidizing at the desired operating conditions for several minutes, abruptly turning off the air and then the sound, and then carefully vacuuming out thin layers of the bed material, with each layer captured in a small filter bag (Figure 1.3). Each layer is then weighed and analyzed to determine total carbon content. The amounts of naturally occurring unburned carbon in the ash and of the activated carbon in each sample collected from the bed will also be determined. The experiments are being carried out with various air velocities to determine the combination of process conditions which yields the sharpest separation.

Figure 1.3: Sketch Showing Layering Technique for Analysis of Carbon Stratification in Fluidized Bed.

Task 2: Removal of Hg from Activated Carbon and Fly Ash. In 1999 Hassett et al. (Ref. 9) reported on experiments in which samples of fly ash were tested for vapor phase Hg release in a thermal desorption apparatus. An earlier paper (Ref. 10) reported results of Hg thermal desorption experiments on contaminated soil samples performed inside of a pyrolysis apparatus. The Hassett study concluded that the temperatures at which most of the Hg was released ranged from about 230°C to close to 380°C, depending on the nature of the fly ash and the predominant form of Hg on the ash. Similar desorption temperatures were reported by Biester and Zimmer (Ref. 10) for Hg contaminated soils.

This task is determining the potential for removing Hg from spent activated carbon and fly ash, using a heated bubbling fluidized bed. There is an extensive internal micropore structure in activated carbon, and the rate of Hg removal is likely to be limited by decomposition temperature and by mass transfer processes within the particles. The majority of fly ash particles are solid, having formed as molten ash solidifies in the colder sections of the boiler. As a consequence, the kinetics of Hg removal from fly ash is more likely controlled by decomposition temperature and mass transfer coefficient at the particle surface.

Gas fluidized beds operated with superficial gas velocities well in excess of minimum bubbling velocities are characterized by excellent gas-solid contacting, which results in high rates of both heat and mass transfer between gas and solids. Combined with the ability to fluidize fine particles with very low gas velocities (and, as a consequence, very low gas flow rates), the fluidized bed becomes the logical choice for removing Hg from the large volumes of ash and activated carbon which flow out of a boiler. Hg desorbed from the AC or ash will be in a highly concentrated form in the fluidizing gas and will be readily amenable to capture.

The experiments are being performed in a 15 cm diameter batch fluidized bed equipped with an in-bed cylindrical electrical resistance heating element to raise the temperature of the bed material to temperatures in excess of 400°C. As with the equipment used in the previous task, this bed is fluidized with air, and it has a loud speaker above the bed vessel to allow acoustic excitation of the bed material. Thermocouples immersed in the bed are used to measure bed temperature, and air flow rate is measured with a rotameter.

The experimental procedure involves loading the material to be tested into the bed, turning on the loud speaker and the room temperature fluidization air, and then turning on the in-bed electrical heater. As the bed material gradually heats up, small samples of material are removed from the bed. This process is continued until the maximum desired temperature is reached. After being cooled, the samples are analyzed for Hg content using Atomic Absorption Spectroscopy. The data are then arranged in the form of % Hg removal as a function of bed temperature.

Task 3: Microstructural and Chemical Analysis of Fly Ash and Activated Carbon

Samples Produced in Tasks 1 & 2. The experiments in Tasks 1 and 2 require microstructural and spectroscopic analysis of fly ash and AC samples. Specimens of fly ash and AC produced by the Task 1 separation experiments and Task 2 Hg removal experiments are being subjected to some or all of the following types of analyses:

