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ROLE OF FLY ASH IN HEAVY METAL REMOVAL FROM FLUE GAS

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by

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EXECUTIVE SUMMARY

The primary objective of this work is to study the fundamental phenomena involved in the sorption of trace chalcophilic elements by fly ash at high and medium temperatures. Chalcophiles are the low-boiling trace elements that are volatilized during pulverized coal combustion and are transferred to the gas phase, e.g., As, Pb, Cd and Se. Fly ash acts as a sink for some of these volatile trace toxics and a great deal of chemical interaction is speculated to take place under furnace conditions. This fly ash-chalcophiles interaction, though crucial to the control of chalcophilic emissions, is still very poorly understood. This is due, in part, to the lack of experimental studies and data on the behavior of fly ash and chalcophiles.

The main focus of this work is investigating the sorption phenomena of a representative chalcophile, arsenic (As) on fly ashes at temperatures representative of the upper-furnace region (850-1200°C) and the economizer section (375-600°C). Arsenic is chosen because it is a highly toxic chalcophile and shows some affinity for fly ash but is also emitted from the stack as vapor and aerosol particles. The two temperature zones have been chosen because most of the dry-sorbent injection technologies are being developed for application in these two regions. Also, various fly ash samples from different sources are being studied because their chemical composition and subsequently their chemical sorption characteristics would show a great deal of variation depending on their source.

In the first year of this project, it was proposed to conduct isothermal sorption experiments in a differential reactor system. The first year's work was divided into two phases; namely 1) design, construction, testing and trouble-shooting of the differential reactor assembly and the analytical instrumentation, and, 2) designing experiments and conducting sorption studies in the differential reactor system. The first phase was completed, not before encountering a number of challenges and making quite a few design modifications to tackle them. The two most important challenges were: the need to generate reactant gas containing a fixed and low (order of 1-10 ppm) concentration of the arsenic species, and the need to prevent or minimize condensation of the arsenic species in the transport lines and tubes (for achieving mass balance).

The second phase of first year's work has yielded some interesting results which are discussed here. Two fly ashes, NIST Certified fly ash and from Zimmer utility station near Cincinnati have been tested. Both the fly ashes exhibit high levels of arsenic capture, a significant portion of which is not water leachable. The fraction that is not leached with water is believed to be captured by some chemical reaction. NIST shows increased capture by chemisorption at 900°C compared to 500°C, which indicates an activated chemical reaction as the primary sorption mechanism. Zimmer seems to exhibit little effect of temperature on the amount of arsenic captured by chemisorption.

Differential reaction studies were also carried out at a higher concentration of As_2O_3 in order to explore the effect of concentration. Zimmer fly ash showed increased capture after 2 hours of exposure at 1173 and 773 K, with majority of the capture being water leachable. Increased concentration of arsenic will lead to increased physisorption and thereby water leachability.

XRD studies have shed more light on the chemical nature and structure of the captured species and have confirmed chemical interaction. In addition to As_2O_3 itself (which may be physically adsorbed), XRD results show the presence of Ca-arsenate as well as Al-arsenate. These compounds could only have been formed by some chemical interaction.

I. DIFFERENTIAL REACTOR ASSEMBLY & PROCEDURE

The first year's work was divided into two phases:

1) design, construction, testing & trouble-shooting of the differential reactor assembly, and,

2) differential reactor experiments to study the sorption of arsenic by fly ashes.

Phase 1 has been successfully completed, a fully assembled and working differential reactor set-up is in operation and is being used for performing experiments.

A schematic of the complete reactor assembly is shown in Figure 1. This set-up is the final outcome after a number of testing and trouble-shooting operations performed with previous set-up's (refer to First and Second Quarterly reports for Year 1). The main components of the assembly are briefly described below:

Microbalance (ATI Cahn Instruments, Model D-200) - hangdown-type, digital recording balance with a maximum sensitivity of $0.1 \mu\text{g}$ and interfaced with a 486SX PC for data acquisition. The arsenic sample is suspended from the hangdown wire into the vaporization tube and its weight change is continuously monitored and displayed on the PC.

