**SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULFUR SPECIES
FROM COMBUSTION.**

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INTRODUCTION

This report presents work done on a laboratory combustor in an attempt to identify mechanisms that govern the simultaneous capture of alkali and sulfur species using sorbent injection techniques. The mechanisms of capture fall into two broad categories i.e Physical transport of alkali species (in vapor or condensed phase) to the sorbent surface and Surface reaction between the alkali species and the sorbents. Water solubility, though not specific, has been used to get an indication of relative significance of these two broad mechanisms. It is assumed that the physically adsorbed alkali species on sorbents are predominantly water soluble while the chemically reacted alkali content is predominantly water insoluble. In order to infer possible dominant mechanisms, specific parameters have been varied during experimentation. Such parameters include, speciation, particle time-temperature history, and furnace burning conditions.

Effort has been expended to obtain time-resolved sorbent/alkali interaction data in the temperature region above alkali species dewpoints (approximately above 800°C). The laboratory, 6" X 240" downflow combustor for this work has been described previously. One advantage of this combustor is that large time-temperature scale experiments can be achieved. In this report, we present both the theoretical and the experimental work done in this quarter. The theoretical work is presented in terms of dewpoint calculations and possible transformations of the sorbent in the high temperature region. Experimental work done this quarter consisted of a total of 54 impactor samples. Finally, preliminary results are included although a detailed discussion of these will be done in the next quarter once more results become available.

THEORETICAL CONSIDERATIONS

(i) Equilibrium dew point calculations:

The dew-point which characterizes multicomponent vapor mixture is a temperature of practical importance. The appearance of a condensate will change the gas phase concentration of the alkali species of interest. This will result in an unfavourable shift of the gas phase-solid reaction. Condensation on sorbent surface may also result in sorbent pore blockage thus 'freezing' any further gas phase capture reactions. In order to exploit the large pore surfaces characteristic of Kaolinite, it is necessary that the gas phase alkali species diffuses substantially into the pore structure before the onset of condensation. This, inevitably, means Kaolinite has to be injected at a temperature above the dewpoint of the most significant alkali species. Injection at too a high temperature may also result in the collapse of the pore structure thus reducing the available pore surface. The dewpoint theoretically sets a lower injection temperature limit. The upper temperature limit may depend on factors such as pore collapse with temperature, and the deactivation of metakaolinite with temperature. The dewpoint depends on burn conditions, combustor flow mixing characteristics and on the most significant alkali condensate species present. For example the dewpoints for $\text{Na}_2\text{CO}_3(\text{s})$ is significantly different from that of $\text{Na}_2\text{SO}_4(\text{s})$. In this regard compare Figure 1. and Figure 2.

Thermodynamic dewpoint calculations were carried out for a combustion flue gas environment of $\text{SR}=1.2$ (Natural gas air flame), using the computer codes of the NASA-CEC program (Gordon & McBride, 1971). Figure 1 shows dewpoints for Potassium and Sodium species in the absence of sulfur. Figure 2. shows similar calculations for a sulfur level of 300

ppm (typical of a coal flame environment). In both cases, the alkali source was the alkali acetate. The major gas phase component of the alkali species, in the absence of sulfur, is the hydroxide (KOH, NaOH), and the main condensate component is the carbonate ($K_2CO_3(s)$ and $Na_2CO_3(s)$). In the presence of sulfur, the main condensate component is the sulphate ($K_2SO_4(s)$ and $Na_2SO_4(s)$). Figures 1 and 2 show that there is a significant shift (about 200 K) in the dewpoints due to the presence of sulfur.

Figure 1: Equilibrium dewpoint temperature for sodium and potassium in a flue gas environment of SR=1.2.

