SORBENT-BASED RECOVERY OF SULFUR FROM REGENERATION TAIL GASES

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The U.S. Department of Energy (DOE), Morgantown Energy Technology Center (METC) is sponsoring research on advanced methods for controlling contaminants for hot coal gas streams of integrated gasification combined-cycle (IGCC) systems.(1) The programs focus on hot gas cleanup technologies that match or nearly match the temperatures and pressures of the gasifier, cleanup system, and power generator. The purpose is to eliminate the need for expensive heat recovery equipment and to avoid the efficiency losses associated with fuel gas quenching. DOE/METC has originated the Gasification Island concept for IGCC systems, which combines temperature and pressure matching, modular shop fabricated construction, and steam and air integration of the gasifier and turbine. Figure 1 illustrates the simplified IGCC system that can be achieved with hot gas cleanup. For the control of sulfur in the coal gasifier gas, DOE/METC continues to conduct and to sponsor work toward the development of a zinc ferrite absorption process. Absorption capacity of the zinc ferrite is highest at temperatures of 800 to 925 K compatible with the operation of a fixed-bed gasifier turbine system.

The hydrogen sulfide laden fuel gas passes through a fixed bed of zinc ferrite, in the form of 3/16-inch extrudates, which absorbs sulfur up to 25 percent of its weight. The clean gas contains less than 5 ppm, well below New Source Performance Standards (NSPS) and also enhances corrosion and erosion protection for the downstream turbine. The sulfided sorbent is regenerated with a dilute typically less than 2 percent oxygen containing gas. The oxygen content of the regenerator gas is limited to avoid overheating and sintering the sorbent due to the highly exothermic oxidation of the sulfide to sulfur dioxide. The tail gas from the regeneration process must be further processed to remove the sulfur and recover it in an environmentally acceptable manner in a salable or readily disposable form.

This paper will discuss the results of experimental/theoretical research on two novel process concepts for elemental sulfur production from regeneration tail gases. Both concepts utilize a highly efficient sodium/aluminum (Na/Al) based SO_2 sorbent at elevated temperatures (800 to 1,000 K) and pressures (1 to 3 MPa). One concept involves sulfation of the Na/Al sorbent with the tail gas followed by regeneration with reducing gas to produce a suitable Claus plant feed. The other concept aims for single step sulfur production by reacting the tail gas with a small quantity of raw coal gasifier product gases over the sorbent.

The first concept is schematically shown in Figure 2. The SO_2 in the tail gas is absorbed onto the Na/Al sorbent and the hot diluent is recycled for regenerating zinc ferrite. The sulfated Na/Al sorbent is then regenerated using a small side stream of the coal gasifier gas. The resulting concentrated sulfur stream at elevated temperature and pressure containing from 10 to 50 percent H_2S is a suitable feed for a Claus plant for elemental sulfur recovery.

The preparation of the Na/Al sorbent follows from Beinstock et al. at the U.S. Bureau of Mines for the removal of SO_2 from combustion flue gases.(2) Further development in this study has produced a sorbent as strong 1/16 inch to 1/8 inch extrudates with greater structural integrity, reactivity, capacity, and mechanical strength.(3) Enhancement of these properties is believed to be necessary for successful application at high temperature and pressure conditions.

The sorbent has been tested at atmospheric pressure as well as elevated pressures to demonstrate the potential of the concept shown in Figure 2. Atmospheric pressure tests have been carried out using both a fixed-bed reactor system and a thermogravimetric reactor (TGR) system. Tests have been conducted at 800 to 975 K with a tail gas containing 1 to 2 percent SO_2. These conditions are representative of zinc ferrite regeneration tail gas. Atmospheric pressure tests have shown that the sorbent can absorb SO_2 up to 40 percent of its weight. The sorbent can be regenerated while maintaining a crush strength greater than 13.5 N/mm over 20 sulfation/regeneration cycles. In atmospheric pressure fixed-bed tests, the sorbent demonstrated high efficiency in absorbing SO_2 by reducing it from 2 percent to less than 10 ppmv. This essentially "zero" prebreakthrough level of SO_2 was maintained for over 2 hours at a space velocity of 2000 h^{-1}. Approximately 30 percent by weight SO_2 was absorbed prior to 100 ppm SO_2 breakthrough. Regenerations of the sorbent with coal gasifier gas and hydrogen in separate tests produced H_2S rich gas streams containing up to 16.4 and 60 percent H_2S, respectively.

