Regenerable Solid Sorbents for Claus Tailgas Cleanup: A Treatment Process for the Catalytic Removal of SO₂ and H₂S

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Use of a regenerable solid sorbent can offer advantages over conventional wet scrubbing for Claus tailgas treatment. In this paper, we describe a novel process/catalyst combination for this service. The Mobil Oil SO_x Treatment (MOST) process, demonstrated here on the laboratory scale, consists of first combusting the Claus tailgas with air, converting all sulfur species to SO_2/SO_3. The SO_x is then sorbed onto a solid sorbent, and in a separate step, the sulfur is reductively desorbed as a concentrated stream of mainly SO_2 and H_2S, which can then be recycled to the Claus plant for further processing. Catalyst screening for this application focused on examining alumina and magnesium aluminates, with oxidation promoters including ceria, vanadia, and platinum. The materials with the highest SO_x uptake are a commercial FCC SO_x transfer additive and a vanadia/ceria-promoted, magnesium aluminate ($V/Ce/Mg_2Al_2O_5$) spinel (54 and 46 wt % SO_x uptake, respectively). During most of the adsorption period, the SO_2 level in the effluent from the sorbent bed was below 1 ppmv. When the same base magnesium aluminate was examined with ceria but without vanadia, the SO_x uptake was lower (25 wt %), while the base alone had fairly low uptake (5 wt %). Thus, effective SO_2 oxidation promoters are necessary for this application. Oxidation of CO to CO_2 was also demonstrated over these catalysts. All materials examined were found to be regenerable under hydrogen. The main products observed were SO_2, H_2O, and H_2S. The results indicate that a regenerable solid sorbent-based SO_x abatement system can give lower emissions of sulfur species and of CO than current Claus treatment processes and may allow a capacity increase in a hydraulically limited Claus plant.

Introduction

In conventional petroleum refining operations, sulfur is removed from hydrocarbon streams primarily by reductive processes, such as catalytic hydroprocessing, to yield hydrogen sulfide. Hydrogen sulfide is also produced during catalytic cracking and occurs naturally in oil and gas deposits. In these situations, the hydrogen sulfide is typically collected by contacting the gas stream with an amine-based solution. Subsequent stripping of the amine solution yields a concentrated acid gas stream, which is fed to a Claus plant. In the Claus plant, about a third of the hydrogen sulfide is combusted to form sulfur dioxide, which is then reacted with the remaining hydrogen sulfide to yield elemental sulfur. Because of equilibrium limitations, only about 97% of the feed sulfur is usually recovered in a Claus unit.

The remainder of the sulfur from such processing, in the form of H_2S and SO_2, must be treated prior to release to the atmosphere. Two common types of Claus tailgas processes for SO_2 abatement for this application, which enjoy worldwide use (Kirk–Othmer, 1981), are the Beavon/Stretford and selective amine absorption processes. Both of these processes involve wet scrubbing or absorption steps, require hydrogen, and may be energy and labor intensive. With a Stretford unit, the tailgas SO_2 is reduced to H_2S, and then the H_2S is oxidized to a fine suspension of elemental sulfur in an aqueous solution of sodium carbonate, sodium metavanadate, and anthraquinone disulfonic acid. In selective amine processes, the SO_2 is also reduced to H_2S, and the tailgas is then treated to remove water, CO_2, and traces of SO_2 in a caustic quench and is contacted with an amine solution which has a high selectivity for H_2S removal in the presence of CO_2. After the H_2S is

stripped from this solution, it is returned to the Claus plant for further processing. Both of these processes can reduce sulfur emissions to several ppm but are less effective in removing CS_2 or COS or mitigating any CO which may pass through the Claus plant.

A solid sorbent system which can combust the sulfur-containing species and selectively capture the SO_2 produced offers operational advantages over these wet scrubbing processes. Herein, we describe a novel process and catalyst combination, called the Mobil Oil SO_x Treatment Process (MOST), for achieving these goals. This process consists of the following steps:

(1) Combust the Claus tailgas stream with air, to raise its temperature, convert all sulfur species (H_2S and residual COS and CS_2) to SO_2/SO_3, and convert CO to CO_2.

(2) Adsorb the SO_x onto a high-capacity solid sorbent, in either a fixed, moving, or fluidized bed.

(3) In a separate step (for swinging fixed beds) or in a separate vessel (for moving or fluidized beds), reductively desorb the sulfur from the solid as a concentrated stream of mainly SO_2 and H_2S, which can then be recycled to the Claus plant for further processing.

