Thermochimica Acta, 26 (1978) 241–255

DEVELOPING REGENERABLE SO_2 SORBENTS FOR FLUIDIZED BED COAL COMBUSTION USING THERMOGRAVIMETRIC ANALYSIS*

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ABSTRACT

Exxon Research and Engineering Company, funded by the National Science Foundation RANN Program, is using thermogravimetric analysis as the major research tool in a program to develop for fluidized bed coal combustion (FBCC) regenerable SO_2 sorbents that are superior to limestone or dolomite. In FBCC, powdered coal is burned in a fluidized bed of limestone and the SO_2 produced during combustion reacts with the CaO to form $CaSO_4$. However, only a fraction of the limestone or dolomite reacts (low utilization) and the sulfated limestone is difficult to regenerate because high temperatures (~1100°C) are required and deactivation occurs after repeated cycles of SO_2 sorption and regeneration.

A DuPont TGA was modified to handle reactive gases. Over 100 tests were made in order to compare the relative abilities of different materials to sorb SO_2 and be regenerated. The sample, either in the form of a fine powder or small pellet, was maintained at constant temperature as it reacted in a gas stream of nearly constant composition. Reaction conditions for sulfation were 900°C, one atmosphere pressure and a gas composition of 0.1–0.25% SO_2, 5% O_2, balance N_2. Reaction conditions for regeneration were usually 1100°C, one atmosphere, and 5% CO in nitrogen. Tests were made in which the sample was cycled as many as 50 times between sulfation and regeneration conditions. Conversion of the sample (to sulfate) was determined as a function of time and number of cycles.

Candidate sorbents included simple metal oxides, mixed metal oxides (mostly aluminates and titanates), carbonates, composites containing CaO and promoters, and combinations of CaO and cement. All sorbents regenerated much faster than they sulfated. Deactivation was manifested by a decline in the sulfation rate and utilization of the sorbent. Of all materials tested, barium and calcium titanates were unique in that no measurable loss of activity occurred. All other sorbents deactivated to some extent, although many were superior to limestone. Calcium aluminate cement was also promising because it had good activity maintenance and could be made into hard pellets that would resist attrition in a fluidized bed.

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* Presented at the 7th North American Thermal Analysis Society Conference, St. Louis, Missouri, September 25–28, 1977.

TGA proved to be a very valuable tool for screening large numbers of sorbents at reproducible reaction conditions and at minimim cost. Follow-up testing of the best sorbents will be conducted in a pilot-plant scale fluidized bed combuster and regenerator.

INTRODUCTION

Fluidized bed coal combustion is a new direct combustion technique which promises to provide an environmentally and economically acceptable method of utilizing high-sulfur coal. Programs to develop this technique are being carried out in the U.S. primarily under the sponsorship of the Energy Research and Development Administration, the Environmental Protection Agency, and the Electric Power Research Institute. In the process, coal is burned in a fluidized bed of a granular material which can absorb SO_2. The fluidized bed may be operated either at atmospheric or elevated pressure. Retention of SO_2 by the sorbent depends on a number of variables, the most important of which is probably the ratio of sorbent to sulfur in the feed to the combustor. Retentions of over 90% are readily attainable[1]. Energy can be recovered from heat transfer tubes (e.g. to raise steam) immersed in the fluidized bed and, in pressurized fluidized bed combustion, also from the hot (900 °C), pressurized, flue gases leaving the combustor. Figure 1 shows a pressurized fluidized bed coal combustion system which includes a sorbent regenerator.

A disadvantage of fluidized bed combustion is that large quantities of sorbent are required to achieve low SO_2 emissions when burning high-sulfur coal. In order to minimize the amount of sorbent needed and also reduce the amount of waste solids to be disposed, a practical fluidized bed combustion system will require a sorbent that is capable of being regenerated many times, is resistant to attrition, and is economically attractive. The conventional sorbents which have been used are limestone and

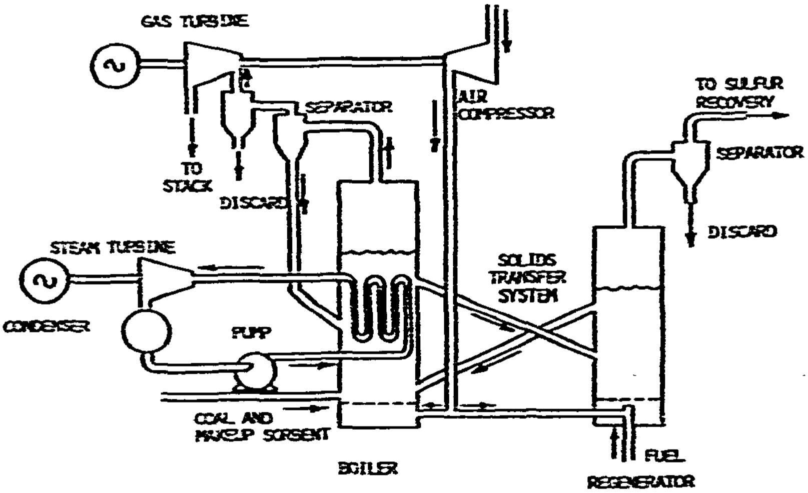

Fig. 1. Pressurized fluidized bed coal combustion system with sorbent regenerator.

