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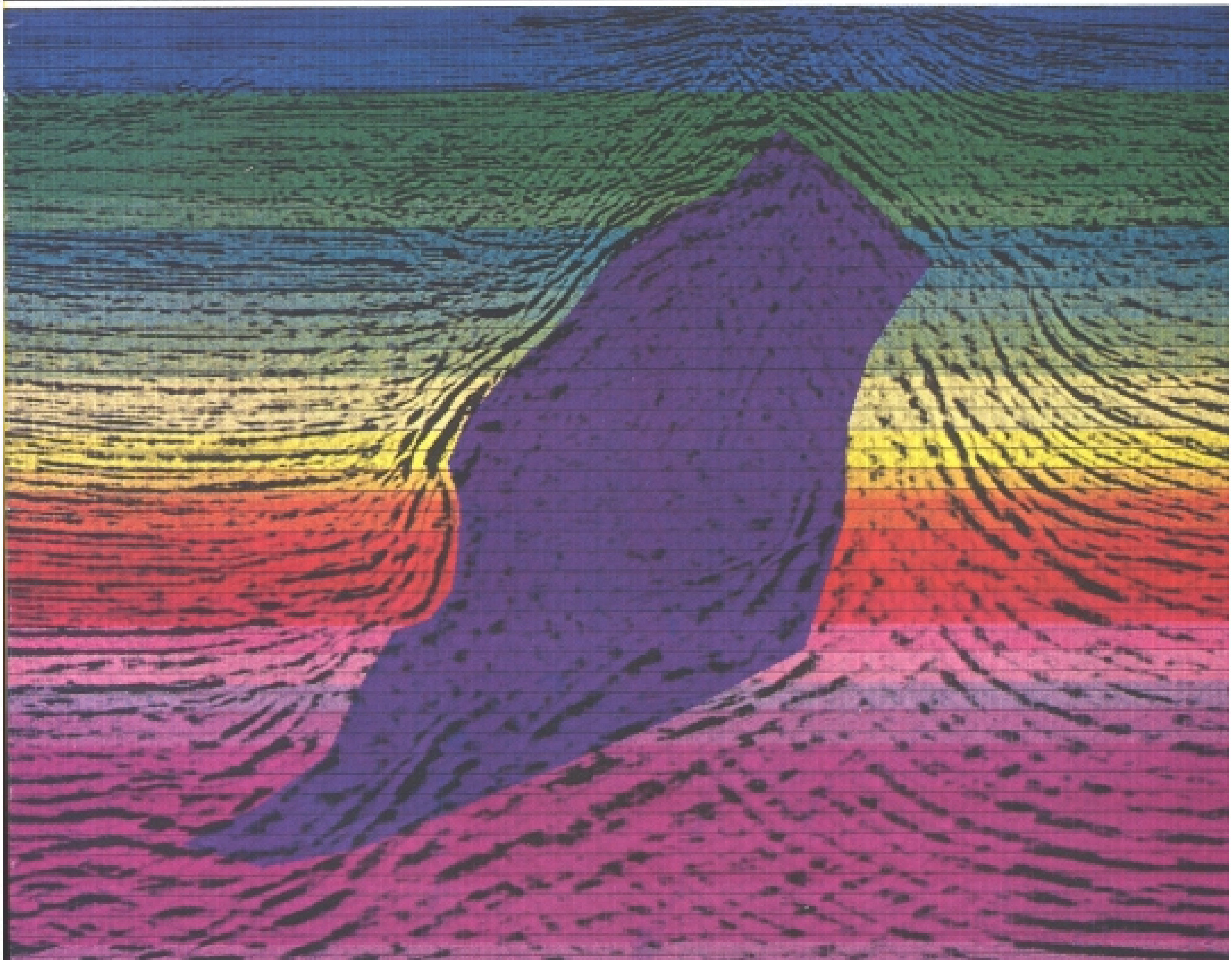

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SO_2-generation process can double refinery Claus unit capacity

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Brown & Root Braun has modified and applied its sulfur dioxide (SO_2) generation process now in commercial operation at a Texas chemical plant-to fit the unique requirements of oxygen-fired sulfur plants.

The new adaptation provides all the benefits of SO_2 quench, with favorable economics. It can be used to double existing sulfur capacity in a refinery, or to provide redundancy, as required by some regulatory agencies.

