FROM SHORE

TO SHIP

UDAY N. PAREKH AND BEVAN HOUSTON, DEVCO, USA, LOOK AT SULFUR RECOVERY TO SHIP LOADING TECHNOLOGIES THAT ARE CLEAN, ECONOMIC AND SAFE.

An important step in oil and gas processing as well as coal gasification is the removal of the sulfur contained in the fossil fuel so as to produce clean burning end products with minimal impact on the environment. The key goal of the enterprises engaged in these activities with respect to sulfur removal is that it be done effectively, cleanly, safely and reliably and that the sulfur be dispatched without impacting the main operation of the facility. This is understandable viewed through the prism of sulfur being a byproduct/waste product of the energy industry. However, on the receiving end at the consuming industries sulfur enjoys some of the sheen of a precious metal of the same colour as it constitutes a vital feedstock for the manufacture of sulfuric acid and fertilisers necessary to feed the world's seven billion.

This article highlights three proven technologies that radically improve the environmental, safety and reliability attributes of sulfur recovery and handling operations:

- COPE technology. Increase capacity and improve environmental performance of the sulfur recovery unit (SRU).
- D'GAASS technology. Safe and efficient removal of dangerous H_2S from liquid sulfur.
- Devco II Forming. Safe and reliable conversion of liquid sulfur to solid sulfur for safe handling, storage and transportation through the long supply chain.

This article also speaks of the significantly changing dynamics in the sulfur markets. These include the emergence of new geographies which will be introducing significant new volumes of sulfur to the world markets as well as other large contributions to sulfur supply from new projects in the Middle East. All of this will exert pressure on current and new producers of sulfur, as demand will fail to keep up with this additional supply. The safe and cost effective operation of a energy

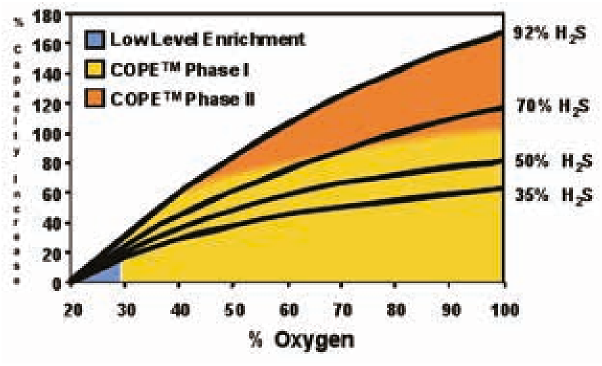


Figure 1. SRU capacity increase with oxygen enrichment.

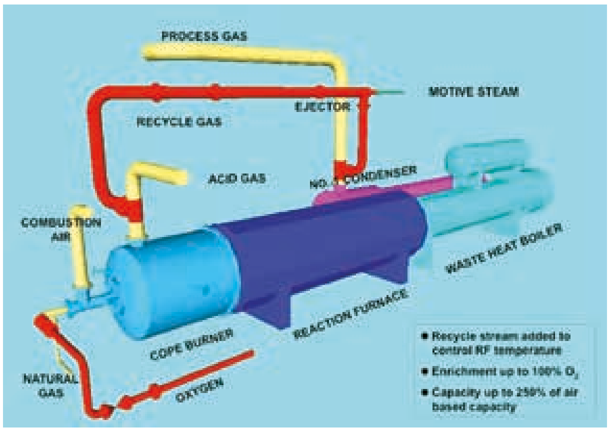


Figure 2. Cope Phase II process.

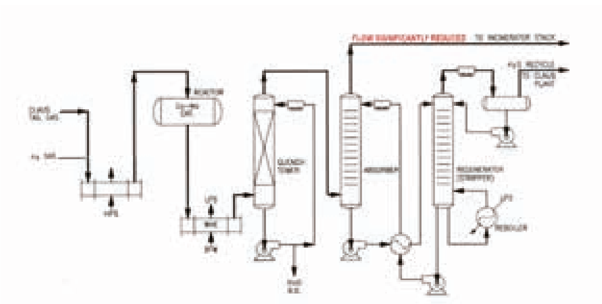


Figure 3. TGTU (hydrogenation - amine).

production of a formed sulfur product that is safe to transport will be of increased importance in the emerging buyer's market.