The MOST process utilizes a solid catalyst and can offer advantages over solution-based systems in terms of reliability, capacity, extremely low H_2S and SO_2 emissions levels, ability to convert COS, CS_2, and CO, and reduction of waste disposal. Although this paper describes the MOST process for SO_2 reduction from Claus tailgas emissions, its flexibility allows for process modifications for mitigating several other stationary SO_x emission sources, such as from FCC tailgas and power plant applications; these will be described in upcoming publications.

In designing catalysts for MOST, both external literature describing the use of FCC SO_x capture materials

and catalyst design principles to maximize the effectiveness of the catalyst systems for use in the MOST process were drawn on. FCC SO_x transfer additives function by oxidatively adsorbing SO_x on metal oxides under the oxidative conditions present during FCC catalyst regeneration and release the sulfur primarily as H_2S under the reducing conditions present in the FCC riser reactor (i.e., react SO_x with hydrocarbons and hydrogen to yield H_2S). Hirschberg and Bertolacini (1988) discuss several materials which are potential SO_x capture agents in FCC regenerator operations. For these applications, platinum- and ceria-promoted aluminas, as well as magnesia-containing catalyst systems, were examined. Further, Bhattacharyya et al. (1988) and Yoo et al. (1991) describe the use of promoted magnesium aluminates for use in FCC SO_x transfer additives.

Herein, we describe laboratory experiments demonstrating the MOST process concept for SO_x removal in Claus tailgas treatment. The performance of solid sorbents for SO_x capture is discussed, as a function of both catalyst and process parameters. We also describe results examining the reductive desorption step, in order to more fully describe the MOST process scheme.

Experimental Section

Catalyst Preparation. CeO_2/Al_2O_3. A ceria/alumina material was prepared by impregnating high pore volume γ-alumina (DYCAT 521, $1/8$ in. extrudate from Dycat International) with a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) in water, using an incipient wetness technique. The material was dried for 3 h at 120 °C and calcined in air for 1 h at 700 °C. This material was crushed and sieved to 14/60 mesh.

$MgAl_2O_4$ and $Mg_2Al_2O_5$. Two Mg–Al spinel base materials were made. The first was made with a composition corresponding to approximately $MgAl_2O_4 \cdot 0.1MgO$, which is close to the stoichiometric spinel. For convenience, this material is referred to below as $MgAl_2O_4$. This method of preparation followed that discussed by Yoo et al. (1991). Two solutions were made. Solution I contained 256.4 g of magnesium nitrate hexahydrate, 68.6 g of concentrated nitric acid, and 500 mL of water. Solution II contained 209.7 g of sodium aluminate, 10.7 g of sodium hydroxide, and 500 mL of water. Solution I was added to 2000 mL of water, and then solution II was added to solution I over $1/2$ h. The resulting mixture was aged for about 16 h, and the slurry was found to have a pH of 8.9. The gelatinous white solids were filtered, repeatedly washed with water, and dried at 120 °C. The second Mg–Al spinel material, with a composition of approximately $Mg_2Al_2O_5$, was prepared in a fashion similar to that of the material described above, except 461.5 g of magnesium nitrate hexahydrate was used in solution I, and the slurry pH was adjusted up from 3.6 to 10.2 by addition of sodium hydroxide prior to aging.

$CeO_2/MgAl_2O_4$, $CeO_2/Mg_2Al_2O_5$, $V_2O_5/CeO_2/Mg_2Al_2O_5$, and 100 ppm $Pt/Mg_2Al_2O_5$. These materials were synthesized by incipient wetness impregnation of the appropriate base magnesium aluminate spinels. Spinels with approximately 10% ceria loading were prepared by adding a solution of cerium nitrate hexahydrate in water to the corresponding magnesium aluminate solid, using an incipient wetness technique. A sorbent with vanadia and ceria was made by adding a solution of ammonium metavanadate and cerium nitrate hexahydrate to $Mg_2Al_2O_5$. The resulting materials were dried for 3 h at 120 °C and calcined for 1 h at 700
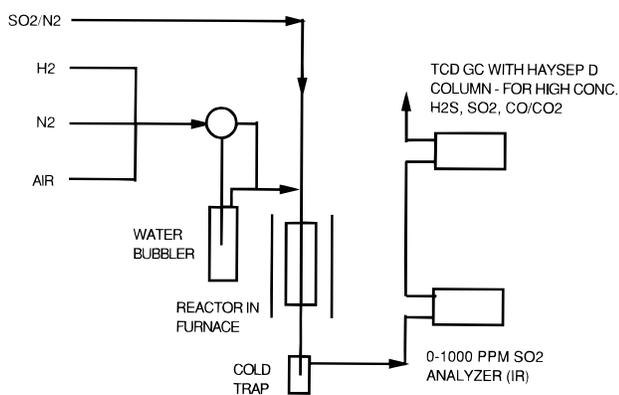