Vaporization tube - 1" OD Pyrex tube with provision for carrier gas (dry N_2) and thermocouple. The vaporization tube is wrapped with heating tape and insulation during experiments to generate arsenic species vapor to be transported by the carrier N_2 gas. The carrier gas enters at the top and leaves the vaporization tube at the bottom.

Transport line from the vaporization tube bottom to the reactor tube - a 1/4" OD flexible stainless steel line with provision for mixing diluent gas with the arsenic-laden carrier gas. The diluent gas is dry air and is preheated with a single-pass through the reactor furnace. The transport line assembly is also wrapped with heating tape and insulation to prevent any condensation of arsenic species during transport. The flexible tubing also helps in isolating the vaporization assembly from the reactor tube assembly.

The reactor tube - 1" OD ceramic (mullite) tube held inside a single-zone, 1200°C furnace. The ceramic tube is cemented to a custom-fabricated stainless steel end-connection at the top which has provision for the diluted reactant gas and a thermocouple. The bottom of the ceramic tube is connected to universal plate joint.

Figure 1: Schematic of Differential Reactor Assembly for Arsenic sorption studies

The fly ash holder assembly - a 1/2" OD stainless steel tube enters from the bottom through the plate joint. This tube is cemented to a quartz tube (slightly smaller than 1/2" OD), the top of the quartz tube has provision to hold a miniature sample holder by means of a quartz T-S joint. The fly ash sample is dispersed on quartz wool inside the sample holder. The sample holder has an OD of 3/8" and is about 1" long. The reactant gas flows through the sample holder over the fly ash sample, then flows through the impinger solutions before being vented to exhaust. The impinger solutions are designed to capture the remaining arsenic in the gas phase by bubbling the gas through two impingers in series. Another flexible stainless steel tubing connects the bottom of the 1/2" tube to the impinger assembly. This flexible tube is also wrapped with heating tape and insulation.

In order to do post-capture analysis, an Atomic Absorption Spectrometer (Perkin-Elmer Model 3110) has been set-up. The spectrometer uses a Graphite furnace atomizer and can analyze both liquid as well as solid samples directly. The AAS detects the total elemental concentration of the species and it has a detection limit of 1 ppb for arsenic species in solution.

Experimental Procedure & Analysis:

The execution of differential reactor experiments poses a number of challenges; two of the most important ones are:

- (1) the reactant gas should contain a very low and steady concentration of the toxic arsenic species, and
- (2) extreme care needs to be taken to avoid any cold spots in any of the transport lines etc., to prevent or minimize condensation of arsenic species.

Most of the experimental set-up and procedures followed for experiments are dictated by the above mentioned considerations.

Vaporization species, temperature and flow rates:

During actual experiments, the platinum sample pan is loaded with a small, preweighed quantity (about 15 mg) of the arsenic species. In our experiments, the arsenic species used was crystalline solid arsenic trioxide, As_2O_3 . This species was chosen based on findings of previous researchers (Germani and Zoller, 1988; Wouterlood and Bowling, 1979). Their findings, though subject to ambiguity, provided some basis for further exploration. Also, we performed some

thermodynamic free energy minimization studies (refer to 2nd quarterly report) in order to assess the exact speciation of arsenic under simulated flue gas conditions. Our studies revealed that As_4O_6 is the dominant species in the medium temperature range, while both As_4O_6 and elemental As_4 can exist in the high temperature range, as can be seen in Figure 2a. The vaporization was decided to be carried out isothermally and the temperature was decided after thorough characterization of the vaporization rate vs. temperature behavior and also from a theoretical estimation of As_2O_3 vapor pressure data. Figure 2b shows the saturation concentration of As_2O_3 in ppm versus temperature obtained from vapor pressure data. As can be seen, 100 ppm is the saturation concentration at a temperature of about 130°C . As_2O_3 sublimates at about 197°C , it was found that a temperature of about 170°C gives reasonable vaporization rate in order to obtain the desired concentration. It was decided to maintain the concentration of arsenic in the reactant gas of the order of 5 ppm (mg/m^3). This compares with the actual flue gas concentration of arsenic measured by some previous researchers at about 150 ppb (Germani and Zoller, 1988). The flow rate used for the carrier gas was 100 ml/min (STP), this was decided based upon the sensitivity and stability requirements of the microbalance reading. The diluent was used at a flow rate of 1000 ml/min (STP). Air was used as the diluent gas, which introduced oxygen in the reactant gas mixture.