Background

Air Products & Chemicals Inc. and Goar, Allison & Associates Inc. jointly offer the Claus Oxygen-based Process Expansion (COPE) process. Since this process was first installed at Conoco Inc.'s Lake Charles, La., refinery in 1985, interest in expanding

Based on a paper presented at Laurence Reid Gas Conditioning Conference, Mar. 1-3, Norman, Okla.

sulfur plants by using oxygen instead of air has grown.

Sulfur plant expansions based on oxygen enrichment can have very favorable economics. In addition, oxygenbased Claus plants emit

about one eighth the SO_2 that air-based plants do.

Today, a number of refinery sulfur plants use modest oxygen enrichment of air to increase capacity. But while enriched air can be used with relatively minor modifi-

cations, the rich acid-gas feeds typically found in refinery applications require limiting the reaction furnace temperature when oxygen concentrations are greater than about 30%.

From a technical view-

Fig. 1

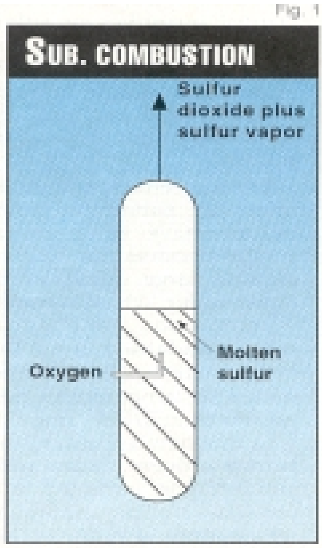


Fig. 2

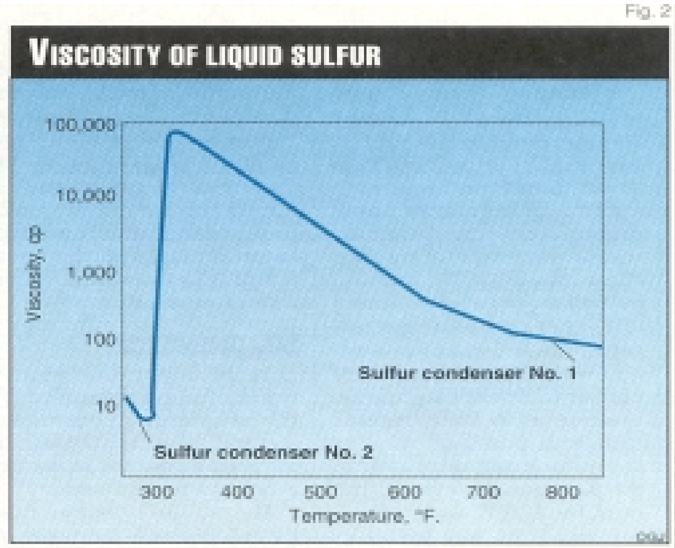


Fig. 3

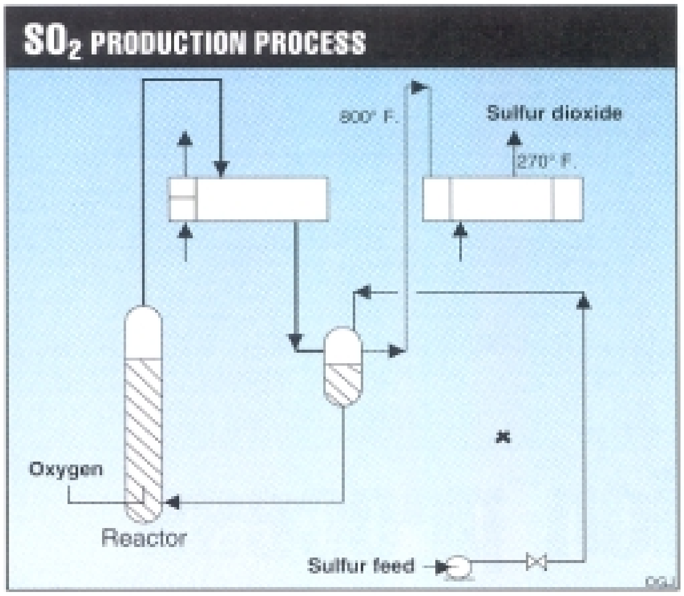
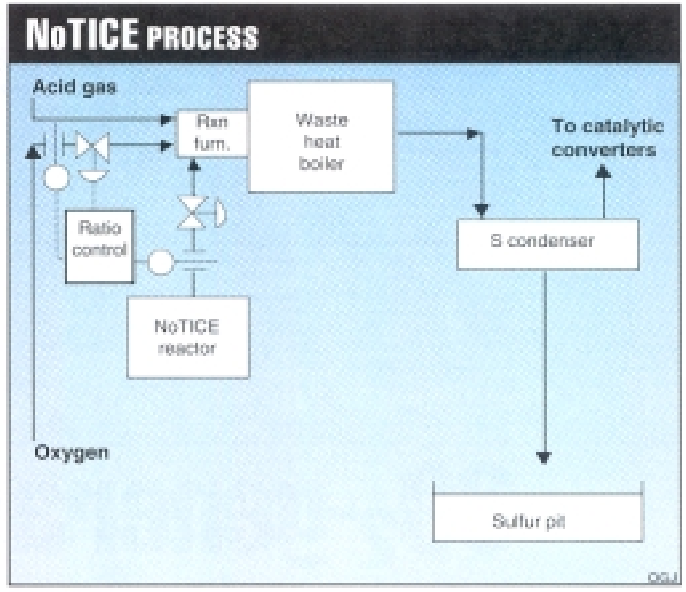