Figure 1. Experimental setup for adsorption/desorption experiments.

°C. A sorbent with 100 ppm Pt was made by adding a solution of 0.013 g of chloroplatinic acid (37% Pt assay) in water to $Mg_2Al_2O_5$ and calcining 3 h at 450 °C.

Evaluation of SO_x Uptake. Samples of these materials were sized to 14/60 or 14/80 mesh for evaluation of SO_x sorption activity. Standard conditions involved loading 6 g of sorbent in a quartz reactor, which was held at 649 °C for both adsorption and desorption. The reactor was 11 mm i.d., with a central thermowell, and was heated in a radiant furnace. The flow rate during adsorption was usually 360 sccm (standard cubic centimeters per minute), with molar concentrations of 1% SO_2 and 4% O_2 and with the balance being N_2 (dry basis). Part of the feed stream was passed through a saturator to add 10–20% H_2O. The flows and temperatures of all runs are listed in Table 1. A schematic of the apparatus used to evaluate these catalysts is shown in Figure 1.

A cold trap in an ice bath was located immediately below the reactor to trap water and particulate products, such as elemental sulfur. The reactor inlet pressure was typically 3–5 psig, and the outlet pressure was 1–2 psig. The effluent from the cold trap passed through a filter and then through a Siemens Ultramat 22P infrared SO_2 (0–1000 ppm) analyzer, for monitoring of SO_2 breakthrough during adsorption. The internal plumbing of the Siemens infrared analyzer was rearranged to bypass an internal pump and reduce dead volume. The adsorption was terminated when the SO_2 level in the effluent exceeded 250–300 ppmv.

Regeneration of the solid sorbent was accomplished by contacting it with hydrogen which was bubbled through the saturator to attain about 20% water vapor concentration. The composition of the off-gas during the regeneration was measured using a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a thermal conductivity detector. A 10 ft long, $1/8$ in. stainless column packed with Hayesep D was held isothermal at 115 °C. This GC system resolved hydrogen, nitrogen, carbon dioxide, water, hydrogen sulfide, and sulfur dioxide in less than 8 min. It also resolved C_1–C_3 hydrocarbons. A sample of pure SO_2 was injected on the GC at the start of a desorption run, to precoat the column.

In order to observe appreciable concentrations of sulfur species in the off-gas, low hydrogen flow rates (7–25 sccm) were used. The standard flow rate was 7–8 cm^3/min, although a higher hydrogen flow rate was often used at the start of a regeneration, when warranted by the higher rates of sulfur desorption at that point, to reduce the time required for regeneration. Regeneration was continued until the concentration of

Scheme 1. MOST Process for SO$_x$ Removal in Claus Tailgas Operations
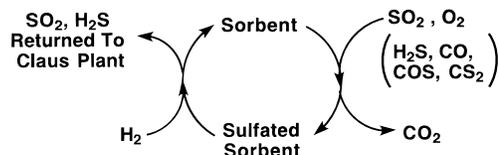
sulfur species in the off-gas dropped below about 2%. The total regeneration time was 2−4 h.

Results

As described in the Introduction, the MOST process scheme for Claus tailgas SO$_x$ reduction consists of three main steps, which can be illustrated in the catalytic cycle shown in Scheme 1. We describe how this process works by separating the individual process steps—the oxidative sorption of SO$_x$ under conditions suitable for Claus tailgas operation, sorbent screening for this application, cocombustion of CO during the oxidative sorption step, and the reductive regeneration of the sorbent.

