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

Quarterly Report No. 11

for period March 1993 - May 1993

DOE Grant Number DE-FG22-90PC90285

Prepared by

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Submitted to

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July 26, 1993

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the Director

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Introduction

Sulfur dioxide is one of the major pollutant from coal combustion application and gasification. The capture of sulfur from flue gas with lime has been investigated and proven to be effective. Previous work concluded that the overall conversion of lime is limited by the micro-structure of the particles and reaction temperature. Due to the larger specific volume of product of calcium sulfate than that of the raw sorbent of calcium carbonate, which may cause pore blockage at the pore mouth and increase the diffusion resistance of sulfur dioxide through the product layer, but this pore plugging will not apply to the particle less than 0.01 cm in diameter. The reaction temperature, which determined the chemical reaction kinetics, between 800°C to 850°C, is recommended to be the best chemical reaction temperature for sulfur removal by lime.

The alkali vapor removal has been the subject of many studies due to the possible application of coal combustion and hot flue gas turbine combined cycle which requires alkali concentration in the flue gas phase of sub parts per billion (ppb) level. But this process will increase the coal utilization efficiency dramatically. Some clay materials such as kaolinite and alumina-silica mixture like bauxite are found to be a very good sorbent for the adsorption of alkali vapor (Shadman et. al., 1988, 1989).

Adsorption is an effective method for the removal of both alkali and sulfur compounds from high-temperature combustion gases. Both of these processes have been extensively studied and sorbents have been suggested. However, the two groups of sorbents suggested and studied for the removal of alkali and sulfur are quite different in both physical and chemical properties. Calcium compounds have been used for sulfur capture while alumina-silicate type compounds

have been suggested for gathering of alkali. Since introduction of a variety of sorbents for different impurities into the same combustor is neither practical nor economical, the purpose of this study is to develop and test multi-functional sorbents that can capture both sulfur and alkali compounds simultaneously.

The main objective of this research is to develop sorbents with alumina-silica base for both as a carrier to calcium and sorbents to alkali. A number of sorbents, with bauxite based and calcium active sites, have been developed and tested in a series of experiments. The experimental results of adsorption of sulfur dioxide, alkali and combined adsorption of sulfur/alkali have been given in the previous report. Following is some of the highlights:

1. A unique reactor system is designed for experimental purpose, which consists of a high temperature furnace and its supporting system, a electronic micro balance, a computerized data acquisitions system and a flow controlling system.
2. The adsorption of SO_2 by the sorbents is tested at 800°C under simulated flue gas condition at various calcium impregnating solution concentration, and different sulfur dioxide concentration. The results show the capacity of sulfur adsorption by the sorbent is proportional to the amount of calcium impregnated on the sorbent. The effect of sulfur dioxide concentration will only change the reaction rate not the final conversion.
3. In the effects of calcium active sites on alkali sorption, results show that with the increase of impregnating solution concentration, in other words the increase of calcium sites, the initial rate is lower and the final converge time is increasing. This can be contributed to the increase of diffusion because of the calcium sites and decrease of effective surface area available for the alkali sorption.
4. In simultaneous adsorption, strong interactions are observed between the two adsorption processes. In particular, the simultaneous capture is found to be of synergistic nature, where the combined adsorption is more effective than the simple application of separate sorbents. One possible reason is the enhanced adsorption of sulfur dioxide by alkali alumina-silicates. Another one could be the formation of alkali sulfate in the gas phase and then condensed on the sorbent surface, and then the condensed species reacts with calcium, alumina and silica, which enhances both alkali and sulfur adsorption.

In conclusion, multi-functional sorbents are proved to be a very unique and effective way for high temperature combined removal of alkali and sulfur generated from fossil fuel combustion. Further works need to be done on the understanding of reaction mechanism, interaction between components, and condensation and solid-solid reaction.

Current report will focus on the further investigation on adsorption mechanism of combined reaction of sulfur/alkali. Major analytical methods used here are computerized high resolution scanning electronic microscopy (SEM), energy dispersive spectrum and x-ray diffraction.

Experimental Approach

A number of sorbents with alumina-silicate base and sulfur capturing active sites have been developed for simultaneous removal of alkali metal compounds and sulfur dioxide. Current report will focus on bauxite sorbents, which includes experiments on sulfur dioxide absorption, alkali capturing and alkali/sulfur absorption simultaneously by bauxite-based sorbents. The alkali compound used here is sodium chloride. Experiments show an effective adsorption of sulfur or alkali separately, and also the combined adsorption of alkali/sulfur. Atomic absorption analysis of reaction products shows that there is a much higher sodium existed in the combined reaction products than that of the single reaction of alkali absorption by bauxite. Further X-ray diffraction analysis shows that there is sodium sulfate in the final products of simultaneous reaction, which indicates the formation and then condensation of sodium sulfate in the reaction system.