Fig. 4



point, $S0_2$ quench is the most desirable method of limiting Claus plant reaction-furnace temperature. Some of the advantages of $S0_2$ quench are:

- $S0_2$ as a Claus reactant enhances conversion.
- $S0_2$ not only acts as a quench by absorbing sensible heat, but also reduces the extent of the exothermic hydrogen sulfide (H_2S) oxidation. that takes place in the reaction furnace. As a result, the waste-heat boiler duty is much less, as compared to other quench schemes.
- The flow of gases through the reaction furnace and waste-heat boiler is much less than in other quench schemes.
- Pumps and compressors are not required for $S0_2$ supply.
- Reaction furnace temperature is controlled easily and safely by introducing oxygen (0_2) in proportion to sulfur dioxide.

In a typical refinery application, simply replacing air with a mixture of 0_2 and $S0_2$ allows an 80-100% increase in sulfur capacity, without any other modifications (except burner modifications) and without taking credit for conservative designs. In practice, a 100-120% increase usually is possible.

The primary drawback of the $S0_2$ quench system has been the lack of an economical source of SO_2 given its $230/ton price. This price, however, fairly represents the cost of manufacturing $S0_2$ by conventional means. Burning sulfur or H_2S in air to produce S02 introduces too much nitrogen, and normal combustion with oxygen results in the same type of temperature problem faced in the Claus reaction furnace.

NoTICE process

Brown & Root Braun's "No Tie In Claus Expansion" (NOTICE) sulfur process relies on a different approach to producing $S0_2$. The first generator to use this technology has been in commercial operation since 1989 at the Calabrian Corp. chemical plant in Port Neches, Tex. Calabrian uses the sulfur dioxide to produce sulfur-based chemicals.

Brown & Root Braun has modified and applied this process to fit the unique requirements of an oxygenfired sulfur plant. This adaptation provides all the benefits of $S0_2$ quench at favorable economics.

S02 generator

In the sulfur dioxide generator, $S0_2$ is produced by the submerged combustion method (Fig. 1). Oxygen is released below the surface of a pool of boiling sulfur.

The sulfur is hotter than its autoignition, temperature (about 500° F.); therefore, the oxygen and liquid sulfur immediately react to form sulfur dioxide. But because the "flame" is submerged in the liquid sulfur, vaporization of the liquid sulfur limits the temperature of the surrounding liquid to its boiling point.

Sulfur dioxide production is easily controlled by regulating the flow of oxygen. Sulfur is always in excess and, without oxygen flow, everything stops. Straightfoward safety interlocks therefore control the flow of oxygen.

The oxidation of sulfur is highly exothermic so that, although reactor temperature is easily controlled, substantial quantities of sulfur are vaporized. In fact, the mass of sulfur in the vapor exiting the reactor is more than 10 times the mass of sulfur required to produce the SO_2.

Previous attempts to commercialize submerged combustion have been unsuccessful because the process requires large quantities of liquid sulfur, which becomes very viscous (93,000 cp) when condensed from the hot reactor effluent and cooled to temperatures just greater than 310° F. (Fig. 2).

In this new approach, the reactor effluent, laden with sulfur vapor, is cooled in a condenser. The minimum temperature of sulfur in this condenser, however, is limited to about 800°F., so that the maximum viscosity of the liquid sulfur effluent is less than 150 cp.

The hot, low-viscosity sulfur is returned to the reactor as continuous recycle (Fig. 3). The hot condenser is cooled with molten salt as the heat-transfer medium. The molten salt is then used to generate steam at any level useful to plant operation. The returning molten salt enters the condenser at 725°F, so that the viscosity of the sulfur condensing on the tube wall is less than 300 cp.