dolomite but there are many problems with these natural materials. Only a small fraction of the calcium contained in limestone or dolomite is utilized (converted to sulfate), attrition rates are high, regeneration requires high temperatures and deactivation occurs after only a few cycles of sulfur sorption and regeneration, and different natural sorbents vary greatly in their reactivity with SO_2 and in attrition resistance. Improved sorbents are needed which are superior to limestone and dolomite in all of these respects.

Our objective is to identify and develop superior sorbents for fluidized bed combustion which can be used to remove sulfur compounds from burning coal in a cost effective manner. The basis for our work was several paper studies in which the thermodynamics of a large number of compounds were screened in order to identify those compounds which could absorb sulfur at the conditions of temperature, pressure, and gas composition which prevail in a fluidized bed coal combuster and be easily regenerated[2-4]. About thirty such compounds were identified but experimental results to confirm the thermodynamic prediction were lacking. Also, there was no information available on sulfation or regeneration rates, or on activity maintenance.

Since the reactions to be studied produced a weight change, thermogravimetric analysis (TGA) was chosen as the basic experimental technique used to determine the reactivity of the various potential sorbents. Using this technique, large numbers of materials could be screened at atmospheric pressure under carefully controlled and reproducible conditions.

This paper describes the TGA equipment used in these studies, including the way in which we modified the equipment to permit its use with reactive (corrosive) gases, and the reaction conditions and procedures used to carry out the tests. The outcome of the work was that two classes of materials were identified as highly promising sorbents; they appeared to be superior to all the other materials tested. The results section describes these materials.

EXPERIMENTAL

Equipment

The TGA equipment used was the DuPont 951 TGA and 990 Thermal Analyzer (control unit). The TGA consists of an electronic balance and a furnace capable of operating at temperatures up to 1200°C; it is used with the 990 Thermal Analyzer, which contains a temperature programmer-controller and an X–Y–Y' recorder. Maximum sensitivity and capacity of the balance are 0.05 mg/in. and one gram, respectively. This sensitivity would permit detection of weight changes corresponding to as little as 0.035% conversion of the conventional SO_2 sorbent, CaO, to $CaSO_4$. Most often, the TGA was operated in the isothermal mode, and the recorder produced a graph of sample weight vs. time. Alternatively, the temperature could be programmed, and a graph of sample weight vs. sample temperature produced. The second pen on the recorder was usually used to plot sample temperature, although it could be used to plot the time derivative of sample weight.

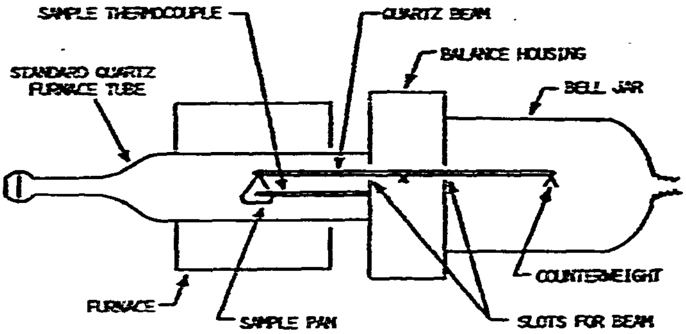

Fig. 2. DuPont 951 thermogravimetric analyzer.

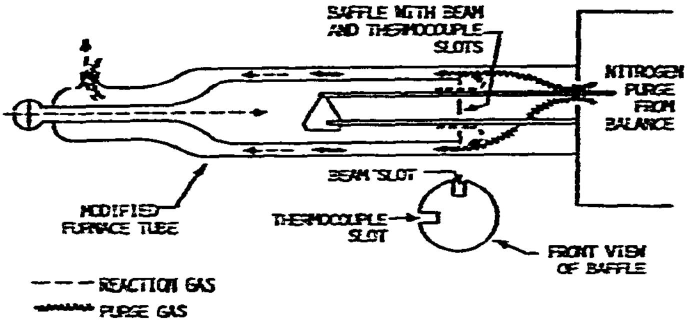

Fig. 3. Modification of DuPont TGA for use with corrosive gases.

Figure 2 is a diagram of the TGA, essentially as supplied by DuPont. Gas flows through the balance and across the platinum sample pan, which is suspended by a horizontal quartz beam at the center of the furnace. The sample temperature is determined by a chromel–alumel thermocouple located about one millimeter above the center of the sample pan. In the form seen in Fig. 2, the TGA cannot handle corrosive gases (SO_2), which would ruin the balance.

