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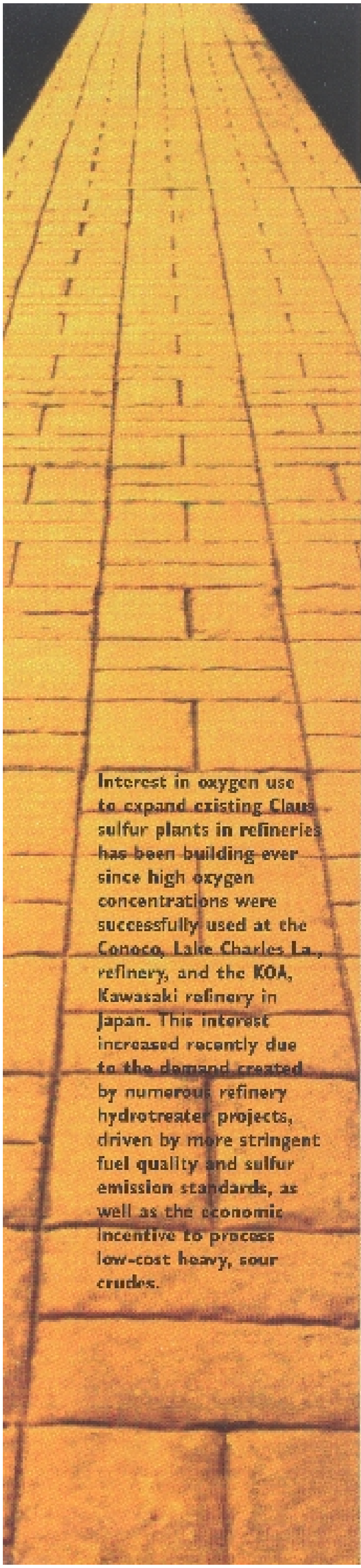
Refining Technology
Auto/Oil Issues
Executive Outlook

Special Report

Expand Sulfur Plant Capacity

Reduce Plant Emissions Using High Oxygen Concentrations Without High Temperature Damage to Refractories



Interest in oxygen use to expand existing Claus sulfur plants in refineries has been building ever since high oxygen concentrations were successfully used at the Conoco, Lake Charles La., refinery, and the KOA, Kawasaki refinery in Japan. This interest increased recently due to the demand created by numerous refinery hydrotreater projects, driven by more stringent fuel quality and sulfur emission standards, as well as the economic incentive to process low-cost heavy, sour crudes.

Various approaches that introduce low oxygen levels have resulted in moderate capacity increases. Oxygen can be added to the air supply stream for concentrations up to 30% oxygen. Beyond the 30% oxygen level, oxygen must be introduced into the reaction furnace through a burner specifically designed to accommodate oxygen, or through a separate oxygen lance. However, higher oxygen concentrations result in higher temperatures, which rapidly approach the furnace refractory design limits.

Methods must be employed to mitigate the reaction furnace temperature whenever high oxygen levels are necessary to coincide with significant capacity increases in refinery operations. Three proprietary technologies are in commercial operation that successfully address this issue.

Combustion Process Technology

One proprietary oxygen combustion technology relies on a recycle stream taken from the No. 1 condenser exit to dilute reaction furnace gases and carry away sensible heat from the reaction furnace. The process requires a recycle blower, and usually a complete change out of the reaction furnace, waste heat boiler and No. I sulfur condenser, due to the higher flows, and heat duties in this plant section,

A second process offers yet another approach. At higher temperatures, hydrogen sulfide partially dissociates into hydrogen and sulfur. Other compounds like carbon dioxide, that are found in the reaction furnace also dissociate at these temperatures. Since the reactions are endothermic, the net temperature rise with oxygen concentration is not linear, and somewhat selflimiting.

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To some extent, these reactions occur in all refinery Claus furnaces, especially when oxygen enrichment is used. Certain burner designs further promote dissociation reactions by producing a hot flame in the presence of high levels of oxygen. However, the furnace refractory must be protected from the high temperatures of this flame by a separate cooler flame that surrounds the hot flame. While the increased level of dissociation allows for higher net oxygen concentrations than normally possible, the maximum oxygen concentration for processing a typical refinery acid gas stream is limited to about 60% oxygen.' Not being able to operate at oxygen concentrations in the 60% to 100% range limits capacity increases. Also, this approach requires a longer residence time (about 2 seconds) in the reaction furnace to allow for mixing of gases from the two separate flames. Complete replacement of the existing waste heat boiler is normally required.