Fly ash

The fly ash was preweighed (15-20 mg) and was dispersed on a preweighed (15-20 mg) quantity of quartz wool inside the sample holder cup. The cup was then placed on the 1/2" OD sample holder tube and introduced into the reactor tube, maintained at the reaction temperature. The experiment is then started by commencing the arsenic species vaporization by quickly raising the temperature to about 170°C and then maintaining it steady at that value. This is done with the help of the temperature controller which controls the heating tape power supply. The vaporization rate is maintained the same for all the experiments in order to generate the same concentration throughout the experiment and between different experiments also. Vaporization was found to be very sensitive to temperature which has to be controlled within $\pm 5^\circ\text{C}$ of 170°C . Any variation of greater than 5°C would immediately be reflected in the form of an aberration in the continuous weight loss curve.

DISTRIBUTION OF As SPECIES IN FLUE GAS WITH TEMPERATURE

Figure 2a: Distribution of arsenic species in flue gas with temperature obtained from thermodynamic free energy minimization studies.

Saturation Concentration of As_2O_3 as a function of temperature

Figure 2b: Saturation concentration of As_2O_3 as a function of temperature obtained from vapor pressure data.

All of the reactant gas flows through the 1/2" OD holder tube over the fly ash, thus ensuring differential conditions, each fly ash particle "sees" the same, uniform concentration of arsenic and there is assumed to be negligible depletion of arsenic species in the gas phase. Each experiment is conducted for the same duration of time. The experiment is stopped by quickly lowering the temperature of the vaporization tube. After the temperature of the vaporization tube has decreased below 100°C or so, there is no appreciable vaporization, the furnace temperature is also reduced and the fly ash sample is removed for analysis along with the impinger solutions.

Post-sorption Analysis:

This analysis is carried out in two steps. In step 1, the fly ash (along with the quartz wool) is leached in deionized water (50 ml) for at least 24 hours, part of the time (about 2 hours) in a small ultrasonic bath. The solution is then analyzed for arsenic elemental concentration in the Atomic absorption spectrometer (AAS). The AAS requires minimal quantity of liquid (20 μ l per detection) so there is negligible loss of solution. The AAS detection is done for 2-3 times in order to obtain consistent results. For the step 2, separate leaching experiments (see 2nd Quarterly report) and some available literature (Hansen et al., 1984; Turner, 1981) helped identify a good leaching agent for the total arsenic. 20% H_2O_2 is used in analyzing the total arsenic captured. 50 ml of 20% H_2O_2 is added to the 50 ml water leached solution. The solution is then leached again for at least 24 hours to extract all the arsenic captured.

The fly ash itself contains arsenic, it is separately analyzed to obtain the total arsenic content and the water leachable fraction. The post-reaction fly ash analysis is corrected for the original arsenic present (both water-leachable and total) to obtain the "net" arsenic capture during experiment.

In order to confirm that the quartz wool itself doesn't capture any arsenic species, separate "blank" run was conducted without the fly ash sorbent. The quartz wool was analyzed to have captured negligible arsenic.