Our modification of the TGA to allow it to be used with corrosive gases is shown in Fig. 3. This is essentially the same approach used earlier by Ruth[5]. A nitrogen purge flows through the balance housing and a redesigned quartz furnace tube and type 310 stainless steel baffle provide separation between the balance and reaction zones. The modification serves two purposes: to keep corrosive gas out of the balance, and to keep purge nitrogen away from the sample, so that the composition of gas in the reaction zone is not affected by dilution with nitrogen.

In the modification, purge nitrogen enters the end of the balance bell jar and flows through a slot in the balance housing for the beam. Reaction gas enters the inner tube of the concentric furnace tube (as seen in Fig. 3) and passes over the sample. The reaction gas leaves the inner tube through slots in the circular baffle held in place at the end of the inner tube by means of a side arm (not shown in Fig. 3) attached to the balance housing. Slots in the baffle provide for passage of balance beam and thermocouple. Reaction gas and nitrogen pass together through the annular space between inner and outer tubes and are discharged through an opening near the end of the outer tube.

The bare chromel–alumel sample thermocouple supplied with the DuPont TGA would be quickly destroyed by exposure to SO_2, so that it was necessary to replace this thermocouple with a chromel–alumel thermocouple in a 0.159 cm (1/16 in.) diameter sheath fabricated of type 310 stainless steel.

Consideration of flow and diffusion in the vicinity of the slot in the balance housing showed that 800 cm^3 (0°C and 1 atm)/min would be adequate to keep reaction gas out of the balance. Greater concern was felt as to the possibility that purge gas might penetrate the reaction zone. Hence, data were obtained on weight gain vs. time for finely powdered copper exposed at 600°C to mixtures of oxygen and nitrogen of known composition. These data permitted determination of the penetration in runs in which oxygen was used as the "purge gas", nitrogen as the "reaction gas", and copper powder as the sample.

Penetration was found to depend on both the rate of flow of reaction gas and the ratio of purge gas to reaction gas. However, at a reaction gas flow of 100–200 cm^3/min, there was negligible penetration at purge gas flows as high as 1000 cm^3/min. The reaction gas flow used in the experiments was 160–200 cm^3/min; the purge gas flow was 800 cm^3/min.

A gas flow system was constructed to permit us to synthesize gas mixtures that would be required in the sorption and regeneration tests. Up to five flue gas components (SO_2, O_2, CO_2, N_2, H_2O) and six reducing gas components (CO, H_2, SO_2, CO_2, H_2O, N_2) could be blended and sent to the TGA. Pure gases from cylinders were metered through rotameters and blended in a glass mixing tube before entering the TGA. Water could be added by metering minute quantities of liquid water with a Sage Model 355 syringe pump through a hypodermic needle and into a heated tube through which the other gaseous components were flowing. The tube was kept hot enough for rapid vaporization of the water to occur. In order to switch between flue and regeneration gases, electrical solenoid valves were used. This was especially convenient during studies on activity maintenance when repeated switching between the two atmospheres was required.

Selection of reaction conditions

For carrying out the TGA experiments, it was necessary to choose standard reaction conditions that were convenient, could be readily reproduced, and were relevant to conditions that would exist in a fluidized bed coal combustor. The temperatures selected for the absorption tests were 870 and 900°C (1600 and 1650°F) since these are typical temperatures at which fluidized bed combustors operate. Choosing gas composition was more involved, partly because it was desired to measure the performance of sorbents which would be used in both atmospheric and pressurized combustors, even though all work in the TGA was performed at a total pressure of one atmosphere. The TGA was operated as a differential reactor, i.e. gases flowed past the solid sample at a rate sufficient to preclude any substantial change in gas composition.

A real flue gas would be expected to contain small amounts of CO, nitrogen oxides and hydrocarbons, in addition to SO_2, O_2, CO_2, H_2O and N_2. However, to keep the experiments simple and avoid the possibility of effects which would make it difficult to interpret data, we decided to use a gas containing only SO_2, O_2 and N_2. Five mole percent O_2 was chosen since this level is typical of a real flue gas. The level of SO_2 chosen for screening potential sorbents was 1000 ppm (0.1 %). For subsequent studies to determine the regenerability (activity maintenance) of sorbents, this level was increased to 2500 ppm, primarily to speed up the reaction and save time. Thermodynamics and reaction rates must be considered in order to relate the significance of these SO_2 levels to the operation of a real combustor at atmospheric and elevated pressures.

The sorption reaction can be written as

$$MO + SO_2 + 1/2\ O_2 = MSO_4 \qquad (1)$$

where MO represents a metal oxide sorbent. Sorption can occur if the level of SO_2 prevailing in the flue gas is higher than the equilibrium level of SO_2, which can be shown to be proportional to $1/P^{3/2}$, where P is the total pressure. Increasing pressure favors sorption; for example, if 1000 ppm is the lowest concentration of SO_2 which reacts with a sorbent at one atmosphere, then $1000/10^{3/2} \approx 30$ ppm SO_2 could react at ten atmospheres.