Claus oxygen based process expansion

Oxygen enrichment of SRUs is a popular, economic, reliable and safe method for addressing the dual needs of providing additional sulfur removal capacity while simultaneously conserving capital for more profitable operations. Devco through its partnership with Fluor offers a full range of oxygen enrichment technologies that provide capacity increases from 10% to 100+% (Figure 1).

Replacing some or all of the combustion air with oxygen via oxygen enrichment decreases its nitrogen content and permits the processing of additional feed while still operating within the hydraulic constraints of the existing SRU. There are three distinct SRU oxygen enrichment technologies specifically designed for the level of capacity increase desired:

- Low level oxygen enrichment: Oxygen is injected into the SRU combustion air line through a custom designed diffuser. Safety considerations usually limit this technology to enrichment levels of about 28% and a capacity increase of 15 - 25%.
- Mid level oxygen enrichment (COPE Phase I): Oxygen enrichment levels exceeding 28% require the use of a special burner with discrete oxygen port(s) to safely handle oxygen as done with the COPE Phase I technology. This technology provides a capacity increase of up to 60% at oxygen enrichment levels of up to 40 – 45% for typical refinery acid gas streams. The maximum allowable furnace refractory temperature sets the upper oxygen enrichment limit of this technology.
- High level oxygen enrichment (COPE Phase II): High reaction furnace temperatures typically encountered above 40 - 45% oxygen enrichment for rich acid gas streams require the implementation of special temperature moderation technologies for further gains in capacity. COPE Phase II is a patented technology in which a portion of the cooled gas from downstream of the first sulfur condenser is recycled back to the reaction furnace to achieve temperature moderation (Figure 2). This technology can be deployed at oxygen enrichment levels up to 100% to more than double the capacity of an existing SRU.

Besides capacity increase, other key COPE/SRU oxygen enrichment process advantages include:

- Significant capital cost savings: 75 - 90% for retrofit installations and 25 - 35% for grassroot installations.
- Quick implementation.
- Improved conversion and reduced emissions.
- Higher furnace temperatures for lean acid gas streams.

Since this article focuses on the environmental and safety attributes of the subject technologies, the environmental benefits of the COPE technology is highlighted below.

The very significant reduction in SRU process flow rates at high oxygen enrichment levels results in a very large decrease in the tail gas treatment unit (TGTU) absorber overhead flow rate (Figure 3). As shown in Table 1, for COPE II operation at 65% oxygen enrichment and despite a doubling in capacity, the TGTU absorber overhead and hence SO_2 emissions are reduced by 62%. On a unit H_2S feed basis, this translates to SO_2 emission reductions of 80%.

Since the first high level SRU oxygen enrichment startup in 1985, the patented COPE technology has been licensed at over 35 SRU trains worldwide.

Sulfur degassing process

Liquid sulfur produced from a Claus SRU typically contains 200 - 350 ppmw H_2S, partially dissolved and partly present in the form of polysulfides (H_2S_x). If liquid sulfur is not degassed, H_2S will be released during storage, loading, and transport and may create an explosive mixture of H_2S in air. Undegassed sulfur can also create a toxicity hazard and a noxious odour problem when H_2S is released from the sulfur. Solid formed