After the hot sulfur recycle, very little pure sulfur remains in the $S0_2$ vapor. A second condenser, operating under conditions similar to the final condensers of a Claus sulfur recovery plant, effectively cools the $S0_2$ and removes the remaining sulfur.

Claus integration

The use of oxygen in a Claus plant presents two process control issues:

- Control of the reaction furnace temperature
- Control of the H_2S-to-$S0_2$ ratio to maintain conversion efficiency.

The reaction furnace temperature is controlled to the desired maximum by using the proper mixture of $S0_2$ and oxygen. The flow of $S0_2$ produced by the NoTICE $S0_2$ generator is measured

Fig. 5

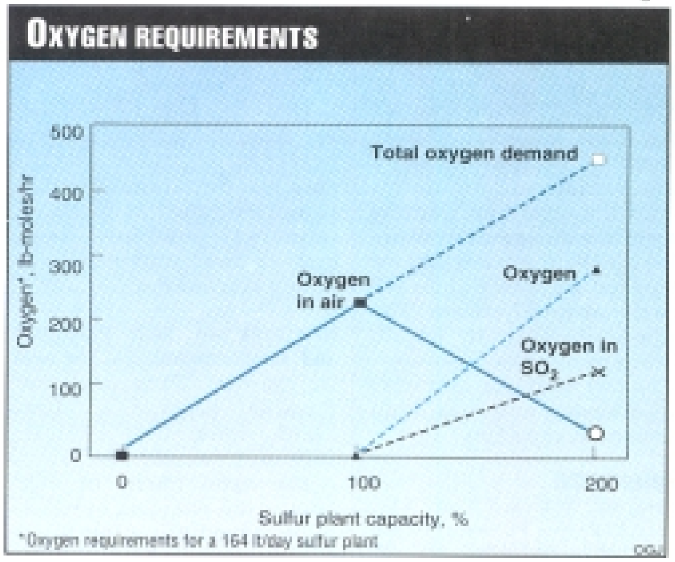
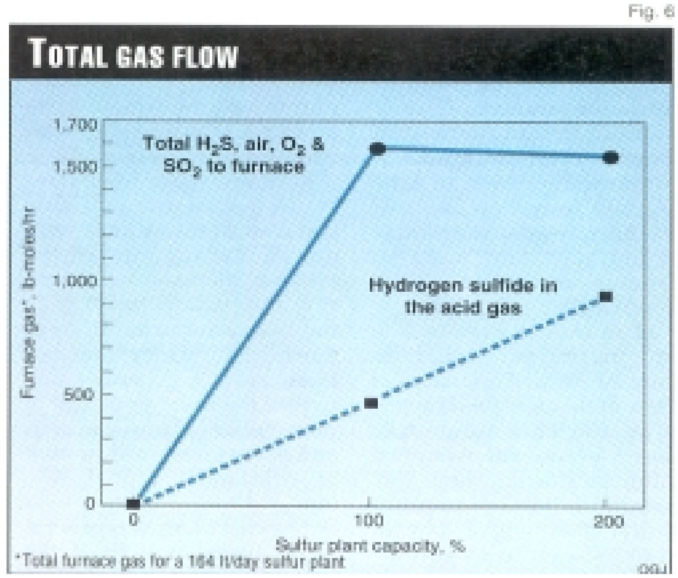


Fig. 6



and the signal is sent to a ratio controller. The ratio controller then allows oxygen to flow to the Claus reaction furnace in proportion to the $S0_2$ flow (Fig. 4).

This control system is inherently safe because there is no oxygen flow to the reaction furnace unless $S0_2$ flow is detected first.

For H_2S-to-SO_2 ratio control, the same controls used in a conventional Claus plant are used with NoTICE. This is typically feed-forward control, based on the acid-gas flow for bulk control and the tail gas H_2S-to-$S0_2$ ratio feedback signal for trim control. The only difference is that these control loops regulate oxygen flow to the $S0_2$ generator, as opposed to air flow to the reaction furnace.

Because there is little holdup in the $S0_2$ generator, these control loops, in effect, control the flow of $S0_2$ to the reaction furnace. Controlling $S0_2$ flow in this manner regulates oxygen flow to the reaction furnace in proportion to $S0_2$ flow

By controlling oxygen flow to the $S0_2$ generator, the control loops regulate the flow of an $S0_2$/0_2 mixture of constant composition to the reaction furnace. This technique is similar to controlling the flow of air (a constant-composition mixture of N_2 and 0_2) in the original plant.