The EPA emission standard applicable to fluidized bed combustors is 1.2 lb. SO_2 emitted per million Btu of fuel burned. For many coals, this standard corresponds to about 600 ppm SO_2 emitted in the flue gas. Hence, a sorbent reacting with SO_2 levels above 1000 ppm in the TGA would not quite be capable of reducing emissions below the standard in a combustor operating at atmospheric pressure. Emissions would be below 600 ppm, however, for a combustor operating pressure above about 1.4 atm.

Reaction rates are, of course, also affected by SO_2 level. The TGA experiments were conducted with 1000 ppm SO_2 at a total pressure of one atmosphere. This represents the same concentration (partial pressure) of SO_2 as 100 ppm at ten atmospheres. Reaction rates would be expected to be comparable for both cases, provided that the reaction mechanism remains the same.

Reaction conditions for regeneration were 1100°C (2012°F) and a gas atmosphere consisting of 5 mole% CO in nitrogen. The reaction which occurs during regeneration is

$$MSO_4 + CO = MO + CO_2 + SO_2 \qquad (2)$$

One should note that the products of reaction (2) are not present in significant amounts when regeneration is carried out in the TGA. Thus, the reverse of reaction (2) does not occur and equilibrium is not a factor. However, in a real regenerator, CO_2 and SO_2 are present and small amounts of these products may stop the regeneration. In fact, high temperatures of about 1100°C are required to regenerate sulfated limestone ($CaSO_4$) in order to produce levels of SO_2 sufficiently high to permit recovery of sulfur from the regenerator off-gas.

The initial evaluation of the sorption and regeneration properties of the compounds and materials selected for sulfation screening was performed on fine powders. In fluidized bed combustion, the bed is granular in nature consisting of particles about 1–5 mm in diameter. The use of powders was preferred for the initial screening, however, as powders (1) minimize sample variability, (2) permit control of particle size (all samples were screened through −100 mesh), and (3) allow direct comparison of different types of materials. The use of powders also eliminated variation which might be introduced by different pellet-forming methods and different binder types used in forming the pellet. We believed, and subsequently demonstrated, that the results obtained for powders would predict directionally the results obtained for pellets fabricated from that powder.

The ability of SO_2 to diffuse into the complete sorbent sample being evaluated was the prime criterion in determining the quantity of sample powder which could be evaluated at one time. For samples larger than 8–10 mg, it was found that the percent sulfation achieved in a given time was in part an inverse function of the quantity of sample utilized. The larger the sample, the lower the percent sulfation level achieved for a specific sorbent. Below the 8–10 mg level for most substances, the percent sulfation was found to be invariant for a given time and SO_2 level. The influence of diffusion was also observed for pellets. However, in this case most pellets were prepared with sufficient uniformity so that pellets of a given sorbent possessed similar mass and size thereby permitting direct comparisons within one pellet type.

Test procedures

In preliminary experiments to screen various materials for their ability to absorb SO_2, about 8–10 mg of finely powdered sample was spread out on the platinum sample pan of the TGA. Later, sorbent pellets weighing from 15 to 40 mg were tested. In all cases, the sample was heated in nitrogen at 20°C/min from room temperature to 900°C, which was the usual temperature at which sulfation tests were carried out. The gas atmosphere was then quickly changed to the sulfating (flue) gas mixture, and sulfation proceeded at constant temperature while a record of sample weight vs. time was plotted. The sulfating reaction was usually allowed to continue for 150 min, or 75 min if regeneration was to follow. In the latter case, the gas atmosphere would be again changed to nitrogen, temperature raised at 20°C/min to the normal regeneration temperature of 1100°C, and regeneration begun by changing the atmosphere to the CO/N_2 mixture. Regeneration at 1100°C was much faster than sulfation at 900°C, and was usually completed in 5–15 min. For runs in which the sorbent was cycled between sulfating and regenerating conditions, nitrogen was readmitted after regeneration and the temperature reduced to 900°C.

RESULTS AND DISCUSSION

The compounds and materials screened for sulfation and regeneration response were those (1) selected from the thermodynamic screening noted earlier, (2) compounds

TABLE 1

SUBSTANCES SCREENED FOR ABILITY TO ABSORB SO_2

Reaction Conditions: 870-900°C, 0.1% SO_2, 5% O_2, balance N_2, 1 atm pressure.