Catalyst Screening for Effectiveness in SO$_x$ Uptake Operations. Several potential sorbent candidates for this application were chosen, based on both their efficacy in FCC SO$_x$ transfer additive applications and a desire to obtain high SO$_x$ uptakes per weight of catalyst employed. The base materials used for the catalysts are high surface area alumina and magnesium aluminate spinels (MgAl$_2$O$_4$ and Mg$_2$Al$_2$O$_5$), with ceria, vanadia, and/or platinum as oxidation promoters. Catalyst screening is described in the Experimental Section. The SO$_x$ uptakes are shown in Table 1. It was assumed that SO$_2$ is oxidized to SO$_3$ before being sorbed, so these uptakes were calculated as grams of SO$_3$ adsorbed divided by 6 g of solid sorbent. The materials were all regenerable under hydrogen, but it has been observed that the SO$_x$ uptake on the first adsorption/desorption cycle may be lower than that seen on later cycles. Therefore, the SO$_x$ uptake values reported here are for second or subsequent cycles.

The first three materials listed in Table 1 all contain ceria. The CeO$_2$/Al$_2$O$_3$ showed the lowest SO$_x$ uptake (6.6 wt % at 649 °C). The CeO$_2$/Mg$_2$Al$_2$O$_5$ gave a somewhat higher SO$_x$ uptake (25.2 wt %) than did CeO$_2$/MgAl$_2$O$_4$ (20.4 wt %). SO$_x$ uptake with Mg$_2$Al$_2$O$_5$ was low but not negligible (5 wt %). These observations suggest that significant SO$_2$ oxidation can occur over the latter material or in the gas phase at our operating conditions, but performance is clearly enhanced by using an SO$_2$ oxidation promoter, such as ceria.

Extending this finding to other promoters, the addition of vanadium to the cerium/magnesium aluminate nearly doubled the SO$_x$ uptake at 649 °C, from 25.2 to 40.7 wt % for V$_2$O$_5$/CeO$_2$/Mg$_2$Al$_2$O$_5$. The SO$_x$ uptake with the 100 ppm Pt/Mg$_2$Al$_2$O$_5$, at standard conditions, was 33.6 wt %. This is somewhat lower than the results using V/Ce/Mg$_2$Al$_2$O$_5$. It is possible that the 100 ppm Pt may become partially poisoned due to metal sulfide formation and thus may be less effective for SO$_2$ oxidation than the vanadia/ceria metal oxide combination.

The amount of SO$_x$ sorbed before breakthrough depends on both the sorption capacity of the material and the rate of uptake. A material which takes up SO$_x$ slowly will have a shallow breakthrough curve, so breakthrough will occur at the bed exit before the

Table 1. SO$_2$ Sorption Results

sorbent material	temp, °C	flow, sccm	feed SO$_2$, %	SO$_x$ uptake, wt %
CeO$_2$/Al$_2$O$_3$	538	360	1.0	5.1
	649	360	1.0	6.6
CeO$_2$/MgAl$_2$O$_4$	649	360	1.0	20.4
CeO$_2$/Mg$_2$Al$_2$O$_5$	593	360	1.0	14.3
	649	360	1.0	25.2
Mg$_2$Al$_2$O$_5$	649	360	1.0	5.0
V$_2$O$_5$/CeO$_2$/Mg$_2$Al$_2$O$_5$	649	360	1.0	40.7
	649	180	2.0	46.4
100 ppm Pt/Mg$_2$Al$_2$O$_5$	649	360	1.0	33.6
	649	180	2.0	40.7
commercial FCC SO$_x$ reduction additive	649	360	1.0	54.0

sorption capacity of the bed is fully utilized. The effluent SO$_2$ concentration remained below 1 ppm for the initial portion of the adsorption runs described above, as confirmed by measurements with Draeger tubes. Once SO$_2$ began to break through the bed, its concentration rose over the course of 5−20 min to 250−300 ppm, at which point the adsorption was terminated. This rise time was generally shorter for the materials with lower uptakes and longer (10−20 min) for the materials with more than 20 wt % uptake.

Results for runs made at lower temperatures (538−593 °C) are given in Table 1 for two materials. In both cases, the amount of SO$_x$ uptake was lower at the lower temperature. The thermodynamics of sorption typically become more favorable at lower temperatures, so the apparent drop in SO$_x$ uptakes observed here with a decrease in sorption temperature is likely due to the impact of temperature on uptake rates, rather than on ultimate sorption capacity. Similarly, using a higher feed concentration and lower feed flow rate should give a steeper adsorption front in the bed, which allows for higher overall adsorption before the effluent concentration exceeds the specified breakthrough value. Two runs, where the SO$_2$ feed concentration is 2% and the feed rate is 180 sccm, illustrate this trend (see Table 1). For example, using V$_2$O$_5$/CeO$_2$/Mg$_2$Al$_2$O$_5$ as sorbent, a SO$_x$ uptake of 40.7 wt % was measured at 360 sccm and 1.0% SO$_2$, while at 180 sccm and 2% SO$_2$ feed, a SO$_x$ uptake of 46.4 wt % was measured (both runs at 649 °C).