A third process which has been in operation at the KOA Osaka refinery in Japan since 1990, is based on double combustion technology. This proprietary process (SURE Tm Double Combustion Process) provides full capacity expansion capability at up to 100% oxygen, without the need for rotating equipment.

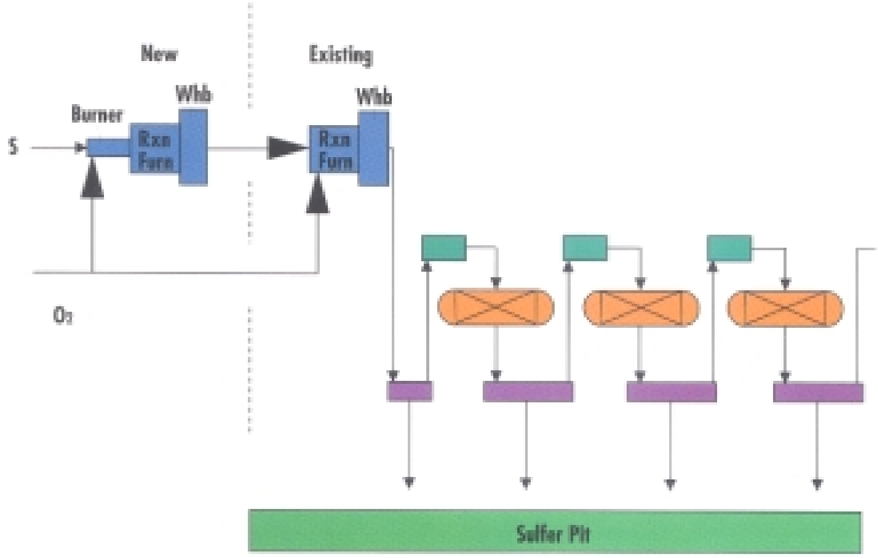

Figure 1. The SURE Double Combustion process uses two reaction stages with intermediate cooling to limit temperature rise to high 02 concentrations.

Double Combustion Process

To limit temperature rise, the combustion reactions are carried out in two stages with intermediate cooling as shown in Figure 1. Acid gases are first subjected to a partial combustion at temperatures well below the safe operating temperature of the refractory, but at temperatures high enough to ensure complete ammonia and hydrocarbon destruction. The first stage of combustion is carried out without attempting to meet the overall stoichiometry requirements, or total oxygen demand. The gases are then cooled in a waste heat boiler, prior to entering a second reaction furnace where the remainder of the required oxygen is introduced.

Significantly, there is no sulfur condenser between the No. I waste heat boiler, and the No. 2 reaction furnace. Also, there is no burner in the No. 2 reaction furnace. By design, the gases exiting the No. 1 waste heat boiler, and entering the No. 2 reaction furnace are substantially above the auto-ignition temperature under all normal operating conditions. This concept allows for a low-pressure drop system, which is easy to install and control.

Since the gases entering the No. 2 reaction furnace are above the auto-

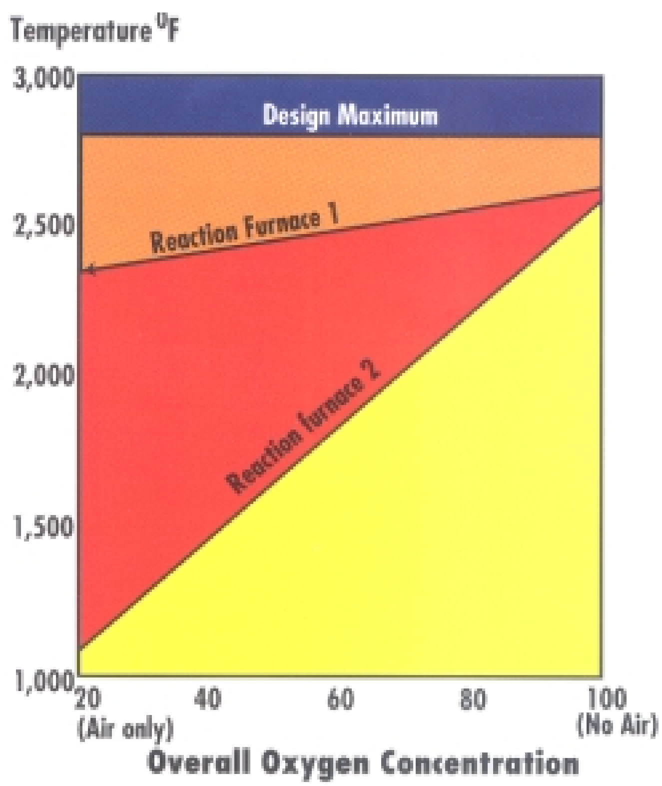

Figure 2. At high acid gas levels, reaction furnace 2 temperature increases with increasing 02 concentration, while reaction furnance I temperature is maintained at high levels, as per maximum design conditions.

