REGENERATION AND REUSE OF A LIME-BASED SORBENT FOR SULFUR OXIDES

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INTRODUCTION

The purpose of this work was to study the feasibility of regenerating and reusing lime employed as a sorbent for sulfur oxides in an industrial, circulating fluidized bed boiler that is fired with petroleum coke. At present ground limestone is supplied continuously to the boiler, and the resulting sulfated bed ash and fly ash are discarded. By regenerating the sorbent, much less limestone would be required and waste disposal would be minimized.

Since the sorbent is converted to calcium sulfate in the boiler, regeneration requires converting calcium sulfate back to calcium oxide. Previous studies showed that such conversion can be achieved by employing reductive decomposition with carbon monoxide as indicated below (1,2):

$$CaSO_4 + CO = CaO + CO_2 + SO_2 \qquad (1)$$

By such means it is also possible to produce by-product sulfur dioxide in sufficient concentration for conversion into sulfuric acid or possibly elemental sulfur.

To study the feasibility of regenerating and reusing the lime sorbent, samples of sulfated bed ash and fly ash from an industrial boiler were subjected to a number of regeneration and sulfation cycles, and changes in the apparent reactivity and sorptive capacity of the materials were observed. The experiments were conducted by employing thermogravimetric analysis (TGA) which made it possible to monitor sulfation and regeneration by observing the change in sorbent weight.

EXPERIMENTAL METHODS AND MATERIALS

The limestone supplied to the boiler is largely calcium carbonate with the principal impurity being silica. Chemical analysis of samples of fluidized bed ash and fly ash from the boiler showed the principal components of the ash to be $CaSO_4$ (58.2%, 33.6%), CaO (30.4%, 29.3%), $CaCO_3$ (1.8%, 21.5%), and SiO_2 (2.1%, 7.2%). For each component, the first number is for bed ash and the second number is for fly ash. Both materials were also found to contain small amounts of iron, vanadium, and nickel oxides arising from the combustion of petroleum coke. Approximately 98% of the bed ash particles were larger than 230 mesh size, whereas 82% of the fly ash particles were smaller than this size. The composition of the bed ash indicates that 37% of the CaO was converted to $CaSO_4$ in the boiler, while the composition of the fly ash suggests a lower level of conversion.

For some regeneration and sulfation experiments larger particles of fluidized bed ash or limestone were used as received, whereas for other experiments the materials were pelletized first, and fly ash was always pelletized first. The pellets were formed in a double-acting stainless steel die by application of high pressure with a hand-operated hydraulic press. The pellets were 6.35 mm in diameter and 1-2 mm thick. For some experiments the pellets were used directly, whereas for others the pellets were crushed, and the material screened.

The experiments were conducted with conventional TGA apparatus consisting of a vertical tubular reactor in which a balance pan for holding the reacting solids was suspended from a Cahn model 2000 electrobalance. Both the 10 mm diameter pan and 25 mm diameter reactor were made of quartz. The reactor was surrounded by a temperature-controlled electric furnace. During operation the reactor was supplied with a mixture of gases produced by combining various pure component gases which were metered separately by calibrated rotameters.

When starting with sulfated particles of fluidized bed ash or fly ash, the particles were first heated in a stream of nitrogen to 1100°C. The particles were then regenerated by treatment with a reducing gas mixture consisting of 2% CO, 5% SO_2, 20% CO_2, and 73% N_2. When the reaction appeared complete, the gas mixture was replaced by nitrogen and the temperature was lowered to 900°C. At this point the particles were sulfated by treatment with a gas mixture consisting of either 1% or 3% SO_2, 5% O_2, and sufficient N_2 to make up the balance. When the reaction appeared complete, the cycle was repeated.

