SOxClean: an alternative to burning sulphur in air

The unique capability of Calabrian's SOx submerged combustion technology to provide in-situ, on-demand pure SO_2 and SO_3 in a safe and reliable manner is creating new opportunities for the use of these critical reagents. **Jeff Hammerstrom** of Calabrian Corporation discusses the key features of the technology and its benefits when applied in a variety of applications, including in-situ production of sulphur trioxide (SO_3), debottlenecking sulphur recovery units (SRUs), and solution mining.

PHOTO: CALABRIAN CORPORATION

SO_2Clean sulphur dioxide plant at Port Neches, Texas.

Sulphur has been burned since antiquity. In 'The Odyssey', Odysseus asked for sulphur to purify his house; and the expression "fire and brimstone" goes back to biblical times. So what in the name of fire and brimstone can possibly be new about burning sulphur or manufacturing sulphur dioxide and sulphur trioxide?

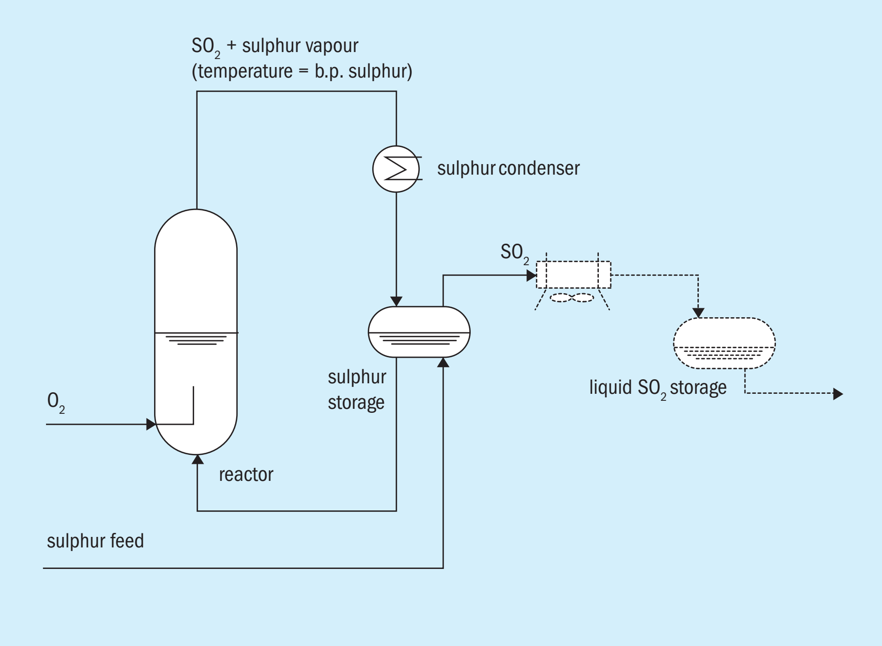
For years, processes requiring sulphur dioxide or sulphur trioxide utilised a conventional air-sulphur burner as the starting point. However, there is an alternative that provides superior economics, operational advantages/flexibility, and improved reliability, namely submerged combustion of pure oxygen in sulphur. Submerged combustion is a safe, environmentally superior and permit friendly way to produce SOx. The good news is that it's not new; it's been in commercial operation for over 20 years. SO_2Clean is a proven, commercial, and proprietary technology developed by Calabrian Corporation to produce high purity SO_2 via submerged combustion.

Above is a photo of the Calabrian Corporation SO_2Clean sulphur dioxide plant at Port Neches, Texas. It consists of two parallel, independently run 50 t/d trains that occupy a 9.1 m x 21.3 m footprint. The Port Neches, Texas plant has been operating for over 20 years.

Submerged combustion production of SO_2

The first step in the submerged combustion process is reacting pure oxygen with sulphur. Oxygen is sparged into a pool of molten sulphur at the appropriate tempera-

Fig 1: **Calabrian's SO_2Clean technology**



ture and immediately reacts to form sulphur dioxide. The heat of reaction causes the pool of sulphur to boil, but the temperature of the system is limited to the boiling point of sulphur at the operating pressure of the reactor. The amount of sulphur vaporised is such that the heat of vaporisation is exactly equal to the heat of reaction. Even at atmospheric pressure, the boiling point of sulphur (444.6°C), is well above the auto ignition temperature (auto ignition of sulphur in air is 243°C). This ensures immediate and complete reaction of the oxygen with sulphur as it enters the reactor. Accordingly, because oxygen is always the deficient reactant, there is no possibility of forming sulphur trioxide. Even if some transient SO_3 is created, it would immediately react with the excess sulphur to form sulphur dioxide.

