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**THE CHEMICAL EFFECT OF ENTRAINED PARTICLES
IN COAL CONVERSION STREAMS**

6th Quarterly Technical Progress Report
for the Period November 1, 1982—January 31, 1983

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Work Performed Under Contract No. AC21-81MC16244

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6TH QUARTERLY TECHNICAL PROGRESS REPORT ON
THE CHEMICAL EFFECT OF ENTRAINED PARTICLES
IN COAL CONVERSION STREAMS

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ABSTRACT

A major objective of the U.S. Department of Energy is to increase coal utilization through the development of combustion stream cleanup technologies. Many of the existing cleanup devices as well as advanced concepts rely on heterogeneous processes (i.e. gas-solid interactions) to achieve efficient stream removal. Examples of such devices include particle injection and granular bed filters for alkali removal, limestone injection for SO_x removal in fluid bed combustors, dry injection for SO_x removal in entrained combustion, and trace metal adsorption and removal on fly ash. Recent studies indicate that the successful use of turbines in combined cycle processes may depend on understanding the interaction between the gas phase alkali and particles in the combustion stream to substantially reduce turbine corrosion. This report documents progress in efforts to model the heterogeneous chemistry of coal combustion streams as well as laboratory studies to obtain critical input data for the model.

1. INTRODUCTION

The purpose of this study is to investigate the chemical effects of entrained particles in coal combustion streams. The specific objectives of the project are: (1) To develop a computer model of gas-particle interactions relevant to the heterogeneous formation and control of alkalis, SO_2 and NO_x ; (2) To measure the critical input parameters required by the model, and (3) To utilize the model and data to predict stream composition and analyze prototype cleanup devices.

In order to meet these objectives, the contract is divided into six major tasks. The first task involves the use of the "PACKAGE" code to analyze data related to gas-particle interactions (e.g., alkali-sorbent interactions) from Curtiss-Wright or other test facilities. Computational problems to be considered include: (1) The effects of gas phase diffusion impedance on absorption and a determination of characteristic times for mass transport limited absorption and bulk enrichment of the absorbing species in the entrained particles; (2) The effects of gas phase diffusion impedance on vaporization and a determination of characteristic times for mass transport limited vaporization and bulk depletion of vaporizing species from entrained particles; (3) A determination of the species identity, concentration, and distribution (gas vs condensed) under equilibrium conditions which result from gas-particle interactions. These calculations will be used primarily to study the release and removal of alkalis from/on ash or sorbent particles under equilibrium and gas phase diffusion limited conditions.

Task 2 is to develop a computer model which describes rate controlled heterogeneous processes. The model will include those processes which control the chemical state of species at the surface of the particle and the distribution of species between the interior of the particle, the surface of the particle, and the gas phase surrounding the particle. Specifically, the

model developed includes the effect of desorption, adsorption, and surface segregation on a semi-infinite solid (i.e., large particle). Upon completion of this phase of the work, the model will be extended to small particles. Using this model, the rates and characteristic times for bulk depletion due to vaporization and bulk enrichment due to absorption will be determined in terms of the kinetic and thermodynamic parameters which describe these phenomena for the particles. The model will also describe the enrichment of the surface of the particle relative to its bulk in terms of these parameters. Under Tasks 3, 4, and 5 these parameters will be measured, and using the model and the data, the effects of rate controlled heterogeneous processes on the formation and control of alkalis, SO_2 and NO_x will be investigated in Task 6.

Task 3 is to measure the rate and thermodynamic parameters describing vaporization of alkali species from ash and ash precursors such as the aluminosilicates illite and kaolinite. The key variables in these measurements include particle size, composition, heating rate, and temperature as well as gas composition. Under Task 6 described below, the vaporization rate data and the segregation data (Task 4) will be used in the models described in Tasks 1 and 2 in order to accurately describe the release of alkalis from entrained particles under equilibrium, diffusion controlled, and rate controlled conditions.