- Particle Identification by Morphological Observation – Scanning Electron Microscopy (SEM) on a systematic matrix of samples is being carried out on an FEI XL30 environmental scanning electron microscope equipped with an EDS spectrometer. We are attempting to determine the relative proportions of fly ash-to-unburnt C-to-AC in the mixtures created by the fractionation experiments in Task 1(a) because the spherical melted fly ash particles have a visibly different morphology from the AC and unburnt carbon particles. It is also possible to distinguish the various particle types by point EDS analyses and utilizing the fact that the fly ash contains Si, Fe, S and Al in addition to C and Hg. In fact, EDS chemical mapping of the binary fly ash/AC mixture in the XL30 SEM is a potential method for producing qualitative visual maps of the relative proportions of fly ash, unburnt carbon and AC. This will allow us to visualize the residual amount of AC in the fly ash after separation in the fluidized bed.
- Particle Size Distributions – a methodology is currently being developed to semi-quantitatively assess the size distributions and volume fractions of the AC, unburnt C and fly ash components of each separated fraction by systematic image analysis of representative scanning electron micrographs.
- TEM analysis of the Fly Ash/AC mixtures – samples of the fly ash/AC powders have been dry dispersed and supported on holey carbon films for TEM examination. A 200kV JEOL 2000FX TEM which is equipped with EDS and EELS is being used for the analysis. A combination of high resolution imaging, electron diffraction and EDS point analyses is being used to characterize the mineral constituents that make up the rapidly solidified fly ash particles, which contain silica, alumina and iron sulfites and unburnt carbon. We have attempted to use EDS analysis to determine whether Hg is preferentially associated with any of these phases or if it is uniformly distributed on the surface of the fly ash. However the Hg levels of the samples examined to date have been below the EDS detectability limit of the instrument.

- Microanalysis of the AC – a combination of high resolution electron microscopy (HREM) and EELS in the JEOL 2000FX TEM is being explored as a way to structurally characterize the porosity and structure of the AC. If the Hg is atomically dispersed throughout the AC network structure, then it will be impossible to image. If however the Hg segregates to form nm scale particulates either on or within the AC, z-contrast ADF imaging in the TEM may allow us to detect their presence.
- Surface Area Measurements (not yet attempted) – BET N₂ gas absorption experiments can be used to determine the surface area and porosity of the AC materials. These will be carried out both before and after Hg thermal desorption, in order to determine if the heat treatment has a deleterious effect on the absorptive properties of the AC.
- Hg Content Measurement - The total Hg content of the samples is only around 20-50ppm level at maximum, so a rather sensitive quantitative composition analysis technique will be required. Atomic Emission Spectroscopy (AES) and/or Atomic Absorption Spectroscopy (AAS) are being used to quantitatively compare the Hg content of fly ash and AC samples before and after thermal treatment, in order to assess the effectiveness of Hg removal.
- Surface Chemistry Analysis – X-ray Photoelectron Spectroscopy (XPS) in a Scienta ESCA instrument is being used to study the surface chemistry of a small selection of samples. For example, comparative studies of the surface composition of samples before and after SCR are underway to look for systematic variations in the surface Cl and S content. Furthermore, Hg contaminated samples are being analysed to see if the Hg is segregated to the material surface.

Task 4: Effect of SCR on Ash Properties. The analyses performed in this task are attempting to determine if the presence of an SCR catalyst affects those fly ash properties which are important for Hg capture.

Samples of fly ash for these analyses have been obtained from two power plants equipped with SCR reactors. In one case, fly ash was obtained by sampling isokinetically across the gas duct both upstream and downstream of the SCR reactor. At the second power plant, there are four coal-fired boilers of identical design, with two equipped with SCR reactors. All four burn the same coal. Samples of fly ash were obtained from the electrostatic precipitator hoppers downstream of the air preheaters. While there might be differences in fly ash properties due to factors such as differences in the coal grind size from one boiler to the next or differences between boilers in O₂ concentrations in the furnace and convective pass, if differences due to these factors are small enough, then this approach should provide additional insight into the effects of SCR on fly ash surface chemistry.

The fly ash samples are being analyzed for size distribution, unburned carbon and mineral constituents, surface chemical composition and total Hg content. Significant differences in surface chemical composition would provide clues to the role of fly ash properties in the Hg capture process and in the possible effects of the SCR reactor.

RESULTS AND DISCUSSION

Task 1: Separation of Activated Carbon and Fly Ash in a Fluidized Bed

Experiments were performed with a mixture of activated carbon and fly ash (AC/fly ash) to determine to what extent the activated carbon and naturally occurring carbon can be separated from the remainder of the mixture. The AC/ash mixture had been obtained from a pulverized coal power plant, but the proportions of AC and ash in the mixture are unknown. Visual identification and counting of particles using SEM images are planned for the coming months.

