

Enhancing SRUs with oxygen-enriched air

As clean fuels regulations become more stringent, refiners looking for new ways to boost the capacities of their existing sulphur-recovery units are turning to oxygen-enhancement technologies

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Most refiners have now moved toward a higher standard of sulphur-recovery efficiency to comply with clean fuels regulations that impose a reduction of sulphur in refined products. While refiners have chosen various avenues and process solutions to address these sulphur cap requirements, reliance on the refinery's previously installed sulphur complex has presented one of the most effective and cost-efficient solutions. Comprised of a Claus sulphur-recovery unit (SRU) and a tail gas-treating unit (TGTU), the sulphur complex processes both lean and rich hydrogen sulphide (H₂S) bearing acid gas streams and ammonia-bearing sour water stripper off-gas streams to recover elemental sulphur.

However, the existing sulphur complex in many refineries may not provide enough process capacity to meet the current regulatory requirements. Current trends indicate that as crudes become increasingly heavier and contain higher concentrations of sulphur, many refineries will need at least two or more Claus units — also referred to as trains — to meet current environmental regulations. This has increased the throughput of many SRUs, which may lead to the SRU reaching its hydraulic limitation (maximum air) and more frequent shutdowns for maintenance. This can force the refinery to shut down its upstream operations unless there is another way to remove sulphur from the acid gas and off-gas streams.

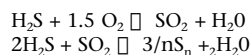
To prevent unscheduled shutdowns of this nature, many refineries have a parallel Claus unit. If one of the trains needs to be taken off-stream for maintenance, the other can handle at least some of the additional throughput. However, in instances where the remaining SRU is unable to provide adequate sulphur-recovery capacity, the refinery may be forced to reduce its upstream operations substantially.

To ensure that a plant's Claus unit complex can meet the demands for increased throughput, even in instances

where one of the trains is not in service, a refiner can do one of two things: either install another SRU or retrofit a unit to provide oxygen enhancement to the Claus process. Since investment in any kind of sulphur-reduction technology is regulatory driven rather than revenue and profit driven, solutions that get the job done effectively for the least amount of money are generally preferred. Oxygen enhancement has become one of the most viable, cost-effective alternatives to installing a new SRU.

Claus combustion process

The classic Claus process has been the most common method for processing H₂S-rich streams and recovering sulphur from both amine acid gas and sour water stripper gas. The Claus process can be broken down into two steps. In the first step, which is called the oxidation process, about one-third of the H₂S contained in the feed is oxidised with oxygen from ambient air to create sulphur dioxide. The oxidation takes place in the burner/thermal reactor of the SRU. In the second step, which is the actual Claus reaction, the remaining H₂S is reacted with the sulphur dioxide to form elemental sulphur. This step takes place in the thermal and catalytic reactor of the SRU. The reactions are listed below:



To obtain the oxygen needed for the combustion process, ambient air is supplied to the SRU burner via an air blower. Ambient air usually contains about 21 per cent oxygen; the balance is primarily nitrogen and some water vapour, both of which are inert in the combustion process. Since these inert components comprise nearly four times as much volume as the oxygen, the unit reaches its hydraulic limitation quickly once these components are introduced, which limits the sulphur-recovery capacity of the SRU.

Sulphur-recovery capacity becomes further constrained by other contaminants in the acid gas feeds, such as ammonia, hydrocarbons, cyanides and carbon-sulphur compounds. Since sour water stripper gas feeds contain more ammonia gas than ever before, it is now necessary for refiners to increase the amount of ambient air supplied to the SRU. This ensures that not only the necessary amount of H₂S is burned to keep the plant compliant with environmental regulations, but also that the ammonia gas contained in the feed is properly destroyed. However, as more air is fed into the Claus unit, the amount of inerts (nitrogen and water) added to the system increases even more rapidly, leading to the hydraulic limitation of the unit and, eventually, to a need to increase the size of the unit or invest in another SRU.

The best way a refiner can avoid this situation is to use an oxygen-enriched air supply, which not only replaces the nitrogen in the ambient air, but also provides enough oxygen to destroy the contaminants in the feed while maintaining adequate oxidation levels. In fact, by substituting pure oxygen for most or all of the ambient air, space is made available to increase the throughput of the acid gas feeds to the SRU, which, in turn, gives the system greater sulphur-recovery capacity.