Task 4 is to measure the rate and thermodynamic parameters describing the segregation of K, Fe, S, and Ca and other measurable species found in ash and ash precursors. These measurements will be carried out over a temperature range meaningful to fluidized bed combustion. Under Task 6 the segregation data and the vaporization data (Task 3) will be used to accurately describe the release of alkalis from entrained ash particles. Moreover, given appropriate data for rates of alkali adsorption, the removal of alkalis by entrained sorbent particles may also be described.

Task 5 is to measure rate parameters for the reaction of SO_2 , NO, and NO_2 on the surface of representative ash material. The measurements will be made over a temperature range characteristic of particle temperatures in a

fluidized bed combustion stream. In these studies, the identity of the surface species formed by the gas-particle reaction will be determined and their rate of formation will be measured. Throughout these studies the potential for catalytic SO_2 - NO_x interactions on the ash particle surface will be investigated. Under Task 6, these data and the models discussed under Task 2 will be utilized to predict the influence of gas-particle reactions on the levels of SO_2 and NO_x in the combustion stream.

Task 6 is to incorporate the data generated by the experimental studies on vaporization, segregation, and gas-particle reactions (Task 3-5) into the model described in Tasks 1 and 2. In this manner, the influence of gas-particle interactions on combustion stream composition may be determined under conditions of equilibrium, mass transport, and chemical rate control. In particular, the data combined with the models will provide detailed insight and quantitative understanding of the effects of gas particle interactions on alkali release, alkali removal, and the levels of alkalis, SO_2 and NO_x in the combustion stream. These results will be compared with data obtained from Curtiss-Wright and other test facilities.

2. TECHNICAL PROGRESS SUMMARY

This quarterly report describes work performed during the period November 1982 through January 31, 1983. A summary of the progress achieved during this reporting period is presented in this section.

Task 1. Exercise "PACKAGE" Code

Completed - July 1982.

Task 2. Model Development

Prior work on this task has focused on implementing and characterizing the combined segregation, evaporation, and adsorption code. In the last quarter, the model was extended to treat small particles. During this quarter, characteristic solutions of the model have been investigated.

Task 3. Measure Alkali Vaporization Rates

In prior quarters, experiments were performed which demonstrate the feasibility of using LIF to measure alkali vaporization rates, and the temperature dependence of the vaporization rate for Na from $\text{Na}_2\text{O} \cdot \text{XSiO}_2$ was determined. In this quarter, a determination of the LIF intensity as a function of Na concentration has been made. From this, the absolute vaporization flux for Na from $\text{Na}_2\text{O} \cdot \text{XSiO}_2$ has been determined.

Task 4. Measurement of Segregation Rates

Installation of the ESCA was initiated during the quarter, however several components were found to be defective and were returned to the manufacturer for repair. Subsequently, these components were returned to ARI and, the installation was completed.

Task 5. Measurement of SO₂/NO_x Rates

ARI personnel met with DOE scientists at the Morgantown Energy Technology Center on November 10 - 12 to outline the work to be performed under this task. This work will be performed at Morgantown in collaboration with ARI scientists. Preliminary work on this task has been initiated and includes baseline studies of SO₂ reactions with Al₂O₃ and SiO₂.

Task 6. Incorporate Data into Model

ARI personnel met with DOE scientific and project personnel at Morgantown on December 10th to outline the work to be performed under this task. The objective of this meeting was to identify the specific combustion stream situations to be modeled and the specific test data against which the model predictions will be tested and compared. From this meeting it has been determined that within the framework of the available data, two sets of "field" measurements will be investigated. These are the Ames alkali measurements at the Curtiss-Wright test facility and the Morgantown measurements of alkali release from illite particles in a laboratory burner.

3. TECHNICAL DISCUSSION

The purpose of this study is to investigate the chemical effects of entrained particles in coal combustion streams. Specifically, we are concerned with the heterogeneous chemistry of naturally occurring coal ash particles and sorbents or gettering agents which may be introduced into the stream to control alkalis, SO_2 , and NO_x . The ultimate objective of the work is to predict the stream composition, especially the alkali and SO_2 concentrations, taking into account the important heterogeneous interactions in which these species take part.