Simple oxides			*Aluminates (sulfated)*	*Other materials*		*Titanates*		*CaO-containing composites and cements (all sulfated)*[b]
Sulfated	*Did not sulfate*			*Sulfated*	*Did not sulfate*	*Sulfated*	*Did not sulfate*	
Na_2O[a]	MgO	Ce_2O_3	$Li_2Al_2O_4$	$BaCO_3$	$(CaO)_3SiO_2$	Li_2TiO_3	$PbTiO_3$	$(CaO)_3Al_2O_3$
BaO	Mn_3O_4	ThO_2	$BaAl_2O_4$	$CaCO_3$		$BaTiO_3$		$(CaO)_3Al_2O_3$-7% Na_2O
SrO	CoO	Bi_2O_3	$SrAl_2O_4$	$CaSiO_3$		$SrTiO_3$		$(CaO)_3Al_2O_3$-1.1% Na_2O
CaO	NiO	Y_2O_3	$Ca_3Al_2O_6$	$BaSiO_3$		$CaTiO_3$		$(CaO)_3(SiO_2 \cdot Al_2O_3)_{1/2}$-14.6% Na_2O
La_2O_3	ZnO			$BaZrO_3$				$(CaO)_3(SiO_2 \cdot Al_2O_3)_{1/2}$-0.5% Na_2O
								$(CaO)_3SiO_2$-3% Na_2O
								85% CaO/10% SiO_2/5% Na_2O
								CaO + Portland type 1 cement
								CaO + calcium aluminate cement

[a] Melted on sulfation.

[b] Formulas indicate stoichiometric proportions of starting materials only, not composition of final sorbent after heat treatment.

with structures similar to those of compounds selected from thermodynamic considerations, and (3) other compounds and materials selected by literature review. The compounds selected included simple oxides, carbonates, and complex oxides such as titanates, aluminates and silicates. Also tested were "composites", mixtures of CaO and Al_2O_3 and/or SiO_2 with or without sodium, as well as combinations of CaO with Portland or calcium aluminate cement. In general, the compounds and materials tested contained at least one element from Groups IA or IIA of the periodic table, and emphasized those containing Ba, Sr, Ca, and Na. The substances evaluated for sorption and the testing outcome are shown in Table 1.

The sorption/regeneration properties of almost 40 potential sorbents were evaluated with the TGA. The criteria which we used to evaluate all potential sorbents tested included: sulfation rate (as measured by the percentage of the theoretically possible quantity of sorbent which could be sulfated, determined for a specified time period), the mass of SO_3 sorbed per mass of sorbent, ease and completeness of regeneration and activity maintenance. Over the 75 min sulfation period utilized, the sulfation levels attained ranged from 20 to 90% for the best sorbents. Regeneration was considerably faster, requiring only 2–5 min for complete regeneration.

The sorbents we found to be the best and most compatible with FBC operation were the titanates of barium and calcium as well as calcium aluminate cement (CAC). In addition, certain composites of $CaO/Al_2O_3/SiO_2$ performed well and served to illustrate important fundamentals of the sulfation/regeneration reactions.

Composites

The composites were combinations of CaO with Al_2O_3 and/or SiO_2 and in certain cases, sodium. The composites were prepared by coprecipitation. For example, materials with the empirical formula $(CaO)_3\text{-}(SiO_2 \cdot Al_2O_3)_{1/2}$ were prepared by adding solutions of sodium silicate and sodium hydroxide–sodium aluminate to a calcium nitrate solution. The resulting slurry was filtered, washed, dried at 150°C, sieved, pelletized, and heated to 1100°C. Samples with two different levels of sodium were prepared by varying the thoroughness of washing the filter cake.

The composites were selected for screening (1) to evaluate the effect of combining CaO with materials commonly used as supports in the catalyst industry which could make CaO more attrition resistant, and (2) to determine the effect of alkali metals as promoters on the sorption and regeneration reactions. In addition, the evaluation of composites seemed to emphasize the acid–base nature of the SO_2–sorbent reaction.

In general, it was found that the reactivity of sorbents decreased in the order $Al_2O_3 > Al_2O_3 \cdot SiO_2 > SiO_2$. The addition of sodium had no effect on the sorption reaction of the composite containing Al_2O_3 but did increase the sorption rates for the other composites. Also, the presence of sodium in all composites prolonged their sulfation/regeneration activity and increased the capacity for SO_3 sorption per mass of sorbent. These observations may be attributable to an acidity effect: the more basic the overall sorbent the more rapid the sulfation reaction. This is in line with the acid–base nature of the SO_2–sorbent reaction. It is also possible that this phenomenon may be attributable to a eutectic melt which is formed by calcium and sodium. The presence of calcium and sodium in the molten form would enhance the reaction rate of these species and should promote the practical reversible nature of the reaction.

However, the presence of sodium in a sorbent has some serious drawbacks. Most important is our observation that some of the sodium volatizes under sulfation and regeneration conditions. In a practical fluidized bed this would result in the highly undesirable presence of sodium which could corrode the system and be highly deleterious to turbine blades in a turbine generator if present downstream. It was also observed that at room temperature the presence of sodium tends to reduce the crush strength of the composites. In addition, in our testing, sodium has attacked the balance beam of the TGA and the furnace tube, both of which are made of quartz, and has necessitated their replacement. As a consequence, we have eliminated from consideration sorbents which contain alkali metal ions.