The impinger solution analysis revealed that they were not very effective in capturing the arsenic from the gas stream. One probable explanation is that the residence time of the gas bubbles in the impinger solution is not sufficient for complete capture. The bubble size could be reduced thereby increasing residence time with a ceramic filter/distributor, but that causes

the pressure drop to rise tremendously. In order to assess the amount of condensation of the arsenic species in the transport or reactor lines etc, all the system components; the vaporization tube, transport line and reactor and fly ash holder tube were "washed" in Na-acetate solution. It revealed that some percentage of the total arsenic vaporized does get deposited inside the transport line. It was found that less than 10% of the total As_2O_3 vaporized was condensed upstream of the fly ash holder. As most researchers in this field have found out, it seems to be a nearly unsurmountable challenge to achieve complete mass balance over the system without making the experimental procedures too cumbersome. In our studies, it was decided to strike a balance between the two; meeting the mass recovery criterion and at the same time performing experiments with reasonable accuracy and ease.

II. RESULTS & DISCUSSION

Differential reaction studies were performed in two temperature windows; the high-temperature range (850- 1200°C), representative of upper-furnace conditions, and the medium-temperature range (375-600°C) representing the economizer section. There exists a lot of variation in the fly ash composition and subsequently its chemical behavior depending on its source. Hence it was decided to test multiple fly ashes from different sources (around Ohio) under the same conditions so as to compare their sorption behavior. The objective of these studies is to understand the complex interactions between fly ash and one representative heavy metal, arsenic, and study the effect of temperature and type of fly ash.

In the results presented in this section, we have studied two fly ashes; Certified NIST (National Institute of Standards & Technology) fly ash and Zimmer utility station (near Cincinnati) fly ash. The NIST fly ash was certified for complete elemental analysis of the fly ash and contains about 140 ppm of arsenic, out of which, about 40 ppm was analyzed to be water-leachable. The Zimmer fly ash was analyzed in our laboratory and found to contain 190 ppm of As with about 60 ppm being water-leachable.

Isothermal experiments were conducted at two temperatures, 900°C and 500°C, all the runs were carried out for about 4 hours. The weight loss vs. time curves are shown in Figure 3 for all the runs. Based on the rate of vaporization and the flow rates used, the concentration of the As_2O_3 in the reactant gas is calculated to be about 7 ppm (mg/m^3).

A. Influence of temperature

Figure 4 shows the results of the AAS analysis for both NIST and Zimmer at both 900 and 500°C in the form of a bar chart. As can be seen from the figure, there is substantial capture of arsenic by both fly ashes, with arsenic ppm in the range of 1000 to 4000 ppm. There is substantial amount of water leachable As. The physically adsorbed arsenic species is bound to the fly ash surface by weak van der Waal's forces and retains its chemical form, As_2O_3 , hence it should be water leachable. Thus, water leached arsenic is a measure of physically adsorbed arsenic (some chemically reacted arsenic might also be water soluble and get leached). The total arsenic leached out should represent both the physically adsorbed as well as the chemically reacted arsenic. Therefore, the difference between the total arsenic and the water leachable

Figure 3: Weight loss vs. time curve for As_2O_3

Figure 4: Water leachable and total arsenic capture by NIST and Zimmer fly ashes at 773 and 1173K.

arsenic is a measure of the chemically reacted arsenic (Uberio & Shadman, 1990, 1991). At 500°C, Zimmer can be seen to have much greater capture of arsenic than NIST, the total capture by Zimmer is almost twice that by NIST. Also, Zimmer shows higher chemically reacted As than NIST. At 900°C, NIST and Zimmer show comparable total capture. Again, the fraction of arsenic that is chemically adsorbed is higher in the case of Zimmer, thus indicating superior capturability of Zimmer by chemisorption at both the temperatures studied. One observation to be made at this point is that even though both the fly ashes originally contained high ppm of chemical As, they still have capacity for taking up more arsenic through some chemisorption.

Effect of temperature on chemisorption of As by NIST indicates the probability of an activated chemical reaction step since the amount chemisorbed increases with temperature. On the other hand, temperature seems to have an intriguing effect on Zimmer fly ash, it shows little effect of temperature on chemisorption. It could be possible that the mechanism of chemisorption is quite different in the case of Zimmer.