CO Oxidation. The CO oxidation activity of two materials was tested by flowing a mixture of 4% CO, 4% O$_2$, and 8% CO$_2$ at a flow rate of 310 sccm over 6 g of each material, while scanning the reactor temperature. With the unpromoted Mg$_2$Al$_2$O$_5$, the CO was half-converted at about 410 °C and nearly all converted at 460 °C. With the Pt/Mg$_2$Al$_2$O$_5$, the CO was half-converted at about 265 °C and nearly all converted at 282 °C. With an empty reactor, there was no detectable CO conversion for temperatures up to 649 °C.

Products during Regeneration. For the first 1−2 h of regeneration, most of the hydrogen was typically consumed, with production of SO$_2$ and water. Later, the SO$_2$ decreased and H$_2$S appeared in the effluent, along with unconsumed H$_2$. For the two runs shown in Table 1 which were made at temperatures below 649 °C (one at 538 °C with CeO$_2$/Al$_2$O$_3$ and one at 593 °C with CeO$_2$/MgAl$_2$O$_5$), the dominant product during the regeneration was H$_2$S. For all other runs, the dominant product was SO$_2$, which, as noted above, may be preferred in practice. In our work, we have noted a tendency for SO$_2$ production to be favored over H$_2$S

when larger amounts of sulfur (>20 wt %) were being desorbed, although exceptions to this generalization were observed. The choice of reducing gas can also affect the effluent SO_2/H_2S ratio. In addition to hydrogen, a variety of hydrocarbons and other reductants were found which effectively reduce the sulfated sorbent. These will be described more fully in upcoming publications.

Discussion

Understanding the reaction chemistry for this process is based on both characterization results, to be published shortly, and discussions as to the functioning of FCC SO_x transfer additives. As mentioned in the Introduction, Hirschberg and Bertolacini (1988) discuss a number of materials which are potential SO_x capture materials for FCC regenerators. In this service, the material adsorbs SO_x under oxidizing conditions in the FCC regenerator and releases it as H_2S in the riser reactor, which is a reducing environment. For the adsorption,

$$SO_2 + 0.5O_2 = SO_3 \tag{1}$$

$$SO_3 + MO = MSO_4 \tag{2}$$

where MO and MSO_4 represent the oxide and the sulfate form of the solid sorbent. For the reduction, both SO_2 and H_2S are possible products, as shown here with hydrogen as the reducing gas:

$$MSO_4 + H_2 = MO + SO_2 + H_2O \tag{3}$$

$$MSO_4 + 4H_2 = MO + H_2S + 3H_2O \tag{4}$$
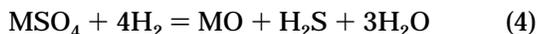
It appears likely that similar reactions are taking place here.

The results presented above indicate that promoters, such as ceria, vanadia, and platinum, are essential for MOST service. A better understanding as to the roles they play in MOST service may be based on previous studies of FCC SO_x transfer additives. Bhattacharyya et al. (1988) have found that, under FCC regenerator conditions, CeO_2 functions as an oxidation promoter for SO_2 oxidation. Further, Yoo et al. (1992) discuss the use of ceria-containing, magnesium aluminate spinels modified with transition metals, as an advanced catalyst for FCC SO_x transfer applications. In their study, they find that the incorporation of iron, vanadia, and chromium, as a solid solution in the spinel, can aid in the reduction of the sulfated catalyst.

The first step of the MOST process scheme (reactions (1) and (2)) is the oxidative sorption of SO_x. Considering that the equilibrium for SO_2 oxidation to SO_3 (reaction (1)) is ca. 50% under the conditions examined here and that this process operates with very low SO_x breakthrough (below 1−2 ppm SO_2), effective oxidation promoters are essential for MOST service. As shown above as well, the oxidation promoters present can also oxidize CO to CO_2 and can likely oxidize H_2S to SO_2, COS and CS_2 to CO_2, SO_2/SO_3, and H_2O, which can then be sorbed. Thus, in addition to the proposal by Bhattacharyya et al. (1988) that ceria functions as an effective SO_2 oxidation promoter, it is likely that other metals such as vanadia and platinum are also essential in MOST service. These metals can also aid in catalyst reduction (reactions (3) and (4)), which is essential for high per pass SO_x uptake (Yoo et al., 1992).