Titanates

Two sorbents which TGA testing revealed possessed excellent properties were the titanates of barium and calcium. Of all the potential sorbents tested, $BaTiO_3$ sulfated the most rapidly. Not only was $BaTiO_3$ the most rapidly reacting sorbent tested, but repeated sorption/regeneration revealed that most $BaTiO_3$ as well as $CaTiO_3$ samples tested exhibited no activity loss on cycling. Most sorbent powders tested, whether naturally occurring sorbents such as limestone or new sorbents under evaluation, deactivated rapidly after the second cycle. This was especially true for calcium-containing substances. In addition, it was found that $BaTiO_3$ could be fully regenerated at a lower temperature than the natural sorbents. Thus, regeneration using CO may be practical for $BaTiO_3$ at temperatures such as 1000°C or lower. This can result in significant energy savings during regeneration.

Thermodynamic calculations have indicated that the SO_2 levels which can be produced during regeneration are much higher for $BaTiO_3$ and $CaTiO_3$ than for sulfated limestone at a given regeneration temperature. Thermodynamics also predict that SO_2 levels suitable for sulfur recovery processes can be produced at lower regeneration temperatures for the titanates than for sulfated limestone. Thus, the cost of energy for regenerating and the cost of sulfur recovery could be reduced using these titanates.

Samples of sulfated and regenerated $BaTiO_3$ were analyzed using X-ray diffraction. The products of sulfation were $BaSO_4$ and TiO_2. After regeneration, only $BaTiO_3$ was found. Thus, the reactions which occur during sulfation and regeneration can be written as

$$BaTiO_3 + SO_2 + 1/2\ O_2 = [BaSO_4 + TiO_2] \tag{3}$$

$$[BaSO_4 + TiO_2] + CO = BaTiO_3 + CO_2 + SO_2 \tag{4}$$

Similar reactions probably occur with $CaTiO_3$.

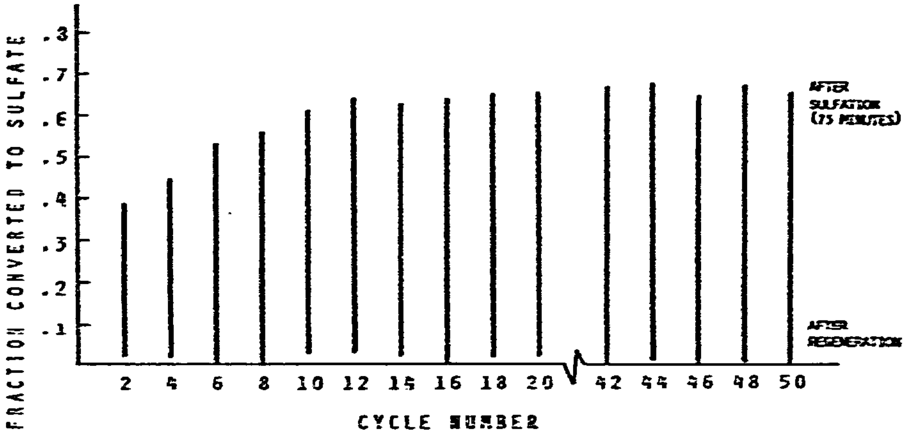

Fig. 4. Cycling of $BaTiO_3$ (+ 6% H_3PO_4) pellets between sulfation and regeneration conditions.

A practical fluidized bed combustor will require a granular or pellet-like sorbent. Pellets of $BaTiO_3$ were made by two methods. The first method, which yielded pellets that were hard but did not react, involved pressing $BaTiO_3$ powder into pellets and heating at temperatures ranging from 980 to 1370 °C. Pellets formed in the lower portion of the temperature range possessed insufficient strength. At the higher temperatures, glass formation occurred making the titanate pellet non-reactive. In the second method, $BaTiO_3$ powder was mixed with either 6 or 12 wt.% H_3PO_4, formed into pellets, pressed at 16,300, 32,600 or 65,200 psig, dried, and heated at 300 °C. This is similar to a technique used in the ceramics industry to pelletize powders. Pellets made with 6% acid and pressed at lower pressure were most reactive.

A $BaTiO_3$ pellet prepared with 6% H_3PO_4 was subject to sulfation and regeneration cycling fifty times. This run demonstrated the ability of $BaTiO_3$ to maintain its activity even in pellet form, as is shown in Fig. 4. The figure shows the sulfation levels after sulfation and regeneration for every even numbered cycle. The sulfation performance of the pellet as measured by the fraction sulfated during the 75 min sulfation phase of each cycle actually increased from about 40% at the start, to about 65% after 10–15 cycles, and remained at this level through the 50th cycle. Swelling of the pellet was noted after the test. The use of H_3PO_4 and pressure coupled with the molar volume change which occurs on sulfation of this and virtually all sorbents may be responsible for this effect. Examination of the pellet by transmission electron microscopy revealed that an apparent loss in crystallinity had occurred during cycling. This change may contribute to the increase in activity by causing an increase in porosity which could be responsible for pellet swelling.

