Abating Sulfur Plant Tail Gases

By DAVID K. BEAVON, Director of Process Operations
Ralph M. Parsons Co., Los Angeles, Calif.

A newly developed process can easily reduce the amount of sulfur in sulfur plant tail gases to 250 parts per million or less. This is a 60-fold reduction from current typical values, and means an increase in sulfur recovery from 95 to 99.9 percent or higher. Using the new process, the estimated sulfur dioxide emission of sulfur plants worldwide might be reduced from the present estimated 3,000-6,000 tons per day to about 12 tons per day.

Today, plants producing elemental sulfur from hydrogen sulfide by the modified Claus process have an output above 30,000 long tons daily, and within two years the total output will exceed 40,000 long tons. Sulfur plants typically recover 90 to 95 percent of the entering sulfur; 5 to 10 percent is lost to the atmosphere as sulfur dioxide. Large units of the latest design will recover about 97 per cent of the sulfur, and lose about 3 percent.

The composition of the Claus plant tail gas typically contains about one-third SO_2 and H_2S, one-third COS and CS_2, and one third elemental sulfur. The total quantity of sulfur corresponds to about 15,000 parts per million of SO_2 in a typical incinerated tail gas (dry basis). The concentration of equivalent SO_2 in the tail gas before incineration is about 50 percent higher. Consistent with trends observed in many locations, a reasonable goal for concentration of SO_2 in the incinerated gas appears to be 250 parts per million or less. This sixty-fold reduction corresponds to increasing sulfur recovery from 95 percent to 99.9 percent or higher.

The new Beavon sulfur recovery process is best described by reference to the modified Claus process. Claus discovered in about 1880 that hydrogen sulfide produces good-yields of sulfur when mixed with air and passed over iron or bauxite catalyst at elevated temperature. The reaction is highly exothermic but completion is opposed by high temperature, so conversion in a fixed bed of uncooled catalyst is relatively low.

I. G. Farbenindustrie, about 1937, approached the problem of heat removal by first burning one-third of the hydrogen sulfide with air in a pressurized boiler, in which about four-fifths of the over-all heat of reaction is removed by generating steam, and some of the sulfur is produced.

After condensed sulfur is separated from the cooled gases, the chemical reaction is carried further toward completion by heating the gases to 400-500 F and passing them over a Claus catalyst (bauxite or alumina, usually). This process of free-flame reaction followed by one or more catalytic conversion steps is known as the modified Claus process. The operating pressure is usually 1.0 to 1.5 atmosphere absolute.

The reaction is exothermic and equilibrium favors formation of elemental sulfur at lower temperatures. It is customary to carry out the reaction in a series of two or three catalyst beds, with cooling, condensation and removal of produced sulfur after each bed. The lower practical temperature limit in the condensing steps is set at 260 F by solidification of the sulfur product, and plugging of the apparatus. A further barrier is set, when water condenses, by the formation of a solution of sulfurous acid and polythionic acids $H_2S_xO_3$, known as Wackenroder's solution. This solution is very corrosive to the common construction metals, with the possible exception of titanium.

Ultimate conversion in the modified-Claus sulfur plant is set by the reverse of the chemical reaction in which water (mostly that formed from hydrogen sulfide) reacts with sulfur to produce gaseous hydrogen sulfide and sulfur dioxide. In general, plants with two catalytic stages can recover 92-95 percent of the potential sulfur; three stages, 95-96 percent; four, 96-97 percent. In addition to losses in the form of unconverted hydrogen sulfide and sulfur dioxide, some elemental sulfur is lost as vapor, and some as entrained sulfur mist or droplets.

Further losses—0.25-2.5 percent of the hydrogen sulfide fed—are experienced in the form of carbonyl sulfide (COS) and carbon disulfide (CS_2). These gases