The conversion during each sulfation step was based on the following relation:

$$\text{Sulfation (\%)} = \frac{\text{moles } SO_3 \text{ adsorbed}}{\text{moles Ca present}} \times 100 \qquad (2)$$

For each regeneration step the conversion was estimated by employing the relation shown below.

$$\text{Conversion (\%)} = \frac{\text{Wt. loss during regeneration}}{\text{Wt. gain during sulfation}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

A number of runs were made with the TGA apparatus to determine the regeneration and sulfation characteristics of the parent limestone, fluidized bed ash, and fly ash. Typical results obtained with bed ash are shown in Table 1. For this experiment the bed ash was pelletized, crushed, and screened to provide -25/+40 mesh particles. The particles were first regenerated and then subjected to the seven cycles of sulfation and regeneration listed. The first sulfation step required 98 min. and resulted in the conversion of 44.6% of the CaO to $CaSO_4$. The subsequent regeneration step only took 25 min. and appeared to result in the complete conversion of $CaSO_4$ to CaO. As the cycles were repeated, both the cycle time and the extent of sulfation decreased gradually from cycle to cycle. The decrease in sulfation indicated that an increasing portion of each particle became inaccessible or unreactive. This result could have been caused by sintering and closure of some of the particle micropores. Nevertheless, even during the eighth cycle of sulfation (recalling that the first cycle took place in the boiler), the capacity of the sorbent was still 26% of the maximum theoretically possible if all of the calcium were converted to $CaSO_4$. Even more encouraging were the results of the regeneration step which always seemed to achieve nearly complete conversion of $CaSO_4$ to CaO.

Similar results were obtained with -25/+40 mesh unreacted limestone particles which were prepared in the same manner as the bed ash particles by pelletizing, crushing, and screening. Upon heating the limestone particles to 900°C in a stream of nitrogen, the $CaCO_3$ was converted to CaO. The particles were then subjected to a series of sulfation and regeneration cycles using the same conditions employed with bed ash. For the early cycles the level of sulfation was nearly the same as that observed with bed ash while for the later cycles it was slightly greater. The similarity in results achieved with the two materials suggests that the small amount of petroleum coke ash present in the bed ash had little effect on the sulfation and regeneration characteristics of the bed ash.

The results observed with -25/+40 mesh fly ash particles differed in several respects from those described above when the particles were prepared and treated like the bed ash particles. For the fly ash particles the time required for the sulfation step was about half that required for the other materials. The level of sulfation achieved in the first TGA cycle was 37.7% compared to 44.6% for bed ash, and in the fifth TGA cycle it was 19.7% compared to 31.4% for bed ash. Therefore, it is apparent that the sorptive capacity of the fly ash decreased more rapidly than that of the other materials. This result was probably due to the difference in grain size of the various materials. The initial particle size of the fly ash was considerably smaller than that of the bed ash. Consequently, when the two materials were heated to reaction temperature, there would have been a greater tendency for the fly ash particles to sinter causing a greater decrease in microporosity.

CONCLUSIONS

The results of this work indicate that it would be feasible to regenerate and recycle the sulfated bed ash produced by burning petroleum coke in a fluidized bed of limestone particles. Although the experimental results showed a decline in the sulfation capacity of bed ash particles as the number of sulfation and regeneration cycles increased, it was still possible to convert 30% or more of the CaO to $CaSO_4$ after five cycles. Regeneration was more rapid than sulfation, and it was nearly always complete. The results also indicate that it would be feasible to regenerate and recycle pelletized fly ash. However, the sulfation capacity of this material declined more with each cycle than the sulfation capacity of bed ash declined.

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Table 1. Results of run made with granulated bed ash*

Cycle	Time, min.	Initial wt., mg	Final wt., mg	Δ wt., mg	Sulf., %	Regen/Sulf., %
1-S	98	39.2	58.5	19.3	44.6	
1-R	25	58.5	39.2	19.3		100
2-S	90	39.2	56.1	16.1	39.1	
2-R	24	56.1	39.3	16.8		104
3-S	89	39.3	54.2	14.9	34.5	
3-R	20	54.2	39.4	14.8		99
4-S	86	39.3	53.6	14.3	33.1	
4-R	22	53.6	39.4	14.2		99
5-S	86	39.4	53.0	13.6	31.4	
5-R	22	53.0	39.6	13.4		99
6-S	88	39.3	51.7	12.4	28.7	
6-R	20	51.7	39.4	12.3		99
7-S	80	39.3	50.7	11.4	26.4	
7-R	20	50.7	39.4	11.3		99

*Particle size: -25/+40 mesh
Weight before calcination: 54.6 mg
Sulfation conditions: 905-910°C, 1% SO_2, 5% O_2, 94% N_2
Regeneration conditions: 1105-1110°C, 2% CO, 5% SO_2, 20% CO_2, 73% N_2.