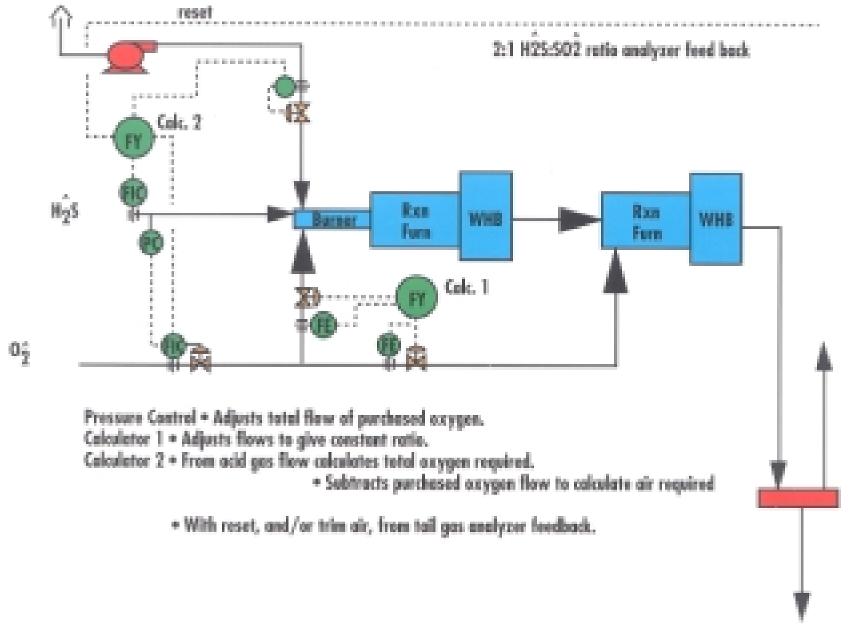

Figure 3. Process control to minimize oxygen consumption.

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ignition temperature, even small quantities of oxygen will react completely, and there is no minimum oxygen flow required to maintain a stable flame. Therefore, a burner is not required, and an oxygen lance may be used to introduce oxygen into the No. 2 reaction furnace. Minimal pressure drop occurs through the system because there still is only one burner.

Reaction Furnace Temperatures

With no burner in the No. 2 reaction furnace, and temperatures above the auto-ignition temperature, there are no minimum flame temperatures, or minimum flows, to maintain. A smooth transition occurs from air-only operation, through partial oxygen enriched air, to 100% oxygen. Even the richest acid gases in refining applications can be processed with 100% oxygen using this process. Oxygen control is safe and simple. Oxygen is fed to the No. 1 and No. 2 reaction furnaces, at a constant ratio between the two furnaces. Oxygen demand is satisfied by increasing the total oxygen flow as required, but since only part of the oxygen flow goes to the No. 1 reaction furnace, temperatures remain well within design limitations.

Figure 2 shows the temperatures in both reaction furnaces for a typical rich refinery gas with significant ammonia present, as overall oxygen concentration is increased from 21% (air only) to 100% (no air). As evident in the figure, temperatures in the No. 1 reaction furnace are maintained at high levels to ensure satisfactory destruction of ammonia and hydrocarbons. The total flow, and therefore residence time, is fairly constant.

Process Control Scheme

In most cases it is desirable to minimize consumption of purchased oxygen to reduce operating costs (Figure 3). Front-end pressure can be used to automatically control the relative amount of air and oxygen used to keep the plant hydraulically loaded. As pressure increases, oxygen flow is increased, while the air flow is reduced to accommodate higher acidic gas flows. Conversely, as the acid gas flow is reduced, pressure falls, oxygen flow is reduced, and air flow is increased. This maximizes air utilization, which results in minimum purchased oxygen consumption.

Retrofit to Existing Plant

When retrofitting to an existing plant, the existing reaction furnace and waste heat boiler become the No. 2 units, and a new burner, No. 1 reaction furnace and No. 1 waste heat boiler are added upstream of the existing furnace. The existing burner is removed during tie-ins.

The BOC Gases acid gas oxygen burner has been operating since 1990. Installed and operating in two refineries, it has been selected for eight more applications currently in various phases of engineering and construction.