Oxygen demand/supply

It may at first appear that more oxygen is required for this scheme than for others because oxygen is used both in the reaction furnace and in the $S0_2$ generator. The total oxygen demand, however, is the same.

If one looks at the overall material balance around the entire sulfur plant, it can be seen that all sulfur species are converted to sulfur. The total oxygen demand equals that required to combine with the hydrogen in H_2S to produce water, plus that required to oxidize other combustible materials, such as hydrocarbons and ammonia, in the acid-gas feed.

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The $S0_2$, in effect, acts as an oxygen carrier. The oxygen entering the reaction furnace as $S0_2$ reduces the amount of oxygen required as free oxygen by the same amount.

For large-capacity plants, an on site cryogenic plant may be economical. But for plants close to an oxygen pipeline, the economics of this process are especially favorable. Even for smaller plants, however, pressure swing adsorption (PSA) presents an affordable solution.

The purity of PSA oxygen typically is greater than 90% and the remaining nitrogen has little impact on capacity increase. This nitrogen level also has no adverse impact on the operation of the $S0_2$ generator.

Oxygen consumption

In refineries where the load on the sulfur plant may vary considerably, it is desirable to use air when low capacities are needed and to use oxygen only when higher capacities are required. With the NoTICE process, it is possible to use any combination of air and an $S0_2$/0_2 mixture.

To minimize oxygen consumption, a single, split range controller regulates both air to the reaction furnace and oxygen to the $S0_2$ generator. The flow of air is increased as acid-gas flow is increased to a maximum of 100% of original capacity.

As the acid-gas flow increases further, the oxygen to the $S0_2$ generator is gradually increased and the air flow is simultaneously decreased (Fig. 5).

Sulfur plant

In this technology, a mixture of $S0_2$ and oxygen replaces air (a mixture of nitrogen and oxygen). The $S0_2$ is produced directly from liquid sulfur and oxygen.

Because liquid sulfur pumped from the existing sulfur pit is the source of sulfur (as opposed to the feed acid gas) and internal recycles are not required, modifications to the existing plant are minimal, involving only burner modification or changeout. Hence the name "No Tie In Claus Expansion" or NoTICE.

The total gas flow is less than the original gas flow throughout the plant, even when minimizing purchased oxygen by increasing the use of air (Fig. 6).

Economics

The total installed cost of a NoTICE modification is about one third the cost of a new equivalent-capacity Claus sulfur-recovery and tail gas unit. With the No-

TICE modification, however, there are greater operating costs in the form of purchased oxygen.

Based on the outflow of oxygen in a NoTICE modification, the amount of time required to recoup the cost (in other words, the simple payout) of a new, more expensive air-based Claus plant can be estimated.

At an oxygen price of $35/ ton, the payout would require 10 years of operation at 100% of the new total capacity. At $50/ton it would take take 5 years. But if annual sulfur production were 75% instead of 100% of total capacity, the simple payout would stretch to 14 years.

Redundancy

Permitting authorities more frequently are requiring refineries to provide redundancy when they apply for capacity increase. The NoTICE process provides an ideal method of providing that redundancy. A single $S0_2$ generator can double the capacity of any one of two or more existing sulfur plants while another is down for maintenance or repair.

In cases where redundancy already exists, an $S0_2$ generator essentially will double the capacity of the existing plants by transferring the backup function to the $S0_2$ generator. In cases where redundancy does not exist, an $S0_2$ generator will reduce the number or size of new sulfur plants needed, and those plants will be built at substantial capital savings.

The cost of an $S0_2$ generator is about one third the cost of a new sulfur plant and, because $S0_2$ is produced only when one of the sulfur plants is down, oxygen costs are minimal. Thus total operating costs are, in this case, actually less than for an air-based plant.

For a rich acid gas containing 92.4% H_2S, increasing the capacity of a sulfur plant from 164 long tons/day(lt/d) to 327 lt/d requires a new airbased sulfur plant of 163 It/ d. The total installed cost of this plant, including tail gas cleanup, is approximately $18-20 million.

On the other hand, an oxygen-based expansion using the NoTICE process can be installed for a total installed cost of about $7 million. The process is easy to install, which minimizes downtime. It is also forgiving and easy to operate, and has high turndown capability.

Reference

1. Hegarty, W.P. and Goar, B.G., "Comparison of Claus Reaction Furnace Performance with Air and COPE 02 Based Operation," unpublished.