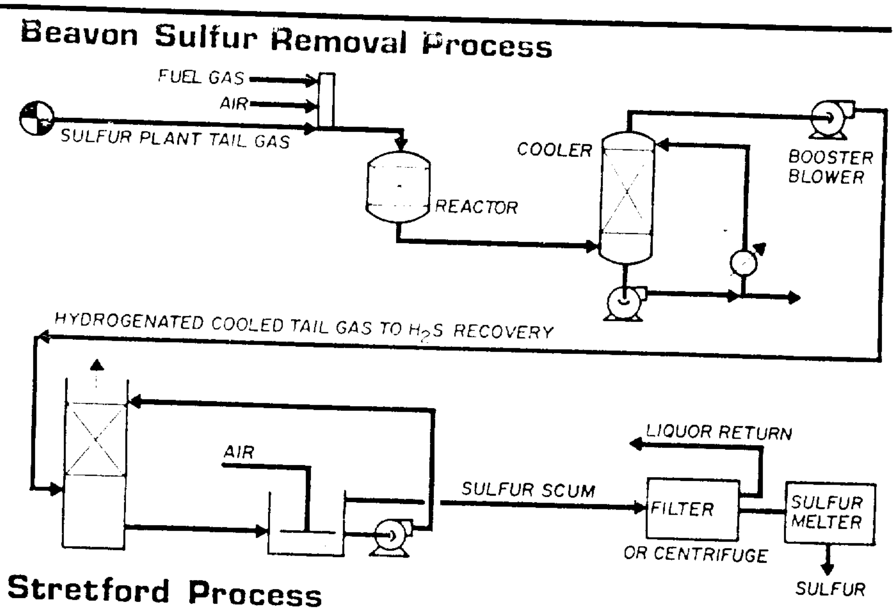

Fig. 1 Flow diagram of processes to eliminate air pollutants from tail gases of sulfur plants.

are formed in the flame zone where hydrogen sulfide is burned with air (generally at a temperature in the range of 1500 to 2500 F) when carbon dioxide or other carbon compounds are present. The carbon-sulfur compounds react slowly under the conditions of the sulfur plant, thus often comprise 30 to 40 percent of the sulfur values lost in the tail gas leaving the sulfur plant.

Tail gas leaving the sulfur plant then contains 1-3 percent of a mixture of hydrogen sulfide, sulfur dioxide, carbonyl sulfide, carbon disulfide, and elemental sulfur vapor and liquid. This mixture is usually incinerated at about 1000-1200 F in an oxidizing atmosphere to convert all the sulfur compounds to sulfur dioxide, their least obnoxious form. The resulting flue gas flows into the atmosphere from a stack.

The new process, Fig. 1, starts by converting all the sulfur in the tail gas into hydrogen sulfide, then cools the gas to condense out water, removing it from the reaction zone. Conversion to hydrogen sulfide is by both hydrolysis and hydrogenation reactions. Tail gas contains about 30 percent water vapor and consequently the hydrolysis reactions are virtually complete at temperatures of 600-700 F when a suitable catalyst is used.

Hydrogenation of sulfur and its compounds proceeds completing according to the following equations:

$$SO_2 + 2H_2 \rightarrow S + 2H_2O$$

$$S + H_2 \rightarrow H_2S$$

Enough hydrogen is usually present in the tail gas to effect the reactions, since both hydrogen and carbon monoxide are formed in the flame zone and persist through the Claus plant. The same catalyst is effective for the hydrolysis of carbon monoxide (the water-gas shift reaction). This reaction proceeds completely and produces more hydrogen. In addition, the supply of hydrogen may be augmented by the partial oxidation of natural gas with air in a simple line burner.

Following the catalytic reactions which convert essentially all the sulfur compounds in the tail gas to hydrogen sulfide, the gas mixture is cooled to as low a temperature as is economic, and condensed water is removed.

Next, hydrogen sulfide is extracted from the hydrogenated, cooled tail gas using the Stretford process. This process is capable of treating the gas to about one part per million hydrogen sulfide content.

The Stretford process uses a sodium carbonate solution which reacts with hydrogen sulfide to form sodium hydrosulfide. The hydrosulfide is oxidized to sulfur by sodium vanadate also in solution. Subsequently the vanadium is oxidized back to the pentavalent state by blowing with air, with sodium anthraquinone disfulonate (also contained) working as an oxidation catalyst. Finely-divided sulfur appears as a froth which is skimmed off, washed, dried by centrifuging or filtration, and added to the product from the parent sulfur plant.

Effluent gas from the Stretford plant contains less than one part per million hydrogen sulfide and small traces of carbonyl sulfide, and does not require incineration. Recovery of sulfur is virtually complete, and the sulfur plant is no longer an air pollution problem.

The law of mass action requires that, for one reagent in a chemical reaction to be consumed essentially completely, there must be an excess of another reagent. For example, the Claus reaction must have an excess of SO_2 to consume all the H_2S, or conversely: either condition is undesirable because it means a loss of sulfur to the atmosphere. In the new process, an excess of hydrogen is supplied, driving reactions to completion. The hydrogen is not an air pollutant, hence the use of a small excess is not harmful. Similarly, the Stretford step applies a very large excess oxidation potential at the top of the absorber column, allowing the conversion of H_2S to be driven virtually to completion. ≋

**For a copy of this article circle 836
on Reader Service Card**