Oxygen levels in the SRU

As previously stated, in an air-based combustion system oxygen typically comprises about 21 per cent of the ambient air, with nitrogen comprising the remaining 79 per cent when the air is dry (water vapour and other small inerts can displace some of the oxygen and nitrogen in humid conditions). By not contributing to the combustion process, nitrogen does nothing more than take up additional space, dilute the Claus reactants and reduce the overall sulphur-recovery process. Thus, in order to increase the capacity in the SRU to

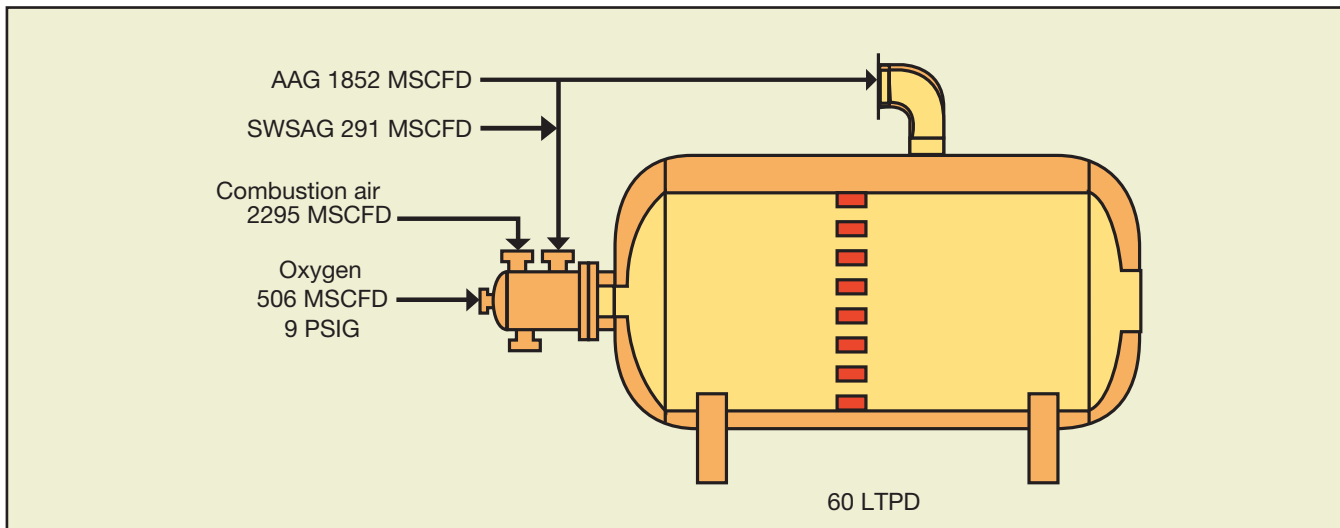


Figure 1 Modified Claus SRU with oxygen injection

process more acid gas, it is first necessary to reduce the nitrogen.

There are various levels of oxygen enhancement that can be applied to increase the capacity of the SRU. Most technologies, however, are grouped into three categories. The first level of oxygen enrichment encapsulates those technologies that increase the oxygen level from 21–28 per cent (low-level oxygen combustion). The second level includes the technologies that raise the oxygen level up to 40 per cent (medium-level oxygen combustion), while the third level of oxygen combustion encompasses those technologies that increase the oxygen concentration to levels in excess of 40 per cent — in some cases, even 100 per cent. It is important to note that for every level increase in the oxygen concentration, certain plant modifications must be made, for both retrofitted SRUs and newly installed units.

Low-level oxygen combustion, the simplest and most cost-effective means of increasing the oxygen concentration

of the combustion air, is often referred to simply as oxygen enrichment. Low-level oxygen enrichment involves the injection of pure oxygen into the combustion air piping system of the SRU, upstream of the burner. This method will typically raise oxygen levels up to 28 per cent and increase SRU capacity by 25 per cent. With a rise in the oxygen concentration levels, a substantial portion of nitrogen is eliminated from the Claus reaction.

While virtually every sulphur-recovery unit at a minimum cost can, in concept and in practice, achieve low-level oxygen enrichment, the system itself has several limitations. For instance, the oxygen level is generally limited to 28 per cent, because anything higher would require special piping system materials and cleaning procedures.

Generally, the existing SRU equipment (including the metallurgy and refractory) can be used without modification, as the combustion temperature should not exceed 2600°F (Figure

1). However, additional safeguards for the oxygen system must be taken into account, and the control system required should be designed to minimise the consumption of pure oxygen to protect the equipment in place.

For newly installed Claus SRUs that are designed for the future installation of oxygen enhancement, safeguards will include a refractory system in the front of the thermal zone, as well as a waste heat boiler tubesheet-protection system, lines/equipment that are designed to withstand the high temperature, and an adequate quench system in the TGTU. For retrofit applications, it is likely that this equipment, after inspection, will require upgrades to handle the increase in oxygen concentration.