Results and Discussion

A schematic diagram of experimental apparatus is given in Figure 1. Two mass flow controller, item #1, from MKS provide accurate flow rate control and deliver desired gas composition for the reactor. Item number 2 of heated water saturator will give required water content in the gas phase by adjusting the heating element temperature. After flowing through the flow controllers and saturator, the gas mixture of oxygen, carbon dioxide and oxygen then is mixed in a gas mixer of 3, and then together, entering reactor 5. The reacted gas mixture will then enter the gas chromatograph (GC) for gas composition analysis, and then pulsed fluorescent sulfur dioxide analyzer, and then to vent.

Figure 2 shows the results of an experiment under the condition of 230 ppm concentration of alkali and 260 ppm of SO_2 at 800°C of reaction temperature and 785°C of alkali (NaCl) source temperature. Sample used here is bauxite with impregnating solution concentration of 5.1 mM. Vertical axis gives the monitored weight change of milligrams per milligram sorbent. Horizontal axis shows reaction time. The result shows a final relative weight gain of about 80% of the initial sorbent, which is much higher compare to the single alkali adsorption of 13% (reference to former report). The first 15 hours of weight gain is about 18%, which is a higher than the combination of sulfur and alkali adsorption (14%). Further more, between 15 to 60 hours, the weight gain is almost linearly respect to time. This is a strong evidence for the physical absorption or deposition. This result leads to the following assumptions of adsorption in the previous report: first is the reaction of sulfur dioxide with calcium; and then reaction of alkali with bauxite; the formation of sodium sulfate in the gas phase and the condensation of sodium sulfate; and then the diffusion and reaction of sodium sulfate within the sorbent. These

assumption are further explained and supported in the following analysis of X-ray diffraction, X-energy dispersion SEM and Atomic adsorption.

Figure 3 shows a back scattering SEM (Scanning Electronic Microscopy) picture. There are four major phases. The brightest one on the upper edge is iron phase with almost 100% iron. The second brightest one on the lower part of the picture between two big particles is the mixture of alumina and silica with alumina rich, the atomic ratio of Al/Si is about 0.15. The third is alumina phase of the particle in the center on the lower edge. The other typical alumina phase is the big particle on the left and upper corner of the former. These particles are pure alumina phase but with different structure. The last phase is the small particle mixture of alumina and silica with a atomic ratio of Al/Si about 1.7-2.0. Sodium is mainly distributed in this phase.

Figure 4 shows a energy dispersive x-ray spectrum (EDX) of alumina phase. The major element in that phase is alumina. There are a little sulfur but no sodium and silica, which may be due to the neighboring contribution because of relative large x-ray diffraction sampling volume. An alumina rich alumina-silica phase (Figure 5) gives atomic ratio of alumina/silica of about 8, the sodium/silica ratio of about 0.43, which is close to the atomic ratio of Na/Si in the sodium alumina-silicate product (Punjak and Shadman). A small sulfur, titania and iron peaks are also detected. The silica rich alumina-silica phase has a higher sodium content (Figure 6). The atomic ratio of Si/Al is 0.57 and the Na/Si atomic ratio is exactly 0.5, which is the same with theoretical product at atomic ratio of this two element. No other elements are detected in this phase.

Figure 7 gives x-ray diffraction result of raw bauxite. X-ray was taken at 30 mA, 40 kV

alpha-Cu. The main peak at 18.29° of two theta is gibbsite. Another major crystal structure is tridymite at 20.51° , a form of silica oxide. After calcined at 800°C under simulated flue gas environment, the products (Figure 8) are mainly alpha- SiO_2 low at theta angle of 26.68° and corundum of alpha- Al_2O_3 at theta angle of 25.6° . X-ray diffraction result of the combined absorption experiment sample is given in Figure 9. There are three major crystal structure. The first one is cristobalite (SiO_2) with two theta of 21.41° . The second one is alpha Al_2O_3 of two theta 35.19° . And the third one is sodium sulfate (Na_2SO_4) with two theta angle of 31.8° . Because of the resolution, sodium alumina silicates are not shown up strongly. The analysis shows strong evidence of sodium sulfate in the sample.

X-ray energy dispersive dot-mapping of calcium, aluminum, silica, alkali, sulfur elements are presented in Figure 10. A uniform distribution of calcium and sulfur (Figures 10a and 10b) is observed, which indicates a successful impregnating process of calcium and a corresponding result of sulfur adsorption by calcium. For alumina mapping, the pure alumina and alumina rich phases have a high alumina intensity, and alumina-silica mixture has a relative low intensity (Figure 10c). Silica is mostly distributed around alumina dense area (Figure 10d), and sodium has similar distribution with silica, which indicates a corresponding relation of these two element and also indicates that silica is the limiting element for the alkali adsorption process as conclude in previous work. Iron is distributed randomly which shoes iron as a impurity nature. Those mapping are in the inner shell of the sorbent, which gives similar results with that of a alkali-only adsorption process. Differences on the edge will be given in the following paragraph.

The EDX line scanning spectrum across the sample (Figure 11) indicates that a much higher alkali and sulfur intensity (line 1 and line 4) occurs at the edge of the sample, which is

most possibly corresponding to the X-ray diffraction detected sodium sulfate. Energy spectrum of the same sample in different area (Figure 12) also shows a major difference in alkali and sulfur content. Line 2 gives alumina distribution, line 3 silica line 5 calcium and line 6 iron. Also noticing the corresponding relationship of silica and sodium in term of peak shapes of these two element excluding edges. Calcium and sulfur are almost uniformly distributed inside the sample which is identical to the x-ray mapping result shown in Figure 10.