A significant operational advantage of MOST is the high SO_x uptake, since less frequent catalyst regeneration is required. As pointed out above, a 46.4 wt % SO_x uptake was observed over $V/Ce/Mg_2Al_2O_5$ while maintaining very low SO_x emissions. Further, a commercial FCC SO_x transfer additive was found to take up 54.0 wt % SO_3. Characterization results, to be published shortly, find that the sites for SO_x sorption in these catalysts are magnesium oxide or magnesium aluminate based and that the mode of sorption is via catalyst sulfation; thus, the maximum SO_x uptake in this system is 76.2 wt % (formation of $Mg_2Al_2O_5\cdot2SO_3$). Taking these results and the SO_x uptake reported above, 71% of these sites react on the $Mg_2Al_2O_5$ base. It is clearly advantageous to have a relatively large number of accessible, basic sites for sorption. This amount of SO_x uptake is higher than generally reported for FCC SO_x transfer additives (Hirschberg and Bertolacini, 1988; Bhattacharyya, 1988). This is in part due to different operating conditions. Claus tailgas treatment involves higher SO_x concentrations and longer exposure times for SO_x uptake than are found in FCC regenerators, so the sorbent can be more efficiently used in the Claus tailgas application.

The reduction step can yield SO_2, S_n ($n = 1-8$), or H_2S as the sulfur-containing products of desorption. Under the conditions used in this study, we describe above that SO_2 is formed in excess of S_n or H_2S (typical product splits are ca. 80/10/10 of $SO_2/S_n/H_2S$). In the MOST process, this stream is then fed back to the Claus unit for further processing. Comparing reactions (3) and (4), an obvious advantage of producing mainly SO_2 rather than H_2S during sorbent regeneration is that less reducing gas is consumed—this is clearly an advantage over wet solution processes (such as Beavon/Stretford and selective amine absorption processes), where hydrogen is used to convert all sulfur species to H_2S before adsorption can occur. Another advantage is that, by supplying some sulfur to the Claus unit in an oxidized form (i.e., as SO_2), the air requirement for the Claus unit can be reduced, which can debottleneck a unit which is operating at a total flow limit.

Application of Regenerable Sorbents. A diagram of the MOST process is shown in Figure 2. H_2S-laden streams such as amine treater acid gas and sour water stripper effluent enter the Claus plant, along with air. Most of the sulfur is recovered as liquid sulfur. The tailgas goes to a burner, where the remaining H_2S is oxidized to SO_2 and SO_3. Excess air is used, such that the effluent from the burner contains 1−4% O_2. The burner effluent is shown going to sorbent bed A, where the SO_x is adsorbed. The cleansed tailgas then proceeds to the stack for release. The regeneration gas circuit is also shown in Figure 2. Reducing gas, diluted with steam, flows through bed B, to desorb the sulfur as a concentrated stream of H_2S and SO_2, which is fed back to the Claus unit. At the end of the cycle, bed A is loaded with sulfur, while bed B has had its sulfur removed. At this point, valve positions are changed, causing the tailgas to flow through bed B, and regeneration gas to flow through bed A.