Medium-level oxygen combustion can be considered when the desired capacity increase exceeds that made available by simple enrichment. Technologies are available that inject oxygen directly into the thermal reactor rather than into the piping system upstream of the burner (Figure 2). Oxygen-injection

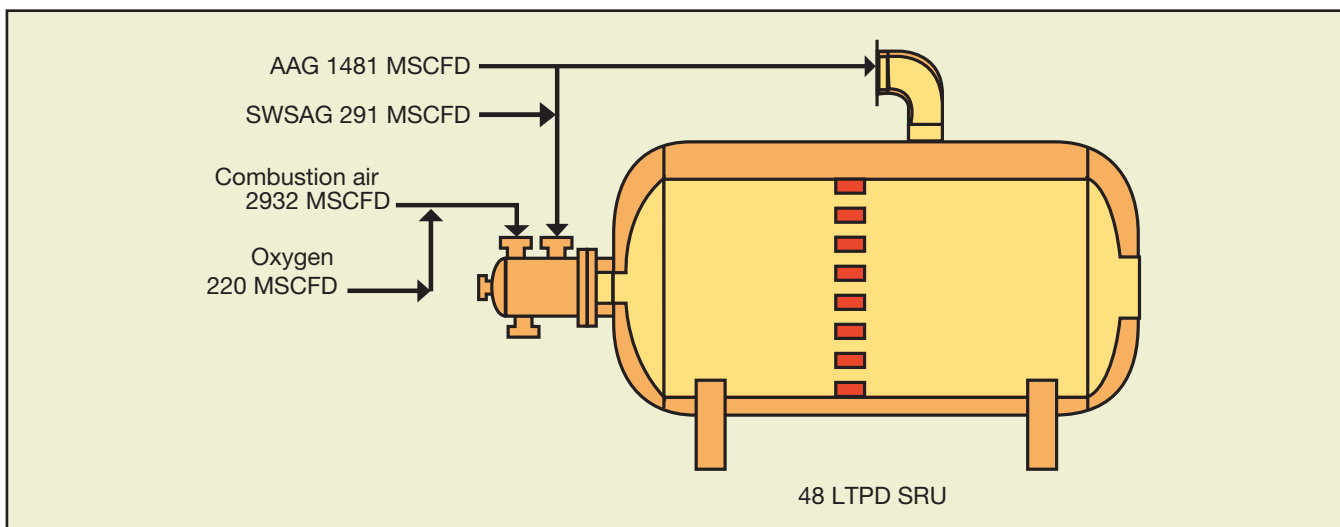


Figure 2 Modified Claus SRU with low-level oxygen enrichment

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systems, which are regarded as medium-level oxygen-enrichment tools, were developed to maximise the amount of acid gas processed in the SRU by replacing the diluent nitrogen in the air with reactants (oxygen and acid gas) to overcome the hydraulic limitations of the existing unit.

Oxygen-injection systems typically are licensed technologies that not only eliminate the metallurgical limitations of low-level oxygen enrichment, but also produce SRU capacity increases of up to 70 per cent for refinery acid gas feeds. This capacity increase further removes nitrogen from the Claus reaction.

Since the oxygen concentration is increased from 28–40 per cent, combustion temperatures are likely to reach at least 2800°F. Careful consideration must therefore be given to the design of the refractory system and the protection of the waste heat boiler tubesheet. In addition, the technology must include a proprietary burner that features an oxygen-injection port separate from the combustion air inlet. The waste heat boiler and the sulphur condensers need to be evaluated to ensure they have adequate heat-transfer capabilities. If the SRU is followed with a TGTU, the quench and amine systems need to be evaluated for the increase in capacity.

To ensure that the thermal reactor of

the SRU is using the proper amount of pure oxygen and not exceeding temperatures of 2800–2900°F, which can cause refractory damage, it is important that refiners install an automated control system. This system should act to minimise oxygen consumption and maximise combustion air consumption, as well as to ensure a smooth transition from air regime to oxygen-enhanced regime and back to air. The thermal reactor combustion chamber temperature controller will limit oxygen feed to the SRU if the temperature gets higher than 2800°F to prevent damage to the refractory system.

Once the necessary adjustments and modifications are made to compensate for the introduction of a medium-level injection system to the SRU, including a new burner configuration, adequate refractory system, proper heat-transfer equipment, and acid gas and other piping that can handle the pressure drops and added capacity, a medium-level system can increase capacity up to 50–70 per cent and can be retrofitted to most Claus designs.