3.1 Exercise "PACKAGE" Code

Work on this task has been completed and reported in detail in the first four quarterly reports. Under this task, characteristic times for enrichment and depletion of the background gas due to diffusion limited vaporization and adsorption were determined. Emphasis was placed on understanding the release and removal of alkali species in the combustion stream in this phase of the work. Additionally, the "PACKAGE" code was used to investigate the equilibrium species formed by gas-surface reactions. In particular, the reaction of gas phase species such as NaCl and NaOH with surfaces representative of ash or sorbent particles was studied.

3.2 Model Development

The objectives of this task are to develop and characterize the combined segregation, evaporation, and adsorption model of Stinespring, Lawson, and Stewart.¹ This model incorporates evaporation and adsorption processes into the segregation model reported by Hofman and Erlewein.² The model has been extended to treat semi-infinite or large particles as well as small particles and to predict the chemical composition depth profiles of these particles.

Using this model, the transport of solute or impurity atoms from the interior of the particle to its surface and the subsequent desorption or evaporation of these species into the gas phase may be described. Conversely, the adsorption of a gas phase species followed by diffusion into the interior of the particle may also be described. The model utilizes data which may readily be measured and, in some cases, estimated from thermodynamic data.

During the last quarter, the mathematical formulation of the small particle model was developed and several example calculations were performed. In this quarter, these calculations were extended in order to characterize the parameterized solutions of the model. Previous studies of the large particle model have shown that when both segregation and evaporation are taken into account, the predicted behavior may be classified as segregation controlled, evaporation controlled, or competitive (segregation and evaporation). Calculations performed during this quarter indicate that this is also true for small particles, and the main focus of the work has been to determine the effects of particle size on this general behavior. To accomplish this, calculations for $\delta = -24$, -4 , and 0 have been performed for $\alpha = -12$, $X_b = 0.1$ and $N-1 = 50, 100, 200$, and 400 layers where δ and α are the evaporation and segregation parameters respectively. This corresponds to particle sizes of $0.025, 0.05, 0.1$, and $0.2 \mu\text{m}$ if the lattice constant is taken nominally as $5\text{\AA}$.

Figure 1 shows a plot of X_1 (surface concentration) vs. τ for a 50 layer particle with $\delta = -24$. The behavior represented here is clearly segregation controlled and is essentially the same as that predicted for a large particle with $\delta = -24$, $\alpha = -12$ and $X_b = 0.1$. That is, the time dependence surface composition is essentially independent of particle size for the segregation controlled regime. It should be noted, however, that for $X_b \ll 0.1$, the maximum surface concentration attained by very small particles may be limited by the low bulk concentration. That is there is simply not enough segregant within the particle to completely enrich the surface. Such low bulk concentrations, however, are generally well below the range encountered in future applications and will not be considered further.

Figure 1. Surface Concentration vs. Time for a 50 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled.

Additional evidence that the behavior is segregation controlled rather than competitive or evaporation controlled is provided by the plot of X_{ave} vs τ for a 50 layer particle with $\delta = -24$ shown in Figure 2. It is evident that X_{ave} is essentially constant and that evaporation is not significant. In addition it should be noted that the same plot is obtained for all particle sizes considered here.

Although the time dependence of both the surface and average concentration in the segregation controlled regime are independent of particle size, the same is not true for the depth profiles. This is illustrated in Figures 3-6 which show depth profiles for 50, 100, 200 and 400 layer particles with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. For the 50 and 100 layer particles, the effects of non-evaporative bulk depletion are clearly evident. For the 200 and 400 layer particle, however, the concentration at the center of the particle remains fixed at $X_b = 0.1$. In addition, only the outer 50 or so layers deviate from the initial bulk composition of 0.1. Thus, for particles larger than approximately 200 layers, the depth profiles as well as the time dependence of the surface and average composition are independent of particle size for the segregation controlled behavior regime.