(ii) Chemical transformations of Kaolinite

In bench scale studies of Punjak and Shadman^[1], the major capture reaction for potassium was proposed to be:

Under this proposed capture stoichiometry, a reduction in capture of alkali species with increased temperature would be attributed to the existence of a 'melt phase' in the Kaolinite which results in reduced pore structure. In our equilibrium calculations, there exists a clear reduction in capture above 1000°C. Since, thermodynamics does not consider transport in pore structures etc, we have to look at the thermodynamic transformation of metakaolinite in order to explain the reduced thermodynamic capture.

Studies on the transformations of Kaolinite with temperature were originally reported by

Figure 2: Equilibrium dewpoint temperature of sodium and potassium sulfates at SR=1.2; SO₂ approximately 300 ppm.

Brindley & Nakahira^[2]. A more recent review of the data on Kaolinite (Al₂O₃.2SiO₂.2H₂O) is presented by Chakravorty^[3]. There is general agreement that above 450°C, Kaolinite progressively loses the hydroxyl bonds to become activated Kaolin (Metakaolinite). It has also been observed that above 950°C, Metakaolinite undergoes an exothermic reaction process and progressively transforms to a more stable structure of Mullite:

The transformation of metakaolinite to a stable 3:2 mullite via a 1:1 mullite is probably accompanied by the slow diffusion of the silicon atoms. The released silicon from this transformation reaction, readily reacts with alkali species to form amorphous water soluble alkali glass as given below:

A complete capture reaction process is thus proposed to consist of five important interaction processes namely:

- (i) Activation of Kaolinite at 450°C and above to metakaolinite.
- (ii) Diffusion of alkali species into the pore structure of metakaolinite.
- (iii) Capture reaction of equation (1)
- (iv) Competing deactivation reaction of equation (2) above 950°C.
- (v) Alkali species reaction with amorphous SiO₂ of equation (3)

The water soluble silicon in our samples will be used as a measure of the extent of mullarisation or deactivation of metakaolinite with temperature.

EXPERIMENTAL WORK

(i) Experimental design:

A schematic of the of the furnace is shown in Figure 3. Typical temperature profiles in degrees centigrade is shown along the furnace .Typical particle residence time scale is shown on the left in seconds. Both temperature and residence time profiles can be varried by changing the burn conditions. Three types of experiments were this performed quarter, namely:

(a) Base runs in which no sorbent is added to the furnace. Alkali species of interest is added to the furnace at an approximate total level of 250 ~ 300 ppm. Impactor samples are taken at selected points along the furnace corresponding to temperatures above, around and below the thermodynamic dewpoint. Analysis of this data will attempt to elucidate:

- Particle size distribution (for alkali species) above and below dewpoints.
- Whether or not there exist a significant identifiable particle size growth with downstream distance after condensation is initiated.
- Significance of on-the sampling line condensation.

(b) The second type of experiments were similar to the base runs but with sorbent added. Kaolinite is injected at a single point at a temperature far above the dewpoint. Impactor samples are taken down stream along the furnace. The results from these runs will be used to elucidate a time temperature resolution of the capture processes. Other results that can be deduced from these runs is whether or not the Kaolinite particles undergoes disintegration upon injection into a combustor. Sensitivity analysis will be attempted to see if Kaolinite particle size distribution is a function of injection temperature.

Figure 3: Schematic of the laboratory 6"X240" combustor, showing a typical experimental temperature profile and sorbent injection and sampling points.

(c) The third type of run attempts to obtain data that may answer whether or not there exist an optimum temperature window of capture. Kaolinite is injected at various temperature windows and impactor samples taken at the bottom low temperature. In analyzing these data, the variation in residence time will be accounted for using results from the first two run types.

(ii) Sampling Techniques:

Figure 4: Isokinetic sampling system using 30 lpm Andersen impactor with air as diluent.