Elevated pressure TGR tests have recently been initiated to evaluate sulfation and regeneration kinetics that could be used to predict fixed-bed sorbent performance at elevated pressure. Figure 3 compares the atmospheric pressure sulfation rate to sulfation rate at 2.5 MPa. As can be seen, the overall SO_2 absorption capacity as a function of time is significantly higher at 2.5 MPa. This indicates that it will be possible to sulfate a fixed-bed of the sorbent to significantly greater levels at elevated pressures than at atmospheric pressure, prior to breakthrough. Following completion of measurement of elevated pressure sulfation/regeneration kinetics, a fixed-bed absorption/regeneration model will be developed to predict sorbent capacity at breakthrough in fixed-bed reactors. Bench-scale tests will then be carried out to demonstrate the concept at elevated pressures.

Elemental sulfur has been observed on the surface of the sorbent following sulfation/regeneration cycles. Also significant amounts of elemental sulfur elutes from the sorbent after breakthrough has been achieved during sulfation. This has suggested a second concept for direct recovery of elemental sulfur from regeneration tail gases which if successful would result in significant reduction of the burden on the Claus plant. Ideally this concept (shown schematically in Figure 4) may allow the complete elimination of the Claus plant. A thermodynamic analysis of potential sulfur forming reactions of H_2, SO_2, CO, H_2S, CO_2, and steam indicates that 96 to 98 percent of the SO_2 can be potentially converted to elemental sulfur at 800 to 1,000 K and 2.5 MPa. A few bench-scale tests will be carried out in the future to assess the potential of this concept.

References

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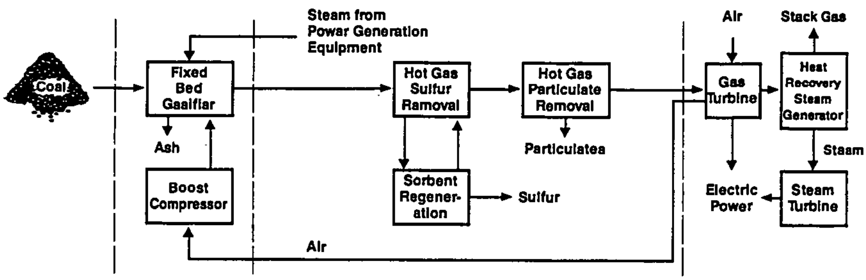

Figure 1. Gasification island concept for IGCC systems.

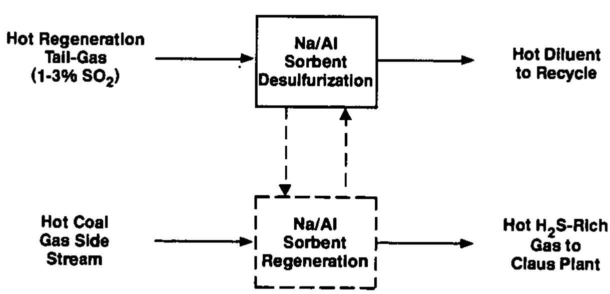

Figure 2. High temperature regeneration tail-gas treatment.

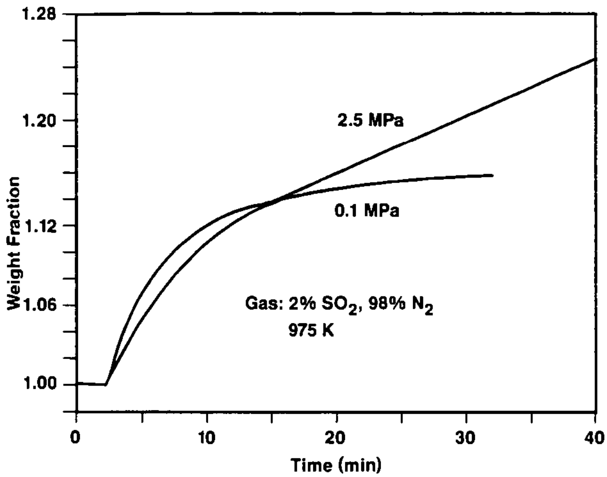

Figure 3. Effect of pressure on sorbent sulfation rate.

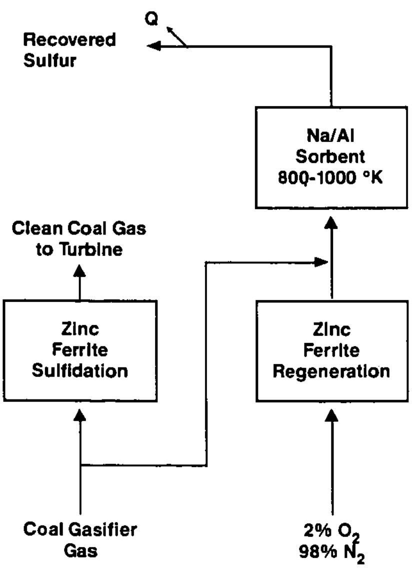

Figure 4. Direct recovery of sulfur from regeneration tail-gas.