The experiments were carried out at room temperature in the 15 cm diameter fluidized bed equipped with an acoustic speaker (loud speaker) positioned at the top of the bed vessel. The settled bed depth was 8 cm and the sound pressure level at the

distributor was 140 db. The superficial velocity of the fluidizing air was varied from 0.6 to 1.1 cm/s.

In each experiment, the bed was fluidized for 10 minutes to assure steady state conditions, and the fluidizing air was then abruptly turned off. As described in the previous section, the bed material was then removed from the bed, layer by layer. Figures 2.1 to 2.7 show how the carbon content of the bed material varied with vertical distance from the distributor, when the bed was fluidized at different velocities. These show the largest segregation occurred at superficial velocities of 0.7 to 0.8 cm/s. At these conditions, the carbon content (LOI) at the top of the bed was approximately 27% and it was less than 17% in the bottom layer. Very little or no carbon segregation occurred at velocities much lower and higher than 0.7 to 0.8 cm/s (Figure 2.8).

Fluidized bed particle segregation, based on particle density and size is controlled by bubbling in the bed. At velocities close to minimum bubbling, there is insufficient bubbling to transport the low-density particles towards the free surface and the high-density particles towards the distributor. At much higher velocities, the bubbling is much more intense, and this maintains the bed material in a well-mixed state and prevents particle segregation. Figure 2.9 shows the minimum fluidization velocity as determined from bed pressure drop experiments was approximately 0.8 cm/s. The minimum bubbling velocity is close to U_{mf} in magnitude. The optimal fluidization velocity will vary depending on the size and density distribution of the particles.

Relation Between Mercury Concentration and Carbon Content

Samples of AC/Ash obtained from each layer of the bed during the tests at 0.6, 0.7 and 0.8 cm/s were analyzed for Hg content using the LECO Hg Analyzer. These results (Figures 2.1, 2.3, and 2.4) show a strong dependence of Hg capture on particle carbon content. The data from all three tests are summarized in Figure 2.10 as Hg content versus LOI level. Note that if the data are extrapolated to low levels of LOI, the Hg content approaches a value close to zero as LOI approaches zero.

Figure 2.1: Vertical Stratification of LOI and Hg. $V_{air} = 0.6 \text{ cm/s}$.

Figure 2.2: Vertical Stratification of LOI. $V_{air} = 0.7 \text{ cm/s}$.

Figure 2.3: Vertical Stratification of Hg and LOI. $V_{air} = 0.7$ cm/s.

Figure 2.4: Vertical Stratification of Hg and LOI. $V_{air} = 0.8$ cm/s.

Figure 2.5: Vertical Stratification of LOI. $V_{air} = 0.9 \text{ cm/s}$.

Figure 2.6: Vertical Stratification of LOI. $V_{air} = 1.0 \text{ cm/s}$.

Figure 2.7: Vertical Stratification of LOI. $V_{air} = 1.1 \text{ cm/s}$.

Figure 2.8: Magnitude of Carbon Stratification Versus Superficial Air Velocity.

Figure 2.9: Minimum Fluidization Velocity From Bed Pressure Drop Test.

Figure 2.10: Variation of Hg with LOI. Boiler A Fly Ash/AC Mixture.

Additional Testing Planned

One activated carbon/fly ash mixture has been tested, so far, in Tasks 1 and 2. This mixture was obtained from a Hg- capture field trial at a utility boiler. The extent of the ability to separate carbon from non-carbonaceous ash constituents in a fluidized bed will vary from boiler to boiler due to differences in particle size and density distributions. As additional Hg-capture field trials are carried out and we are able to obtain additional suitable AC/ash samples, we plan to perform more experiments on carbon separation and Hg desorption.

Task 2. Removal of Hg from Activated Carbon and Fly Ash

Experiments were performed with the AC/ash mixture used in Task 1 to determine the temperature at which Hg is driven off. These experiments were performed in the heated fluidized bed, using the procedure described in the “Experimental” section. Once the bed was fluidized and the electrical heater turned on, an experiment lasted from one to 1.5 hours. As the temperature of the bed gradually increased with time, small samples of bed material were removed from the bed and analyzed for Hg content using the LECO Hg Analyzer.