For staged capacity increase (and staged investment) a BOC acid gas/ oxygen burner can first be added to the existing furnace. This will normally allow oxygen concentrations of up to about 45% with very rich refinery-type acid gases, and a resulting capacity increase of 75% or more. Later, during expansion to the fullest capacity available with the double combustion process, the same burner can be moved from the existing furnace to the new No. 1 furnace.

Oxygen Supply

For large capacity plants, an onsite cryogenic air separation plant may be economical. However, even for smaller plants, adsorption-type plants present an affordable solution.

Adsorption-type oxygen plants, and small volume cryogenic plants have economical advantages when producing oxygen with a purity of nearly 90%. The small amount of remaining nitrogen has little impact on capacity increase.

Investment Cost

The inherent advantages in the operation and maintenance of the double combustion process can be delivered at investment costs which are much lower than a new sulfur plant and significantly lower than other approaches. The new waste heat boiler is about 50% of the work required by other process schemes, which call for total replacement of the existing boiler. Also, there is no need for a recycle blower, ancillary equipment or unusually high residence times in the reduction furnace. Operation at 100% oxygen is practical, maximizing the potential for capacity increase.

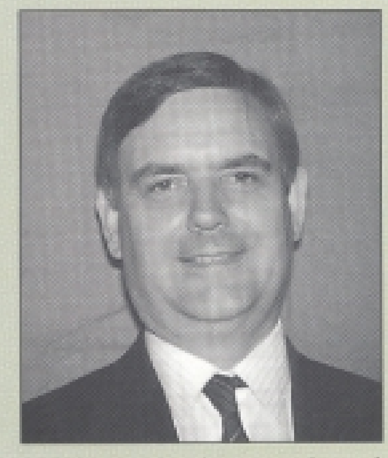
Increasing capacity of an existing sulfur plant with double combustion process technology is more than offset by the substantial savings in investment costs as well as modest operating savings in air blower power consumption.

For new multiple train plants, double combustion technology is an effective means of providing redundancy. The plants may be designed to operate with air at maximum capacity. When one train goes down the overall capacity can be easily restored by switching operation of one or more of the remaining trains to the oxygen mode.

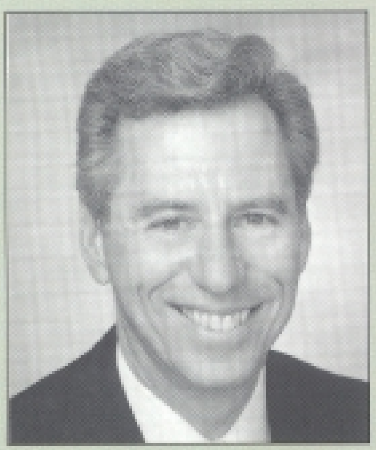
REFERENCE

1. *Hydrocarbon Processing (April 1994) 74.*

Randy Hull currently manages BOC Gases Americas' business and activities for customers within the chemical and refining industries. Hull has 17 years of experience in the industrial gas industry. Prior to joining BOC, he worked at Air Products and Chemicals for more than 10 years and General Electric for more than 3 years. Hull earned a BS in mechanical engineering from Lehigh University and an MBA from Harvard University.



Dick Watson is technical manager in the Chemicals and Petroleum Market Sector of BOC Gases in the UK. He holds a BS degree with honors in chemical engineering from the University of Salford and is a member of the UK Institute of Chemical Engineers. The last 20 of Watson's 25 years with BOC have been developing industrial gas applications in the chemicals and refining industries. He holds several patents on the use of oxygen in Claus sulfur recovery units.



Ron Schendel has an extensive background in gas processing and refining operations (including sulfur recovery). As an independent consultant since 1993, Schendel has assisted refiners with technical evaluations related to capital projects. Recent assignments have included sulfur plant expansion projects, based on oxygen, for two separate clients. His background includes a lengthy career in the engineering and construction industry. His most recent position was manager of technology acquisitions for Brown & Root. Prior to that position, Chendel was vice president of KTI Corp.

Thomas K.T. Chow is director of process engineering for The Ralph M. Parsons Co. He has more than 21 years of experience in supervising chemical engineering endeavors related to process design, process concept development, computer process simulation, field operations, and economic evaluations in the petroleum refining, chemical and hydrocarbon process industries. Chow has authored several articles in the fields of catalysis and synthetic fuels. He earned BS and MS degrees in chemical engineering from the University of Wisconsin and Stanford University, respectively. His PhD program research at Stanford revolved around computer process modeling and heterogeneous activities of various catalysts.