Figure 7 shows a plot of X_1 vs τ for a 50 layer particle with $\delta = -4$, $\alpha = -12$, and $X_b = 0.1$. As described previously, the behavior represented here falls in the competitive regime. This plot is essentially the same as that predicted for a large particle for the same values of α and δ . Thus, just as in the segregation controlled regime, the time dependence of the surface composition is independent of particle size for the competitive regime.

Figure 8 shows plots of X_{ave} vs τ for 50, 100, 200, and 400 layer particles with $\delta = -24$, $\alpha = -4$ and $X_b = 0.1$. From these plots, it is evident that both the rate and the extent of evaporative loss decreases as the particle size increases. The reason for this is made clear by examining the corresponding depth profiles shown in Figures 9-12.

Figure 2. Average Concentration vs. Time for a 50 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled.

Figure 3. Depth Profiles for a 50 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled and shows the effects of non-evaporative bulk depletion.

Figure 4. Depth Profiles for a 100 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled.

Figure 5. Depth Profiles for a 200 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled and shows bulklike behavior in that the concentration at the center of the particle equals the initial bulk concentration.

Figure 6. Depth Profiles for a 400 Layer Particle with $\alpha = -12$, $\delta = -24$, and $X_b = 0.1$. The behavior represented here is segregation controlled and shows bulklike behavior in that the concentration at the center of the particle equals the initial bulk concentration.

Figure 7. Surface Concentration vs. Time for a 50 Layer Particle with $\alpha = -12$, $\delta = -4$, and $X_b = 0.1$. The behavior represented here is competitive.

Figure 8. Average Concentration vs. Time for a) 50, b) 100, c) 200, and d) 400 Layer Particles Each with $\alpha = -12$, $\delta = 4$, and $X_b = 0.1$. These plots show the effect of particle size on the rate and extent of evaporative loss for the competitive behavior regime.

Figure 9. Depth Profiles for a 50 Layer Particle with $\alpha = -12$, $\delta = -4$, and $X_b = 0.1$. The behavior represented here is competitive.

Figure 10. Depth Profiles for a 100 Layer Particle with $\alpha = -12$, $\delta = -4$, and $X_0 = 0.1$. The behavior represented here is competitive.

Figure 11. Depth Profiles for a 200 Layer Particle with $\alpha = -12$, $\delta = -4$, and $X_b = 0.1$. The behavior represented here is competitive.

Figure 12. Depth Profiles for a 400 Layer Particle with $\alpha = -12$, $\delta = -4$, and $X_b = 0.1$. The behavior represented here is competitive.

The depth profiles show that in general, evaporative depletion extends to deeper layers as time increases. As the particle size increases, however, the concentration at the center of the particle approaches the initial bulk concentration, and the fraction of the layers which are actually depleted at any time decreases. Thus, as indicated, both the rate and extent of evaporative loss decrease with increasing particle size.

For the evaporation controlled regime (e.g. $\alpha = -12$, $\delta = 0$) the behavior, with several exceptions, is qualitatively quite similar to the competitive regime. The major difference in behavior is that the surface concentration decreases immediately with time in the evaporation controlled regime. That is, surface enrichment is not observed. In addition, the rate and extent of evaporative loss, as determined from plots of X_{ave} vs τ and depth profiles, is slightly greater for the evaporation controlled regime.

In summary, the small particle extension of the segregation/evaporation/adsorption model has been developed, and characteristic behavior regimes described by the model have been investigated. In particular, the effects of particle size on characteristic behavior have been determined, and the transition from small particle to bulk like behavior has been characterized. This model will, in future work, be used in Task 6 to investigate the loss of alkali species from small entrained aluminosilicate particles.