Figure 2.11 shows bed temperature as a function of time for three of the tests. Temperatures of almost 500°C were reached in each test. Four separate tests were performed where samples were removed for Hg analysis (Figure 2.12). Note that the Hg versus temperature profile obtained in Test HB-1 is different from that obtained in the other three tests. This was the first test performed and the difference in Hg profile may be due to differences in test conditions and measurement and sampling procedures used in the various tests. Each test shows a relatively constant Hg concentration until a temperature of approximately 320 to 380°C was reached, after which the Hg concentration decreased rapidly with temperature. The Hg concentration approached zero at temperatures close to 500°C.

Figure 2.11: Hot Bed Tests. Bed Temperature Versus Time.

Figure 2.12: Hot Bed Tests. Hg Versus Bed Temperature.

When other AC/ash samples become available, we plan to perform more Hg desorption experiments. How the Hg desorption temperature varies with the physical and chemical characteristics of the AC/ash mixture is one of the important aspects of this task. Our ability to do this will depend on our ability to obtain suitable samples of AC/ash.

Task 3(a): Morphology of Fly-Ash/Activated Carbon Mixture From Boiler A

A fly ash/activated carbon sample from Boiler A was chosen as a representative material on which to commence our structural characterization studies. Figure 2.13 shows a typical low magnification SEM micrograph of the fly ash sample in which a diverse range of morphologies and particle sizes can be observed. In order to make progress with evaluating the effectiveness of the separation processes that form the basis of this project, it was essential that we were able to classify the various morphologies present. Hence, a substantial SEM and TEM characterization effort was made on this material in an attempt to gain the ability to recognize the particle types present. Four main types of particles were identified. The first characteristic morphology shown in Figure 2.14a is of large (30-100 μm) irregular shaped particles that were identified by EDS (Figure 2.14b) to be essentially unburnt carbon or charcoal.

A second very characteristic morphology is that of spherical particles that have a hierarchy of sizes ranging from 0.1 to 20 μm in diameter, as shown in Figure 2.15a. The surface of these spheres is always decorated with fine 'debris' of another material. EDS spectra from these spheres (Figure 2.15b) show them to be alumino-silicate in nature. Their smooth shape and minimum surface area configuration suggest that they have at some stage been molten in the boiler.

Figure 2.13: Low Magnification SEM Micrograph of a Fly Ash/AC Sample from Boiler A. Note the Diverse Range of Particle Sizes and Microstructures That Can Co-Exist.

Figure 2.14: SEM Micrograph (a) and EDS Spectrum (b) From a Typical Particle of unburnt carbon.

Figure 2.15: SEM Micrograph (a) and EDS Spectrum (b) From a Typical Spherical Morphology Alumino-Silicate Particle.

The third morphology frequently encountered in the Boiler A sample is shown in Figure 2.16. These are very large (50-100 μm) hollow carbon particles with porous walls. Frequently, the shells are ruptured, allowing a view into their interior. They are usually hollow (Figure 2.16a), but sometimes are seen to enclose some of the smooth spherical alumino-silicate particles (Figure 2.16b). These structures always display smaller (1-2μm) spherical particles embedded within their walls as shown in Figure 2.17a. SEM-EDS mapping experiments, such as that shown in Figure 2.17b have given

Figure 2.16: SEM Micrographs From Large Carbon Particles Having a Hollow Shell Morphology.

Figure 2.17: SEM Micrograph (a) and Corresponding EDS Elemental Map (b) From a Typical Hollow Morphology Carbon Particle.

us some insight into the compositions of the smaller embedded particles. The color coding in Figure 2.17a is as follows; **Green**-Al, **Light blue** -Ca, **Red** - Fe, **Dark Blue** – Si, **Pink** – K and **Yellow** - Ti. It is clear that many of the particles are aluminosilicate in nature, and a much smaller fraction are Fe, Ti and Ca containing particles.

A fourth, all pervasive, morphology present in the Boiler A sample were much finer irregularly shaped particles of activated carbon. TEM imaging experiments (Figure 2.18) showed these particles to be amorphous, typically 50-200nm in size, and to have a tendency to agglomerate into larger clusters. Figure 2.19 demonstrates that these same activated carbon particles also have a strong tendency to cling to the aluminosilicate spheres and decorate their surfaces. Both EDS and XPS chemical analyses on this Boiler A material failed to detect any trace of Hg, suggesting that if present as an adsorbate on the fly ash surface, its concentration is well below the detectability level of either of these two analytical techniques.