Figure 4 shows a schematic of the isokinetic particle sampling system. An Andersen 30 litres per minute impactor is used to segregate the particles into nine discrete size classifications in the range of 1-10 micrometers. Correct particle size classification by the Andersen 30 lpm impactor requires that the total sampling flow rate through the impactor be at one ambient cubic feet per min (1 ACFM). Furthermore, it is important that no water condenses along the sampling line. The saturated partial pressure of water vapour at 21°C is approximately 0.021 atm. Water level in the furnace is approximately 20% by volume. Therefore the sampled flue gas has to be diluted by a minimum of 10 :1, to be certain that no on-line water condensation takes place. In all the experiments carried, the dilution ratio was kept between 20:1 and 15:1. To achieve this dilution ratio control, The furnace was doped with nitric oxide at a level of approximately 700 ppm. Both the furnace total Nox level and the Sample stream Nox level were simultaneously monitored using Chemiluminescence NO/NO_x analyser(Thermo electron model 10 AR) with a stainless steel converter.

Isokinetic sampling (i.e. particles sampled at suction velocity equal to their local flight velocities) reduces the skewing of the particle size distribution. Local flue gas velocities can be calculated from the total mass flow rate, burning conditions, and local temperature assuming ideal gas relationships. A higher flue gas velocity is calculated assuming a laminar flow profile assumptions while a lower flue gas velocity is calculated assuming a plug flow profile. Isokinetic sampling velocity is taken to be between the two above. Dilution air flow rate is calculated from the amount necessary to make up the total flow rate to 1.00 ACFM. The sampling process itself involve presetting the dilution air flow rate and the total sample flow rate using available flow rate calibration curves. A final adjustment is achieved by monitoring furnace and sample NO_x levels to maintain a consistent dilution ratio as required.

Figure 5: Schematic of the impactor stage assembly, as assembled for both water and acid solubility analysis.

An impactor stage assembly is shown in Figure 5. The impactor consists of eight stages and an after filter. For stages 0 to 7, two symmetrical half circular polyethylene sheets are placed on the stainless steel impingement plate. It is assumed that the weight distribution on the two collection media is equal consequently one is used in water solubility tests, while the other is used in acid solubility analysis. Stage F contains the collection plate for stage 7 and the backup total filter for collection of fumes of particle size less than 0.43 microns. The collection surfaces are assembled with a small amount of grease sprayed sparingly to reduce particle bounce and re-entrainment. For Kaolinite of particle bulk density of 1.1 gm/cm³, the stage size range

classification is given as:

Stage	Particle diameter range (Microns)
Cup	10 Microns and above
0	9.0 - 10.0
1	5.8 - 9.0
2	4.7 - 5.8
3	3.3 - 4.7
4	2.1 - 3.3
5	1.1 - 2.1
6	0.65- 1.1
7	0.43- 0.65
F	0.00- 0.43

PRESENTATION OF RESULTS

No attempt has been made to determine the alkali condensate composition. All species are presented as oxides. Although equilibrium studies indicate that the water soluble component may be an alkali carbonate or sulphate, it is both convenient and in line with the manner in which coal study data has been presented by other workers, to present all species as oxides.

(i) Data Analysis

The water and acid dissolved samples are both analyzed using Atomic absorption spectrophotometer for the elemental concentrations of Si, Al, Na and K. The mass ppm readings are then converted to mass readings in terms of SiO_2 , Al_2O_3 , Na_2O , and K_2O . The mass for each oxide is added for all stages to obtain total mass sampled. The fraction of the total for each species in each stage is calculated and tabled. The pre-separator fraction is added to stage 0. The pre-separator does not give an additional size range, but prevents particle bouncing and re-entrainment so that the impactor stages perform properly.

Since each stage does not represent an equal size range partition, the normalised mass fractions are divided by the 'Bin-Width' to obtain a particle ' mass density ' in *mass fraction per unit micron range (bin-width)*. In fact, if the impactor could give uniform size range cuts, the resulting mass fraction data would be similar to this density data. For consistency, an upper maximum particle size is assumed. At present a Kaolinite maximum size value of 50 microns has been selected arbitrarily and will be used in all data analysis. The lower cut off diameter is used as the assumed particle size for each size range. All subsequent plots, data analysis etc, will be represented with the lower cut off diameter as the effective particle size.