3.3 Measurement of Alkali Vaporization Rates

The objectives of this task are to measure the rate and thermodynamic parameters describing the vaporization of alkali species from the surface of ash and ash precursors. In prior work, experiments have been performed which demonstrate the feasibility of using laser induced fluorescence (LIF) for this purpose, and the temperature dependence of the vaporization flux of Na from $\text{Na}_2\text{O} \cdot \text{XSiO}_2$ ($X \sim 6$) has been determined. From these data, the activation energy for the vaporization process was determined. During this quarter, measurements of the LIF intensity as a function of Na concentration (i.e. calibration of the LIF signal) were performed using pure metallic Na as a

source, and, from these measurements the magnitude of the Na vaporization flux was determined for $\text{Na}_2\text{O} \cdot \text{XSiO}_2$ ($X \sim 6$).

Absolute calibration of the LIF yield for Na atoms was accomplished using a sodium metal whose vapor pressure is well known as a function of temperature. The sodium sample was placed in a resistively heated cylindrical tantalum crucible, and the crucible and associated heater and thermocouple leads were mounted in the same vacuum apparatus used previously to measure the sodium flux from sodium silicate glass. LIF experiments were then conducted at a series of temperatures over the range of 400-500 K, using the $3S_{1/2} \rightarrow 3P_{3/2}$ transition at 589.8 nm and the same collection optics as before. From these measurements, the plot of LIF intensity, I_F , vs. T^{-1} shown in Figure 13 was obtained. Also shown in Figure 13 is a plot of sodium atom density, X , vs. T^{-1} . This plot was calculated using the known vapor pressure vs. temperature relationship for elemental Na,³ the geometry of the apparatus and laser beam, and the modeled angular distribution of the sodium atoms escaping from the crucible. This last quantity was derived from a Monte Carlo calculation describing free molecular flow through a cylinder. The details of this calculation are given by Bird⁴ who also provides a FORTRAN IV program required to perform the calculation. The slope of this calculated curve is determined by the enthalpy of Na vaporization. The fact that the plot of I_F has the same slope indicates that LIF measurements performed here yield essentially the same value for the enthalpy of Na vaporization.

Knowing both the sodium atom density in the laser beam and the LIF signal, I_F , as a function of temperature as shown in Figure 13, the relationship between sodium density and LIF signal is readily established. This result is shown in Figure 14 which represents the calibration curve and is given by

$$X = \phi I_F$$

Figure 13. Observed LIF Intensity, I_F , for Na and Calculated Na Density Plotted As a Function of T^{-1} .

Figure 14. Log-Log Plot of Na Density vs. I_F for Elemental Na.

where $\phi = 4 \times 10^5 \text{ mV}^{-1} \text{ cm}^{-3}$. This calibration may be applied to the previously reported LIF data on the sodium flux from the silicate glass. This yields the plot of $\log X$ vs. T^{-1} shown in Figure 15. In the last report, it was shown that

$$X = J_v \left(\frac{b}{r}\right)^2 \sqrt{\frac{\pi m}{8 kT}} = \phi I_F$$

where J_v is the temperature dependent sodium vaporization flux, b is the radius of the source particle, r is the distance from the source particle to the source (measurement) volume, m is the mass of the sodium atom, T is the source temperature, and k is the Boltzman constant. Using this equation and Figure 15, the sodium vaporization flux is found to be

$$J_v = 6.1 \sqrt{T} \exp[-80 \text{ kcal } K^{-1} / RT] \text{ moles} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$$

It is this equation which describes the rate of sodium evaporation per unit area of particle surface.

Experiments to provide an absolute LIF calibration for potassium are presently under way and will be used in studies of potassium evaporation from illite. The data obtained from their studies will be used in Task 6 to model the release of alkalis from entrained particles.

3.4 Measurement of Segregation Rates

The objectives of this task are to measure the rates and thermodynamic parameters controlling surface segregation of alkali and other species in ash and ash precursors. These data, combined with the alkali vaporization data, will be used in Task 6 to describe the release of alkalis from entrained ash particles.

Figure 15. Plot of $\log \text{Na}_2\text{O} \cdot \text{XSiO}_2$ ($X \sim 6$) Density vs. T^{-1}

In these studies, x-ray photoelectron spectroscopy (XPS) will be used to monitor the surface concentration of alkali and other species on the surface of representative materials as a function of both temperature and time. From these data, ΔH_S will be determined.