The particle morphologies identified in this task will be used to characterize the nature of the various samples we will be working with in Tasks 1 and 2.

Figure 2.18: TEM Micrograph of a Typical Agglomerate of Activated Carbon Particles.

Figure 2.19: TEM Micrograph of an Alumino-Silicate Sphere Decorated with Activated Carbon Particles.

Task 3(b): Morphology of ‘Pure’ Activated Carbon

A sample of ‘pure’ activated carbon was also subjected to detailed SEM and TEM examination. Figure 2.20 shows an SEM micrograph of ‘pure’ AC. It is clear that the morphology is very different to that of the Boiler A sample. Large (20-50 μm) angular particles are apparent which are decorated with a population of smaller (brighter) particles. Figure 2.21 shows an EDS spectrum taken from the entire field of view shown in Figure 2.20. The ‘pure’ AC clearly contains impurities as evidenced by the presence of Al, Si, Fe, S, Mg and Ca. It should be noted that the very low intensity of the C K_α signal in this spectrum is an artifact, because the particular EDS detector used is insensitive to very low energy X-rays. EDS point spectra were also acquired from much more localized positions on the specimen, which indicated that the larger irregular particles are the carbon, whereas some (but not all) of the smaller brighter particles are the contaminant mineral phases. TEM imaging experiments were also carried out on these ‘pure’ AC samples as shown in Figures 2.22 and 2.23 which largely confirmed these findings.

Figure 2.20: An SEM Micrograph Showing the Typical Morphology of a 'Pure' Activated Carbon Sample.

Figure 2.21: EDS Spectrum Obtained From the Entire Area Imaged in Figure 2.20.

Figure 2.22: Bright Field TEM Micrograph Showing an Irregular Carbon Particle in the Pure AC Sample Decorated with Smaller Carbon Particles.

Figure 2.23: Higher Resolution Electron Micrograph of the Smaller Decoration Particles in Figure 2.22, Showing Them to be Amorphous Carbon.

Task 4: Microstructural Characterization of Fly Ash Passing Through SCR Catalysts

Fly ash was obtained by sampling isokinetically across the gas ducts, both upstream and downstream, of SCR reactors. The two materials obtained have been subjected to comparative TEM and XPS studies to see if there is any significant difference in their microstructure or surface chemistry.

The morphology of the 'before' and 'after' SCR fly ash samples were essentially identical as observed by TEM observation. Figures 2.24 to 2.26 show some representative images of the various morphologies observed in both samples. Figure 2.24 is a low magnification micrograph showing an intimate mixture of large agglomerates of tiny carbon particles and spherical fly ash particles. Figure 2.25 shows a spherical fly-ash particle about 0.7 μm in diameter whose surface is decorated with

Figure 2.24: Bright Field Low Magnification Micrograph of the 'After' SCR Samples.

Figure 2.25: Bright Field Micrograph of a Typical Spherical Fly Ash Sample Showing Surface Decoration with Carbon.

Figure 2.26: High Resolution Bright Field Micrograph of an Agglomerate of Amorphous Carbon Particles.

much finer carbon particles. Figure 2.26 shows a higher magnification image of an aggregate of carbon particles showing that the primary particle size is the 20-50 nm range. Electron diffraction images from such regions showed these carbon nanoparticles to be amorphous in nature.

Chemical analyses of the 'before' and 'after' SCR samples were attempted by both TEM-EDS and XPS. The EDS analysis was fairly inconclusive, showing the existence of C, Si, Al, O, Fe and Ca in both samples. The XPS analysis, which is much more surface sensitive, was more interesting. Figure 2.27 shows the widescan survey spectra from both samples, indicating the additional presence of Cl and S along with some another minor peaks. Higher resolution spectra over a more limited (0 -500ev) binding energy range are shown in Figure 2.28, in which characteristic transitions from Na, Ti & N can also be seen. The most significant differences between the surface chemistries of the two fly-ash samples are as follows:

- The 'after' SCR material has a significant surface Cl content, while the 'before' SCR material is essentially devoid of Cl.
- The surface S signal in the 'after' SCR sample is about half of that observed in the 'before' SCR sample.
- The surface Fe content shows the opposite trend to the S signal. It *increases* by about 50% in the 'after' SCR sample.