Table 1. Why oxygen enrichment decreases SRU emissions

Rich acid gas feed (93.7% H_2S)	Air based operation, 100 ltpd	COPE operation (65% O_2), 200 ltpd	COPE versus air based, % increase	Comments
Contained S in feed, ltpd	100	200	100%	
SRU tail gas flow, million ft^3/h	353	322	-9%	
Contained S in tail gas, ltpd	2.7	4.2	56%	
Feed gas to TGTU amine absorber million ft^3/h	257	104	-60%	Feed to absorber 60% lower despite 2X capacity
Absorber off gas to incinerator, million ft^3/h	255	98	-62%	Feed to incinerator 62% lower despite 2X capacity
H_2S level in absorber off gas, ppmv	80	80	0%	
Contained S in gas to incinerator, lbs/h	1.72	0.66	-62%	
SO_2 emissions from incinerator stack, tpy	15.05	5.78	-62%	SO_2 emissions 62% lower despite 2X capacity

sulfur from undegassed sulfur is more corrosive and friable. Overall, the storage, loading, transportation and unloading of undegassed sulfur pose serious risks along the long sulfur supply chain.

Process description

The D'GAASS Process (Figure 4) offered by Devco in partnership with Fluor accomplishes the removal of H_2S and polysulfides (H_2S_x) from liquid sulfur outside of the sulfur pit in a pressurised vertical vessel. The undegassed sulfur is pumped from the sulfur rundown collection pit/tank to the vessel where it is intimately contacted with pressurised process air counter currently across special fixed column internals. The contactor vessel may be located at any convenient location between the sulfur pit and forming/loading. Undegassed sulfur and process air are the only feeds to the degassing contactor. For existing SRUs, the sulfur rundown pit/tank acts as the degassing unit feed tank. No changes other than the installation of new sulfur feed pumps are required to an existing sulfur pit.

The D'GAASS process removes H_2S and H_2S_x through two mechanisms, oxidising some of the H_2S and H_2S_x to sulfur, and stripping the balance of the H_2S from the sulfur. The H_2S content is reduced to less than 10 ppmw without addition of a chemical catalyst to the sulfur feed. Further, operation at elevated pressure and a controlled temperature accelerates the oxidation of H_2S and H_2S_x to sulfur and SO_2. The degassed sulfur can be sent to sulfur storage, sulfur forming, or directly to loading without additional pumping.

The overhead vapour stream from the contactor vessel, which is pressurised air with low concentrations of H_2S, SO_2, and sulfur vapour, can be sent to the SRU thermal stage or tail gas unit burner thus eliminating the degassing unit as an SO_2 emission source.

Other key D'GAASS process advantages include:

- Easy to retrofit to an existing SRU.
- Low capital investment and operating cost.
- Simple operation and low maintenance.
- Very small footprint.
- Better sulfur quality compared to degassing processes that use catalysts.

These features have contributed to establishing D'GAASS as the leading technology for the degassing of liquid sulfur with over 90 licensed units and total capacity of over 60 000 long tpd (LTPD).

Sulfur forming technology

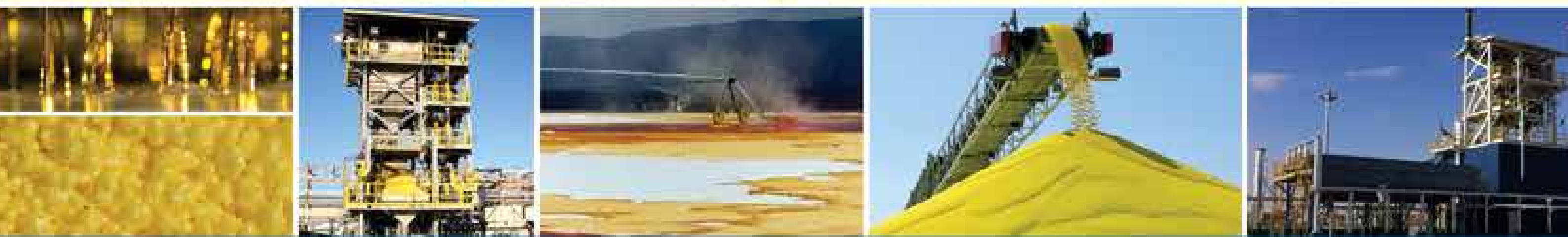
Sulfur is transported long distances from where it is produced as a byproduct to where it is used for the production mainly of sulfuric acid and downstream to fertilisers. For example, China, which is the world's largest importer of sulfur, counts among its suppliers Canada and Saudi Arabia over 6000 and 4000 miles distant respectively. Conveying sulfur for this and even for much more moderate distances requires that the liquid sulfur produced in the SRU be converted to a solid form for safe and cost effective transport. Highlights of the vast global sulfur trade are illustrated in Figure 5.