(ii) Preliminary results:

Figures 9-21 (appendix) are preliminary summary results of impactors so far analyzed. presented are particle density distributions for Kaolinite, total alkali content, water soluble alkali content and water insoluble alkali content. A total of 54 impactors were taken in this quarter. Figures 9 and 10 represents base runs for combustor environment with a total alkali level of 250 ppm (125

ppm Potassium and 125 ppm Sodium). Figure 9. was sampled at 900 °C corresponding to a temperature just above dewpoint while Figure 10 was sampled at a temperature of 700°C(below dewpoint). The residence time scales between the two samples approximately two seconds. For the sample taken at 900°C, both sodium and potassium exist predominantly in the after filter stage as sub-micron fumes. For sample taken at 700°C, there is a clear shift in size distribution with the bulk of the alkali species found in the 0.4-1.1 micron size range.

Figure 6 shows percent weight gain of Kaolinite due to the water insoluble total alkali fraction plotted against particle size. There seems to be no difference (so far) for all the three samples taken at different locations with different residence time. This may suggest that the weight gain by the insoluble alkali content probably depends only on Kaolinite injection temperature. There is also a possibility that pore blockage is taking place.

Figure 6: Percent weight gain due to water insoluble alkali oxides.

Figure 7, on the other hand, is a similar plot of percent weight gain of Kaolinite due to the water insoluble alkali content, plotted against the inverse of the particle diameter. The alkali content here is shown to be some function of both residence time and inverse particle diameter. It may be noted in passing that, while these are preliminary results, they none-the-less show interesting trends which will be used in future modelling approaches.

A detailed discussion of these results will be carried in the next quarter.

Figure 7: Percent Weight gain due to water soluble alkali oxides plotted against the inverse particle diameter (micron^{-1})

FUTURE WORK

Work in the next quarter will focus in detailed compilation and data analysis of the results from the samples so far taken. Modelling of transport mechanisms will also be undertaken. It is likely that as more data becomes available, the experimental approach will have to be modified in order to study, in detail, specific issues arising.

CONCLUSION

- A significant fraction of water insoluble alkali content in the Kaolinite is observed after a very short residence time (1.4 secs for sample 92). This is shown to be a mass gain in the region of 5 % to 15% . Complete reaction should show a mass gain between 28% and 42% .
- Kaolinite weight gain due to the water insoluble alkali oxide seems to be independent of particle size.
- The water soluble alkali content seems to be a linear function of the inverse of the particle size especially in the above micron range.
- Particles sampled from temperatures above dewpoints did show a significant amount of water soluble alkali content. This phenomenon requires further investigation as it suggests that either

there is a significant amount of on-the-sampling line condensation, or that there exists a significant shift from the thermodynamic dewpoint. Shifts in dewpoint may be induced by transport effects when particles are injected into a furnace.

(e) The water soluble silica is of the order of 1 ~ 5%.

These are preliminary observations and will be discussed in detail in the next quarter.

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APPENDIX

Figures 8...21

TOTAL ALKALI MASS DENSITY DISTRIBUTION

Figure 9: Sample at 900 C (No.82)

Figure 10: Sample at 700°C (No. 83).

Figure 8

Figure 11: Sample at 850°C (No:92).

Figure 12: Sample at 800°C (No. 93).

TOTAL ALKALI MASS DENSITY DISTRIBUTION

Figure 14: Sample at 850°C (No. 92)

Figure 15: Sample at 800°C (No.93)

Figure 13

WATER SOLUBLE ALKALI MASS DENSITY DISTRIBUTION

Figure 17: Sample at 850°C (No. 92)

Figure 18: Sample at 800°C (No. 93)

Figure 16:

WATER INSOLUBLE ALKALI DISTRIBUTION

Figure 20: Sample at 850°C (No. 92)

Figure 21: Sample at 800°C (No. 93)

Figure 19.

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