Calcium aluminate cement

Calcium aluminate cement (CAC) has a number of advantages as an FBC sorbent. CAC is known for its high strength at high temperatures; it can be made into pellets by reaction with water; porosity required to accommodate the molar volume change occurring on sulfation can be incorporated into CAC pellets. Commercially available CAC contains primarily $CaAl_2O_4$, lesser amounts of other calcium–aluminum oxides and minor quantities of iron oxides, SiO_2 and TiO_2. CAC is available in large quantities from a number of manufacturers.

CAC pellets have been prepared using two different methods. In the first, the CAC powder is mixed with water and the resulting paste extruded into pellets. In the second, the powder is pressed into a pellet using a pilling machine. The resulting pellet is then sprayed with a mist of water. With both methods, the pellet is then cured in a moisture-saturated environment and subsequently heated. Proper initial curing is required if high pellet strength is to result.

Extruded CAC pellets were prepared using water-to-cement ratios over the range of 0.22 (stoichiometric) to 0.5. In general, the higher the water-to-cement ratio, the weaker, but more reactive the pellet. This is not surprising since higher porosity is obtained as water content is increased. Although pellets prepared by extrusion were found to be attrition resistant, especially at the lower water-to-cement ratios, pellets prepared using pilling were even more attrition resistant. The compacting action of the pelletizer was apparently responsible for the increased attrition resistance.

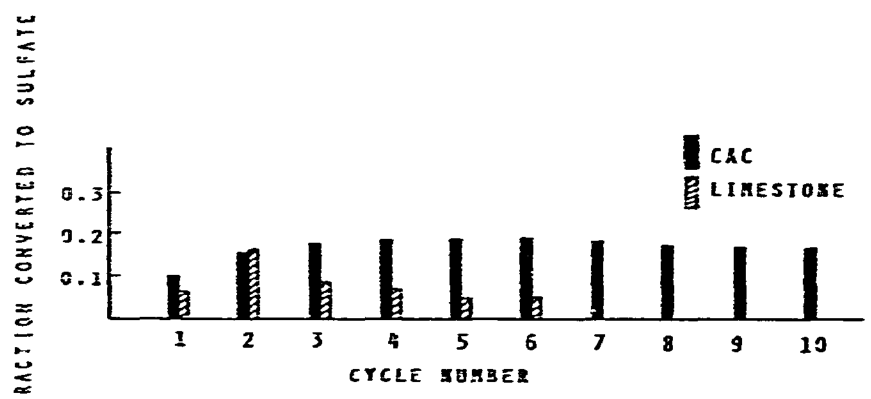

Fig. 5. Comparison of pressed CAC pellets with Grove limestone.

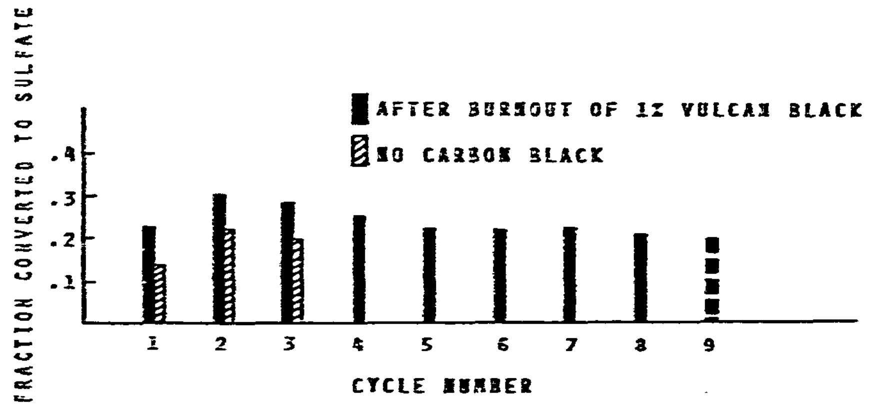

Fig. 6. Comparison of CAC pellets without and after carbon-black burnout. SO_2 level = 0.1% for cycle 1, 0.25% for cycles 2–9.

In general, CAC pellets possessed better activity and activity maintenance than limestone granules of comparable size and weight. Figure 5, which shows the sorption–regeneration cycling for limestone and a CAC pellet prepared by pilling, indicates that the rate of sorption for limestone (and for most other Ca-containing substances) is a maximum on the second cycle, and declines rapidly thereafter. This is not the case for the pilled CAC, however, probably because much of the porosity which is induced during cycling is maintained.

Porosity may be added to pellets manufactured by either method by the use of burnables. These include carbon black, starch and even pulverized nut shells. The burnable is mixed with either the cement paste or powder depending on the preparative method utilized. Porosity is created when the organic powder has burned off. The pore size distribution can also be controlled by adjusting the size of the combustible powder. The activity of CAC pellets has been increased by using carbon black in the cement paste. This is illustrated in Fig. 6 which shows pellets formed by burnout of a water–CAC–carbon black paste compared with similarly formed pellets without carbon black. The dashed line for the last cycle indicates that the pellet was not regenerated.