During this quarter, the installation of the ESCA was completed. This work was scheduled for completion early in the quarter. Unfortunately, during the initial setup, several defective components were discovered. These were returned to the manufacturer for repairs and subsequently returned to ARI. The installation was then completed late in the quarter.

During the next quarter, segregation measurements will be initiated. Preliminary studies will focus on the temperature dependence of the surface composition of Beavers Bend illite. From these studies, the segregation enthalpies (ΔH_S) for segregating species will be determined. In addition, similar measurements will be performed on illite previously heated to high temperature (e.g. simulated ash). The surfaces characterized here will correspond to those investigated in the gas-surface reaction studies under Task 5. The data obtained in the measurements will be used as input parameters for the modeling studies of alkali release in Task 6.

3.5 Measurement of SO_x/NO_x Rates

Work on this task is being performed at the Morgantown Energy Technology Center in collaboration with ARI personnel and will be reported elsewhere. The objectives of this task are to determine the rates and mechanisms by which SO_2 , NO, and NO_2 react with the surface of representative ash materials.

During the quarter, ARI and METC personnel met in Morgantown (10-12 November) to outline the experiments to be performed under this task. The agreed upon studies are shown in Table 1. Preliminary studies of the base line systems are currently in progress.

Table 1 - Gas-Surface Reactions Relevant to Entrained Particles¹

Phase 1 - Baseline Studies

- (i) $\text{Al}_2\text{O}_3 + \text{SO}_2$
- (ii) $\text{Al}_2\text{O}_3 + \text{NO}$
- (iii) $\text{SiO}_2 + \text{SO}_2$
- (iv) $\text{SiO}_2 + \text{NO}$

Phase 2 - Model Systems²

- (i) $\text{Al}_2\text{O}_3/\text{Fe} + \text{NO}$ and SO_2
- (ii) $\text{Al}_2\text{O}_3/\text{Na} + \text{SO}_2$ and NO
- (iii) $\text{SiO}_2/\text{Fe} + \text{SO}_2$ and NO
- (iv) $\text{SiO}_2/\text{Na} + \text{NO}$ and SO_2

Phase 3 - Simulated Systems

- (i) Illite + SO_2 ³
- (ii) Illite + NO ³
- (iii) Ash + SO_2 ⁴
- (iv) Ash + NO ⁴

¹Experimental conditions cover the temperature range of 25-500°C and SO_2/NO exposures of 0-500 langmuirs at 10^{-7} torr. This pressure range may be extended to 10^{-4} torr.

²The system $\text{Al}_2\text{O}_3/\text{Na}$ represents an Al_2O_3 surface doped with Na, etc. Gases are listed in order of greatest interest at this time.

³The illite used in these experiments will be preconditioned by heating to high temperatures under a variety of gas flows. The specific pretreatment will be established by the results of task 4.

⁴Ash prepared for illite.

3.6 Incorporation of Data Into Model

The objectives of this task are to incorporate the data generated under Tasks 3-5 into the models developed under Tasks 1 and 2. In this manner a detailed understanding of the effects of entrained particles on alkali release, alkali removal, and the levels of SO₂ and NO_x in the combustion stream will be obtained.

ARI and METC personnel met on December 10th to outline several key combustion stream situations to be modeled and to identify specific field data against which the model predictions can be tested and compared. Based on the available data, two sets of "field" measurements will be investigated. These are the Ames alkali measurements at the Curtiss-Wright test facility and the Morgantown measurements of alkali release for illite particles in a laboratory burner.

Data from the Ames measurements are currently being reviewed and data from the alkali release measurements are being obtained from Morgantown. It is anticipated that the small particle model developed under Task 2 can be used to model the alkali release measurements, and PACKAGE code calculations can be used to model the Ames measurements. In the next quarter, these calculations will be initiated.

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