The second step of the process is SO_2 and sulphur separation. In addition to forming SO_2 gas, significant amounts of sulphur are vaporised and carried out of the reactor where the gases are cooled in a condenser. The resulting SO_2 gas and condensed molten sulphur are returned to the sulphur feed tank. The SO_2 gas continues downstream to feed other chemical processes or to be condensed for storage or sale as 100% pure SO_2.

In the condensing step, any remaining minor amounts of non-condensed gases are vented to a system where residual trace amounts of SO_2, if any, are scrubbed using a caustic solution. Given that there is no nitrogen, like there would be with air, there is no NOx generation so permitting requirements are minimised. Figure 1 shows a process flow diagram for submerged combustion production of SO_2.

Perhaps the most compelling operational advantage of the process is its start/stop and turn-up/down capability. It essentially provides on-demand inventory capability. The productive capacity of the process is controlled by oxygen flow. For increased capacity simply open the valve, for less close the valve, it's that simple and that fast. A 100 t/d facility can be cycled up and down between 25% and 100% of nameplate capacity in minutes just by the opening and closing of the oxygen valve. Start-up in "hot hold" takes minutes and a full start-up from a cold state takes less than six hours.

Advantages of oxygen over air

How can SO_2 generation via submerged combustion with purchased oxygen be cost competitive with burning sulphur with free air? The answer is inert gas removal. By utilising pure oxygen rather than air, all of the inert gases (approximately 80% of the inlet gas stream) that come along for the ride are eliminated, as are all of the costs, complexities and problems they create. To name a few, the benefits include:

- Smaller downstream equipment size and plant footprint.
- Reduced maintenance downtime – no refractory, no blower, no air drier, no sulphur pumps.
- No burner management system or complicated oxygen ratio schemes – just straight oxygen flow.
- Greatly reduced electrical costs – the incoming oxygen pressure drives gas flow so there is no blower in the process.
- No corrosion – since the process runs in an excess of sulphur not oxygen, i.e. no SO_3 to make condensable sulphuric acid in the process, maintenance downtime and expense is reduced.
- There is no NOx generation – reducing emissions and dramatically simplifying air permitting.
- High turndown capability allows "on demand" production of sulphur dioxide, enabling small liquid on-site storage for uninterruptable supply of sulphur dioxide downstream.
- Highly reliable – 98%+ documented onstream time.

Applications for pure SO_2 and SO_2Clean

There are many markets and applications where the SO_2Clean system and on-demand SO_2 can be deployed. The process' unique attributes and small footprint make it ideal where traditional burners may be impractical. The applications highlighted include in-situ production of sulphur trioxide (SO_3), debottlenecking sulphur recovery units (SRUs), and solution mining.

SO_3Clean for gas/liquid SO_3, oleum and sulphuric acid

Sulphur trioxide (SO_3) and oleum are essential intermediates in the production of many important products. For hazardous inhalants, supply chain risks and the rapidly rising cost of transportation are quickly becoming serious areas of concern for users. SO_3 production in situ, near the point of use, minimises the consumers risk and reduces transportation costs.

Calabrian and Chemithon Corporation, a leading expert in sulphonation processes, have partnered to offer a new solution to produce liquid SO_3 supply by integrating Calabrian's SO_2Clean process with Chemithon's SO_3 converter technology. This new technology platform is called SO_3Clean.

Chemithon's SO_2 to SO_3 converter uses a conventional catalyst in a unique tube converter design that overcomes the heat generation issues present in traditional converter designs. Accordingly, SO_3Clean produces an undiluted, 100% pure SO_3 gas stream from a 100% pure SO_2 gas stream. It does so economically and at very high efficiencies without producing large quantities of excess sulphuric acid like conventional acid plants. The process can also be tailored to produce SO_3 derivatives including oleum and sulphuric acid in varying strengths and quantities.

The SO_3Clean process enjoys all of the operational flexibility and benefits inherent in SO_2Clean. The ability to cycle SO_3 productive capacity up and down in seconds is particularly relevant to sulphonation customers who routinely operate multiple processes with product change-overs.

The benefits of on-site production of on-demand SO_3 using SO_3Clean technology are:

- all the cost, operating and environmental benefits of SO_2Clean vs. air sulphur burning;
- elimination of exorbitant transportation costs and risks;
- on-demand capability allows for less SO_3 storage;
- small footprint that can easily integrate with existing processes;
- expandable modular design providing redundancy and flexibility.