CONCLUSIONS

Advantages of using TGA

Our application of thermogravimetric analysis has shown it to be a convenient, flexible, low cost tool fully capable of rapidly evaluating the sorption/regeneration characteristics of candidate sorbents in a controlled manner. The advantages of TGA analysis in performing this type of assessment in terms of sample size required, gas quantity utilized, time needed and sample type flexibility are noted below.

The TGA evaluation of potential sorbents can be accomplished using minimum quantities of material. We generally used less than 10 mg in performing our evaluations. The ability to completely determine the sorption/regeneration characteristics of a small quantity of material is of incalculable value if only a small amount of a sorbent is available to the researcher.

The evaluation procedure itself is rapid. Because of the relatively small mass and volume of the heated area of our TGA, initial heating and changes in temperature could be accomplished rapidly. As the TGA is a very sensitive instrument, minute weight changes can be monitored routinely. This means that the sorbent evaluation period need not be prolonged in order to reach a workable conclusion regarding the efficacy of the candidate sorbent. Typically, 2–3 h were required for a complete sorption/regeneration cycle, with sorption being performed for a uniform 75 min period, and regeneration requiring no longer than 10 min. In addition, simulated combustor gas can be generated relatively easily using gas cylinders and rotameters. Because of the small size of the TGA cell, relatively small quantities of gas are required. Thus, because the TGA can evaluate a small sample in a relatively brief time using minimal quantities of gas, it can be considered to be a cost effective technique.

The flexibility of the TGA permits the evaluation of both powdered and pelletized sorbents. Evaluation of a sorbent as a powder permits the determination of the "pure" sorbent properties of the material. This may not be possible when pellets are used. The preparative method and/or binder utilized could influence the sorbent characteristics being determined.

Cost of new sorbents

Any sorbent not obtained from natural sources will surely cost far more than limestone on a $/ton basis. However, only through a complete analysis of the total costs of using a sorbent in fluidized bed combustion can it be possible to determine if that sorbent is competitive with limestone. The cost factors which must be taken into account, in addition to the cost for fresh sorbent are

(*1*) Quantity of fresh sorbent actually needed. (This will depend on the number cycles of sulfation and regeneration which are practical for a sorbent).

(*2*) Regeneration cost, particularly energy cost.

(*3*) Sulfur recovery cost.

(*4*) Waste sorbent disposal cost.

As a first step in determining the overall costs of new sorbents, the preparation cost of barium and calcium titanates, and CAC, have been estimated. Barium titanate can be prepared by heating $BaCO_3$ with TiO_2 in a kiln. Calcium titanate can be prepared similarly by heating $CaCO_3$ with TiO_2. Based on the current cost of these raw materials, plus the costs associated with manufacturing the sorbent in the form of pellets suitable for fluidized bed combustion, we have estimated that $BaTiO_3$ and $CaTiO_3$ would cost $1000–1500 per ton. It may also be practical to form $BaTiO_3$ from $BaSO_4$ and TiO_2 using CO at an elevated temperature. Solid raw materials cost about $200/ton and an ultimate sorbent cost in the $500–600 range is not unreasonable.

CAC is commercially available in quantity at $150 per ton. The cost of preparing pellets and calcining was estimated at $30 per ton. Thus, the total cost of producing pellets from CAC would be about $180/ton.

FUTURE WORK

Our efforts are now being directed toward improving the properties of pellets of the titanates and CAC and preparing to evaluate them in a coal burning fluidized bed combustor and regenerator.

The attrition properties of barium and calcium titanate pellets will be improved. The activity of CAC pellets and their attrition resistance will also be improved through, respectively, the use of new formulations of burnables and aggregates. TGA will continue to be used as the primary experimental tool in assessing sorbent activity. TGA evaluation will assure that attrition properties of sorbent pellets are not improved at the expense of sorbent activity.

Pellet attrition resistance determinations will shift from the use of a small room temperature fluidized bed to the use of a similar bed operated at FBC temperatures.

It is anticipated that the use of a high temperature test will provide a more realistic evaluation of pellet attrition resistance.

Evaluation of only the best all-around sorbents will occur in a coal burning pilot scale fluidized bed combustor and regenerator. Correlations will be established between sorbent performance as measured using the pilot-scale FBC and the large body of sorbent performance data obtained using the TGA.

ACKNOWLEDGEMENT

The studies reported in this paper were carried out by Exxon Research and Engineering Company under a grant (No. AER75-16194) from the National Science Foundation RANN Program. We wish to thank the members of the review panel for this program for their invaluable suggestions. The members are: A. Jonke (Argonne National Laboratory), H. Phillips (Fluidized Combustion Company), P. Turner (EPA), G. Weth (ERDA), and T. Wheelock (Iowa State University). Technical direction has also been supplied by Dr. Andrej Macek of ERDA, Fossil Energy Research. The laboratory assistance of Mr. T. C. Gaydos and Mr. D. T. Ferrughelli is gratefully acknowledged.

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