When is high-level oxygen combustion feasible? If low-level oxygen enrichment can increase capacity by 25 per cent and medium-level injection systems can increase capacity by up to 70 per cent, what are the implications

for refiners that want to increase their capacity to more than 100 per cent? To achieve such capacity levels, it is necessary to increase the oxygen concentration to levels in excess of 40 per cent and, in many instances, approaching 100 per cent. When the oxygen concentration reaches these levels, the ambient air is almost completely eliminated from the combustion process.

It is important to note that any oxygen injected into a thermal reactor in the absence of ambient air will quickly cause combustion temperatures to exceed the limits of the refractory system. To prevent this, several proprietary technologies are available that can handle 100 per cent oxygen.

The use of a 100 per cent pure oxygen system may require additional equipment, including a specialised burner to handle the pure oxygen, as well as the normal requirements for the oxygen-injection (mid-level oxygen) system. While this extra equipment will increase SRU plant costs, it will also boost the SRU capacity by 100 per cent or more.

Impact of oxygen processes on SRU

Whether refiners replace part or all of the ambient air with pure oxygen, the concept of using oxygen-enriched air to expand existing Claus units or of

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building peaking capacity into new units has become widely accepted. However, despite the enormous benefits an oxygen-enhanced system provides, especially as crudes get sour and environmental regulations become more stringent, the addition of oxygen to combustion air requires careful consideration of numerous design and operational features to ensure desired safety and reliable operations. When determining whether to retrofit a unit or install an SRU designed for the future installation of oxygen enhancement, it is important to review the following:

- Oxygen control system
- Elevated combustion temperatures
- Heat-transfer equipment
- Increased pressure drops
- TGTUs
- Safety considerations.

The control system for oxygen injection is designed to accomplish the following main objectives: provide safe and efficient operation, maximise unit throughput and minimise oxygen consumption.

To do so, it is imperative that additional safeguards are implemented along with the oxygen-injection system. Such measures include an interlock, which is used to shut off oxygen in the event that temperatures exceed their normal levels in the thermal reactor or

when the entire SRU needs to be shut down. When processing oxygen, the shutdown system needs to be fully implemented and functional to ensure that the SRU will be operated in a safe and reliable manner.

The control system for oxygen injection is designed in such a way that the oxygen is only supplied when the SRU reaches its hydraulic limitations from using the maximum air provided by the air blower. Once the oxygen is introduced in the burner, a portion of ambient air is taken out, thus creating a hydraulic capacity to feed more acid gas to the SRU. As soon as this portion of ambient air is taken out of the process, the temperature in the reactor will increase. The climbing temperature needs to be carefully monitored, so that when it reaches certain high levels the oxygen flow can be promptly reduced to prevent any refractory damage.

As more “inert” nitrogen is replaced by pure oxygen, the combustion temperature will steadily increase. For this reason (with elevated combustion temperatures), it is necessary to review all materials of construction beforehand — including the refractory fire brick, insulating brick and castable refractory— to ensure that all materials have the acceptable chemical composition and physical properties required for

higher operating temperatures. The waste heat boiler tubesheet is particularly susceptible to high temperatures, which can lead to rapid deterioration of the tubesheets. To prevent this, refiners can install a tubesheet-protection system (a patented licensed technology) that improves the protection of the tubesheet against the high process temperatures of oxygen enhancement. This system can be used on new units, as well as retrofit applications.

As temperatures rise in the combustion chamber with the use of oxygen, the load on the downstream heat-transfer equipment is substantially increased. Also, when pure oxygen is added to the SRU, the mass flow decreases more rapidly with each condensation cycle, resulting in lower pressure drops in the latter stages of the unit, as well as slightly higher mass flows in the waste heat boiler and first sulphur condenser. This combination of higher temperatures and higher mass flows should lead to an evaluation of the waste heat boiler to ensure it can handle the extra flow and higher temperatures, as well as an evaluation of the sulphur condenser’s heat-transfer capabilities. Accordingly, these items and their safety valves must be inspected before installing an oxygen-enhanced unit to determine whether they need to be upgraded.

It also is important to note that the increased temperature in the combustion chamber will subsequently affect downstream temperatures. For instance, the temperature rise in the catalytic reactor beds will be higher for the oxygen-enhanced unit because the concentration of the reactants (hydrogen sulphide and sulphur dioxide) has been increased, while the inert nitrogen (which absorbs the increased temperature) has been decreased. Also, each condenser load will be greater because of the higher temperature and increased sulphur condensation. In general, sulphur-recovery efficiency can be expected to improve in the oxygen-enhanced unit.