Figure 2.27: Widescan XPS Survey Spectra of the 'Before' and 'After' SCR Materials.

Figure 2.28: Higher Resolution XPS Spectra From the 'Before' and 'After' SCR Materials.

The other surface concentrations of the other elements were essentially the same in both the 'before' and 'after' SCR specimens.

We have ash samples from other boilers obtained from upstream and downstream of SCR reactors which we will be analyzing using TEM and XPS in Year 2. We will defer discussion of the significance of surface chemistry differences until we obtain those results.

SUMMARY AND CONCLUSIONS

Task 1: Separation of Activated Carbon and Fly Ash in a Fluidized Bed

Experiments were performed with a mixture of activated carbon and fly ash to determine to what extent the activated carbon and naturally occurring carbon can be separated from the remainder of the mixture in a fluidized bed. The data show segregation is very sensitive to superficial gas velocity, with the strongest segregation

occurring at superficial velocities of 0.7 to 0.8 cm/s. At these conditions, the carbon content at the top of the bed was approximately 27% and it was less than 17% in the bottom layer. Very little or no carbon segregation occurred at velocities much lower or higher than 0.7 to 0.8 cm/s.

Relation Between Mercury Concentration and Carbon Content

Samples of AC/Ash obtained from each layer of the bed during the tests at 0.6, 0.7 and 0.8 cm/s were analyzed for Hg content using the LECO Hg Analyzer. These results show a strong dependence of Hg capture on particle carbon content, with the Hg content approaching zero as LOI approaches zero.

Task 2: Removal of Hg from Activated Carbon and Fly Ash

Experiments were performed with the AC/ash mixture in a heated fluidized bed to determine the temperature at which Hg is driven off. The data from each test show a relatively constant Hg concentration until a temperature of approximately 320 to 380°C was reached, after which the Hg concentration decreased rapidly with temperature. The Hg concentration approached zero at temperatures close to 500°C.

One activated carbon/fly ash mixture has been tested, so far, in Tasks 1 and 2. This mixture was obtained from a Hg- capture field trial at a utility boiler. The extent of the ability to separate carbon from non-carbonaceous ash constituents in a fluidized bed will vary from boiler to boiler due to differences in particle size and density distributions. We also suspect the Hg desorption temperature varies with the physical and chemical characteristics of the AC/ash mixture. As additional Hg-capture field trials are carried out and we are able to obtain additional suitable AC/ash samples, we plan to perform more experiments on carbon separation and Hg desorption.

Task 3: Microstructural and Chemical Analysis of Fly Ash and Activated Carbon Samples

During this last year, considerable effort went into using Scanning Electron Microscopy and Transmission Electron Microscopy to study the physical and chemical characteristics of the AC/ ash mixture used for the Task 1 and 2 experiments. Four distinct morphologies have been identified: large (30-100 μm), irregularly-shaped carbon particles, 0.1 to 20 μm spherical alumino-silicate particles, 50-100 μm hollow carbon particles with porous walls, fine 50-200 nm amorphous carbon particles, and large 20-50 μm angular activated carbon particles. With this background, we will now be able to carry out a semi-quantitative evaluation of how the various components redistribute during the fluidized bed separation experiments.

We've been searching for Hg in the ash and AC, but the Hg concentrations are too small to detect by either TEM or XPS analyses. We plan to artificially dope samples of ash with Hg to high enough levels to make it possible to detect the presence of Hg. If we are successful in doing this, we hope to be able to determine the nature of the carbon particle to which Hg attaches and the type of Hg compound which is captured.

Task 4: Effect of SCR on Ash Properties

We have obtained preliminary results from XPS analyses on the effects of an SCR reactor on fly ash surface chemistry. The data show differences in Cl, S and Fe, but further analyses are needed to reach firm conclusions. It is planned to carry out these analyses in the next several months.

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