Expanding SRU capacity

In a conventional Claus sulphur recovery unit, hydrogen sulphide (H_2S) or "acid gas" is combined with air in the reaction furnace. The H_2S reacts with the available oxygen in the air to produce sulphur dioxide. The sulphur dioxide then reacts with the remaining hydrogen sulphide to produce sulphur and water vapour via the Claus reaction.

$$H_2S + 1\frac{1}{2}\ O_2 \rightarrow H_2O + SO_2 + \text{heat}$$

$$2\ H_2S + SO_2 \rightarrow 2H_2O + 3S \text{ (Claus reaction)}$$

Pure oxygen rather than air is often used to increase SRU capacity. By replacing air containing oxygen with pure oxygen, inert gases in air are removed. The result is more volumetric capacity available for processing acid gas. However, the combined effect of more acid gas processing (heat) and the removal of "heat absorbing" inerts results in furnace temperatures that limits the amount of oxygen that can be used. This limits the capacity increase that is available by use of oxygen alone.

If sulphur dioxide is produced external to the SRU's reaction furnace and is instead introduced as a feed stream, the heat of formation is removed in the production process.

$$S + O_2 \rightarrow SO_2 + \text{heat (outside RF)}$$

Therefore, if no air were added to the SRU feed gas and only the stoichiometric requirement of sulphur dioxide provided, the reaction would operate at very moderate temperatures and inert gases would be absent. The result is a significant increase in the ability to process acid gas. The capacity of a conventional SRU can be more than doubled.

The production of sulphur is not the only function of a typical sulphur recovery unit. Destruction of ammonia and hydrocarbons is also required. Therefore, operation of the reaction furnace with some air or oxygen, in conjunction with the SO_2, may be necessary to achieve the high temperatures required to completely destroy these contaminants.

Oxygen enrichment is commonly used to increase SRU capacity. There are several significant advantages to using SO_2 injection. Typically, oxygen enrichment requires significant burner modifications or even complete replacement as well as an increase in quench tower cooling capacity. These modifications are common to all O_2 enrichment projects (beyond simple enrichment). However, high levels of oxygen enrichment require further modification to limit temperature in the reaction furnace. These modifications to allow higher levels of enrichment (and increase in plant throughput) require process changes and normally the use of additional equipment. Many refineries do not have space for this new equipment. With SO_2Clean, the sulphur dioxide can be produced outside the refinery gate, so there is no additional plot space required inside the refinery. This can be a significant advantage in many refineries where space is severely limited.

Refineries with multiple SRUs are the perfect candidates to gain additional capacity and/or redundancy through SO_2 enrichment. High level oxygen enrichment using conventional methods requires significant modification to each of the units in order to realise additional capacity. With the SO_2 approach, a single sulphur dioxide plant can feed and debottleneck multiple units.

If the refinery does not wish to install and operate the SO_2 plant within its battery limits, Calabrian would build/operate a fence-line plant to manufacture SO_2 and deliver it via pipeline analogous to the current practice of supplying other industrial gases (e.g. hydrogen, oxygen, nitrogen).

SO_2Clean in solution mining and leaching of metals

The use of sulphur dioxide in solution mining and leaching of metals (particularly uranium, gold, silver, cobalt, nickel and manganese) is generating great interest for yield improvement and cost reduction. SO_2 is also the best choice for destruction of cyanide in the leaching of precious metals. Despite its overwhelming technical advantages, the transport of SO_2 is a logistical challenge and the inability to dependably source low cost, pure SO_2 gas/liquid at the mine site has limited its usage. In addition, there are many remote areas where smaller amounts of sulphuric acid are required and transportation costs are prohibitive.

The compact size, operational flexibility, and reliability of the SOxClean system make it ideally suited for production of sulphur dioxide and sulphuric acid at the mine site. Intermittent power outages which can severely impact the performance of sulphur burners are not problematic for the shutdown/start-up capability of a submerged combustion system which is controlled by oxygen flow. When power returns, the system can go from cold start-up to nameplate capacity in a matter of hours. Additionally, the system has significant and rapid turndown/up capability – maximum rates to 25% and vice versa in seconds. The limited potential for maintenance outages due to essentially no internal corrosion and no rotating equipment in the process is also extremely beneficial.

A SO_2Clean plant can operate either inside or outside the fence line of the mine and deliver SO_2 via pipeline directly to use points; the leaching unit, the pretreatment plant or the cyanide destruction system.

The future of SOx manufacture

Calabrian will build, own and operate "fence-line" SOxClean facilities that can provide gaseous or liquid SO_2 and SO_3 and/or oleum and sulphuric acid via pipeline directly to the consumer's operations. Licensing of the technology for captive use facilities is also an option. In-situ production provides long term supply chain security, eliminating the risk/cost of hazardous chemical transportation. ■