B. Influence of concentration

Differential reaction studies were also carried out at a higher concentration of As_2O_3 in order to explore the effect of concentration. Zimmer fly ash was used and the experiments were performed at two different temperatures, 773 K and 1173 K, for a duration of 2 hours. The concentration of As_2O_3 was 11 ppm and the results are shown in Figure 5. At 1173 K, the total capture was of the order of 2000 ppm in 2 hours with nearly 90% of it being water leachable. Similar behavior was observed at 773 K, with most of the capture being water leachable. This can be explained by the fact that at a given temperature, increased concentration of arsenic will lead to increased physisorption and thereby water leachability.

C. Chemical Characterization Work

Efforts to explore the chemical nature and structure of the captured species have been carried out by means of XRD analysis. Results of a sample XRD analysis are shown in Figure 6. In addition to As_2O_3 itself (which may be physically adsorbed), XRD results show the presence of Ca-arsenate as well as Al-arsenate. These compounds could only have been formed by some chemical interaction. The particular sample used for XRD analysis was obtained by

Arsenic Capture by Zimmer fly ash
As₂O₃ : 11 ppm, 2 hours

Figure 5: Arsenic capture by Zimmer fly ash at a As₂O₃ concentration of 11 ppm for 2 hours.

Figure 6: Results of the XRD analysis indicating the presence of As_2O_3 along with Ca-arsenate and Al-arsenate.

conducting a very long-duration run of 24 hours with 7 ppm arsenic concentration.

III. CONCLUDING REMARKS

The main objective of this work is to investigate the sorption phenomena of a representative chalcophile, arsenic (As) on fly ashes at temperatures representative of the upper-furnace region (850-1200°C) and the economizer section (375-600°C). In the first year of this project, it was proposed to conduct isothermal sorption experiments in a differential reactor system. The first year's work was divided into two phases; namely 1) design, construction, testing and trouble-shooting of the differential reactor assembly and the analytical instrumentation, and, 2) designing experiments and conducting sorption studies in the differential reactor system. The first phase has been completed, not before encountering a number of challenges and making quite a few design modifications to tackle them. The two most important challenges were: the need to generate reactant gas containing a fixed and low (order of 1-10 ppm) concentration of the arsenic species, and the need to prevent or minimize condensation of the arsenic species in the transport lines and tubes (for achieving mass balance).

The sorption experiments were conducted to study the influence of temperature, concentration and explore the chemical nature of capture species. We have studied two fly ashes; Certified NIST (National Institute of Standards & Technology) fly ash and Zimmer utility station (near Cincinnati) fly ash. The NIST fly ash was certified for complete elemental analysis of the fly ash and contains about 140 ppm of arsenic, out of which, about 40 ppm was analyzed to be water-leachable. The Zimmer fly ash was analyzed in our laboratory and found to contain 190 ppm of As with about 60 ppm being water-leachable.

The temperature effect experiments were carried out at temperatures of 773 and 1173 K for a duration of 4 hours. Both fly ashes captured substantial amount of arsenic in the range of 1000 to 4000 ppm, with significant amount of water leachable As. The physically adsorbed arsenic species is bound to the fly ash surface by weak van der Waal's forces and retains its chemical form, As_2O_3 , hence it should be water leachable. Thus, water leached arsenic is a measure of physically adsorbed arsenic (some chemically reacted arsenic might also be water soluble and get leached). The total arsenic leached out should represent both the physically adsorbed as well as the chemically reacted arsenic. Therefore, the difference between the total

arsenic and the water leachable arsenic is a measure of the chemically reacted arsenic. Effect of temperature on chemisorption of As by NIST indicates the probability of an activated chemical reaction step since the amount chemisorbed increases with temperature. Zimmer fly ash shows little effect of temperature on chemisorption. It could be possible that the mechanism of chemisorption is quite different in the case of Zimmer.

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