Due to the increased flow rate of the feed gases to the SRU, all of the acid gas feed lines and the knockout drums need to be evaluated. Increases in pressure drops in all feed lines and front-end equipment — including the control valves and flow meter — can create the hydraulic limitation for processing more acid gas in the SRU. This needs to be reviewed before retrofitting an SRU for oxygen enhancement. Also, with the increased sulphur production, it may be necessary to check the performance of the sulphur seals, sulphur piping and pumping capacities.

Since the mass flow decreases more rapidly with each condensation step in an oxygen-enhanced SRU, TGTUs usually receive less mass flow when oxygen enhancement is added. However, because there is a higher percentage of hydrogen sulphide and sulphur dioxide and less nitrogen, the temperature rise across the TGTU is higher than the unit is typically designed to handle. In addition, because the quench water equipment has to handle a greater load of condensing water, this must also be reviewed for the increased workload. To compensate for a large increase in the upstream feed capacity, the tail gas amine system circulation capacity may need to be increased as well.

For safety considerations, the unique properties of pure oxygen should be given full consideration when installing pure oxygen piping in the unit. In high oxygen content atmospheres, materials normally not combustible in atmospheric air can burn rapidly. To curtail the risk of fire or injury, it is crucial for all components introduced into the system to be clean for oxygen service. Grease, oil, particulates and iron scale present a serious hazard due to combustibility and impingement, which could result in a pipe fire or other injury. Particular care must be taken during the maintenance activities to ensure that only proper materials and parts are used.

SRU capacity increases using both low-level and medium-level oxygen enhancement (as compared with regular ambient air)

	Combustion air 21% oxygen	Air enrichment 26% oxygen	Injection system 35% oxygen
AAG, MSCFD	1184	1481	1822
SWS AG, MSCFD	291	291	291
Combustion air, MSCFD	3384	2932	2295
Oxygen, MSCFD	0	220	506
Total, MSCFD	4859	4924	4944
Capacity, LTPD	40	48	60

Table 1

Care must also be taken to ensure that all new systems, parts and components are appropriately cleaned.

These features are the most prominent ones that need to be reviewed with respect to oxygen-enrichment applications in existing plants. It cannot be overemphasised that these adaptations for increasing oxygen and supply must be carefully planned, designed, controlled and implemented by experts with practical experience.

Case study

Oxygen-enhancement technologies have been successfully implemented in various sulphur complexes throughout the world. To maximise efficiency, some of these systems are configured to automatically increase or decrease the level of pure oxygen being injected directly into the burner, depending on the capacity level of the SRU.

One such system was recently introduced to a US refinery. This refinery has three SRUs, each one designed to process sulphur in the amine acid gas and sour water stripper gas feed using ambient air. Each unit also is designed and equipped with mid-level-type oxygen-injection systems, in which pure oxygen is directly injected into the burner. With an oxygen level of 36 per cent, each unit can process up to 50-60 per cent more acid gas load (capacity) in the amine acid gas and sour water stripper gas feed.

When the refinery throughput is near normal levels, the SRU relies on ambient air to process the sulphur in the feed. However, once these units reach their maximum capacities through the use of ambient air, the patented oxygen-control system used in the sulphur complex automatically introduces pure oxygen into the burner to process the excess acid gas feed. As soon as the refinery throughput is reduced back to a level that no longer requires the enhanced capacity, the control system automatically switches back to the ambient air regime to minimise the operational costs of the SRU.

This patented advanced control system not only helps the refinery reduce costs, but also allows it to remain

compliant with current regulations. In the event that one SRU becomes inoperable, the feed going to that SRU is automatically redirected to the other two trains. Once these units reach their hydraulic limitations, pure oxygen is automatically injected into the SRU to satisfy the oxygen requirements for the increased feed. Since all of this is achieved with the advanced oxygen-control system, operator intervention is not required, ensuring the refinery remains compliant with environmental regulations at all times.

Meeting future needs

As refiners continue to meet clean fuels regulations for diesel and install more SRU trains for redundancy purposes, SRUs designed for the future installation of oxygen injection may provide a sound capital investment. Whether this capability is installed in a new unit or a retrofit, oxygen has become a cost-effective and efficient solution for the inevitable capacity increase required in SRU throughput. The challenge for the future lies with ensuring the control systems work well with the oxygen-enhanced systems and implementing the necessary safety features to ensure refiners experience a smooth transition.

Table 1 provides an example of how SRU capacity is increased using both low-level and medium-level oxygen enhancement (as compared with regular ambient air). For illustrative purposes, typical (rather than maximum) oxygen levels have been used within each of the scenarios to show the capacity increases. In this example, an oxygen level of 21 per cent is used for combustion air, 26 per cent for the low-level air-enrichment mode of operation, and 35 per cent for the injection system mode.

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