The Shell Flue Gas Desulfurization (SFGD) process, as described by Dautzenberg, Nader, and van Ginneken in 1971, functions in a similar manner to that envisioned for the current MOST process. The SFGD process is a dry sorbent-based process for flue gas SO_x removal in which SO_2 is oxidatively sorbed onto a copper on alumina acceptor to copper sulfate and is reductively
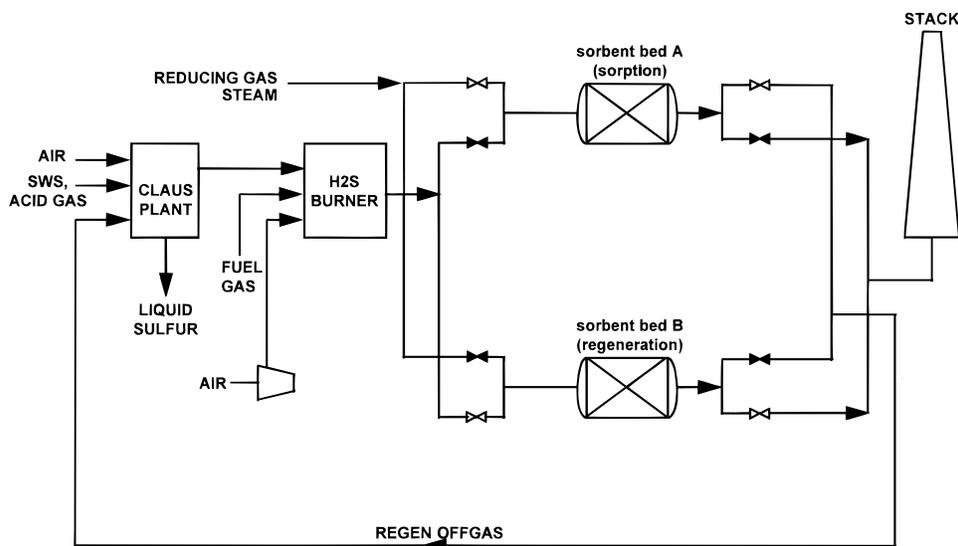
Figure 2. MOST process flow diagram.

desorbed with hydrogen to net mainly elemental copper and sulfur dioxide. SO_x loadings on this catalyst, however, appear to be less than 20%, a distinct disadvantage as compared to the MOST process.

When promoted with strong oxidizing catalysts such as Pt and vanadia, the magnesia–alumina sorbents discussed here can potentially convert all carbon in the Claus tailgas to nontoxic CO_2 and all sulfur species to SO_x. If somewhat shortened adsorption cycles are employed, so as to avoid the start of the SO_2 breakthrough coming through the end of the bed, the results reported here indicate that SO_x emissions can be kept below 1–2 ppm.

The process conditions used for the laboratory experiments described here were chosen with consideration given to catalyst performance and so as to allow for integration into the existing refinery SO_x handling scheme. The results show that high SO_x uptake could be achieved at temperatures of 1100–1300 °F and 3500 GHSV for SO_x sorption and 100 GHSV for reductive regeneration, using the catalysts shown in Table 1. For a Claus plant which handles 100 long tons/day of sulfur and recovers 97% as elemental S, 6600 lb/day of S leaves in the tailgas. Assuming two beds operated in swing mode (one bed adsorbing while the other is being regenerated) on a 6-h cycle and assuming an effective SO_x uptake of 40 wt %, the two beds would each contain 10 315 lb of sorbent. This amount of material could be accommodated in reactors similar to those used in the Claus plant itself.

The regenerable SO_x sorbents discussed here, which also have CO and H_2S oxidation capability, may be used in applications other than Claus tailgas treatment. For example, a fixed bed (preferably in monolith form) downstream of an FCC regenerator might allow better SO_x capture than the current practice of circulating the sorbent with the FCC catalyst. If a SO_x sorbent bed were used to treat the fluegas from an oil or coal combustor, both SO_x and NO_x emissions could be reduced. The sorbent bed would serve to oxidize CO in the fluegas, so the combustor could be run with less excess air and hence lower NO_x make. Because of its simplicity, a solid, regenerable SO_x sorbent/oxidizer may have use in numerous other applications.

Conclusions

Regenerable solid sorbents offer several potential advantages over conventional wet-scrubbing Claus tailgas processes. In this paper, we describe the MOST process/catalyst combination for this application.

Several candidate catalysts were screened for this application, with the objective of achieving low SO_x concentrations in the effluent (below 1–2 ppm) and a high total SO_x uptake. The best materials examined were a vanadia- and ceria-promoted, magnesium aluminate spinel, which sorbed up to 46 wt % SO_3, and a commercial FCC SO_x transfer additive, which adsorbed 54 wt % SO_3. Breakthrough of SO_2 through the fixed bed in our laboratory reactor is sharp; for the first 80–90% of the sorption period, the level of SO_2 in the effluent from the bed is less than 1 ppmv. This represents at least an order of magnitude improvement over conventional Claus tailgas scrubbers in terms of total sulfur emissions. Emissions of CO are dramatically reduced as well. Since sulfur can be recycled to the Claus plant in an oxidized form (i.e., as SO_2), it is possible to gain a capacity increase in a plant which is operating at a hydraulic limit.

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