A SEM picture on the sample edge (Figure 13) shows a flower-type pattern crystal structure. This is likely to be the result of surface condensation. An EDX spectrum on it (Figure 14) shows two strong peaks of sodium and sulfur with an atomic ratio of $\text{Na/S}=2$, which indicates a possible product of Na_2SO_4 ($\text{Na/S}=2$). This result is in line with x-ray diffraction and line scanning EDX results, which leads to a conclusion of sodium sulfate formation and condensation on the sample surface. Atomic adsorption (AA) analysis of the sample also shows a very high sodium to silica ratio (in Figure 15, B-Ca-Na-S: stands for bauxite-calcium-sodium-sulfur system) or absolute sodium value in this sample compare to the bauxite-sodium reaction (B-Na) or the theoretical value calculated based on silica limitation.

Those evidences suggest that sodium sulfate is condensed on the sorbent surface. There are two possible explanation for this phenomena. First the vapor pressure of sodium sulfate is very low, and second the sodium sulfate formation in the gas phase is over saturated, it forms a over saturation sodium sulfate vapor. So that soon after the formation, it will condensed on the porous bauxite sample. This is explained by the equilibrium calculation of gas phase reaction of sodium chloride and sulfur dioxide. In the system, an excess SO_2 is presented, theoretically all the sodium chloride will convert to sodium sulfate which has a much lower vapor pressure

than the sodium chloride at the same temperature, which results in the system temperature is far below the dew point at that concentration. That is when the condensation happened.

Conclusions

Current work is mainly focus on the analysis of products of combined adsorption of sodium and sulfur by calcium impregnated bauxite. Those studies give a clear microstructure of the solid sample and lead to the following conclusion.

The combined adsorption of alkali/sulfur consists of three main steps. First, the adsorption of sulfur and possibly some reaction of alkali; second, combination of gas-phase reaction of alkali with sorbent and condensation of sodium sulfate; the last one is the possible condensation of sodium sulfate and molecular diffusion of alkali through the particles and finding of active sites and then reaction. This sequences need to be further confirmed.

References

- Sams, D.A. and Shadman, F., AIChE J. 32 (7), 1132, 1986.
- Punjak, W.A.; Uberoi, M. and Shadman, F., AIChE J., 35(7), 1989.
- Punjak, W.A. and Shadman, F., PhD Thesis, Univ. of Arizona, 1988.
- Punjak, W.A. and Shadman, F., Energy and Fuel, 2, 702, 1988.
- Uberoi, M. and Shadman, F., PhD Thesis, Univ. of Arizona, 1989.
- Uberoi, M. and Shadman, F., Ind.Eng.Chem.Res., Vol.30, No.4, 1991.
- Smith, J.M., Chemical Engineering Kinetics, 3rd Edition, McGraw Hill Book Company, New York, 1981.
- Goldstein, J.I. et al, Scanning Electron Microscopy and X-ray Microanalysis. Plenum Press, New York, 1984.

Figure 1 A Schematic Diagram of Experimental Apparatus

Adsorption of Alkali/Sulfur

by CaO Impregnated Bauxite

Sulfur Dioxide Concentration: 260 ppm
Sodium Vapor Concentration: 230 ppm

Figure 2 Simultaneous Adsorption of Alkali and Sulfur

Figure 3 Back Scattering SAM Picture for Reacted Bauxite

1. Fe Phase;	1. Alumina Rich Phase
3. Alumina Phase	4. Alumina-Silica Mixture

Figure 4 EDX Spectrum on Alumina Phase

Figure 5 EDX Spectrum of Alumina rich Alumina-Silica Phase

Figure 6 EDX Spectrum of Alumina-Silica Mixture Phase

Figure 7 X-ray Powder Diffraction of Raw Bauxite

Figure 8 X-ray Powder Diffraction Spectrum of Bauxite
Calcined at 800 °C Under the Simulated Flue Gas Condition

Figure 9 X-ray Diffraction Spectrum of Na/S Adsorption Sample

e.

f.

Figure 10 EDX Dot Mapping of:

a. Ca; b. S; c. Al; d. Si; e. Na; f. Fe

a.

b.

c.

d.

Figure 11 Cross Section EDX Line Scanning Spectrum

1. Na; 2. Al; 3. Si; 4. S; 5. Ca; 6. Fe

Figure 12 Line Scanning of EDX Spectrum on Another Place

Line 1. Na; Line2. Al; Line 3. Si
Line 4. S; Line 5 Ca; Line 6. Fe

Figure 13 SEM Photo on the Edge of Na/S Adsorption Sample

Figure 14 EDX Spectrum of Elements on the Edge

Figure 15 Atomic Adsorption Analysis

B-Ca-NA-S : Bauxite Calcium Sodium Sulfur Reaction
 B-Na : Bauxite Sodium Reaction
 Theoretical : Theoretical Ratio of Na/Si Based on
 Suggested Mechanism (Shadman)

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