Devco transforms liquid sulfur into an optimal solid form using the Devco II forming technology (Figure 6), which is one of the most economic, reliable and safe sulfur forming technologies in the world today with 25 plants globally. Some of the largest operating facilities in the world today use Devco's technology including Jubail in KSA (10 500 tpd) and Puguang in China (8640 tpd). Devco's sister company River Consulting specialises in storage and materials handling projects with experience in over 55 countries. With experience in the conveying, storing, loading and unloading of sulfur, fertilisers and grain, River brings valuable capabilities for the long and vital supply chain from an energy byproduct to food.

Process description

Liquid sulfur is fed through heated piping to the top of the prilling tower and distributed on to forming trays mounted above a sulfur forming tank filled with water. The trays are designed with a predetermined number of holes of a specific diameter making up the floor of the trays, through which the feedstock flows in continuous fine streams into the water below. The trays have sidewalls and the depth of the feedstock in the tray creates a hydraulic head, which dictates the rate at which prills are produced.

As the feedstock flowing through the trays falls into the water in the forming tank small prills are formed with the outer surface forming a crust as it quickly solidifies in the water. As the prills drop through the water and are cooled, they are annealed into hard and



Lowest Capital Cost

Proven Marketability

Lowest Operation, Utility and Maintenance Cost

Highest Operational Reliability

Safety is Vital

Smallest Footprint

HOUSTON INTERESTS

Devco Process Heaters | Devco | RIVER CONSULTING | S & R Technical Services

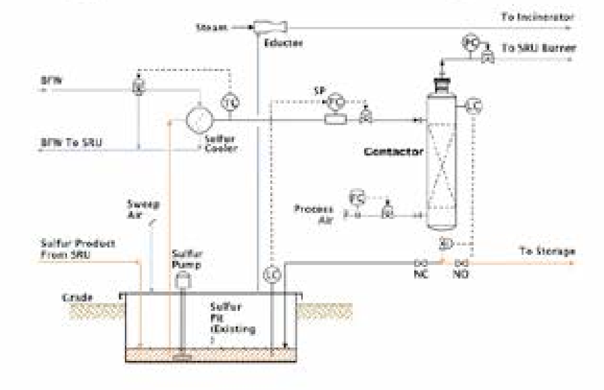


Figure 4. Typical D'GAASS flow diagram.

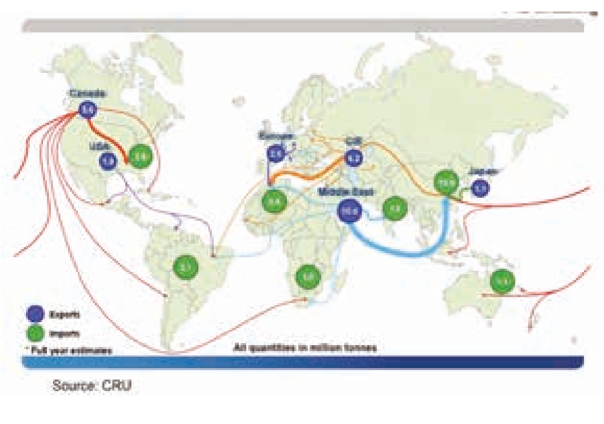


Figure 5. Key sulfur trade routes (>50% of sulfur produced).

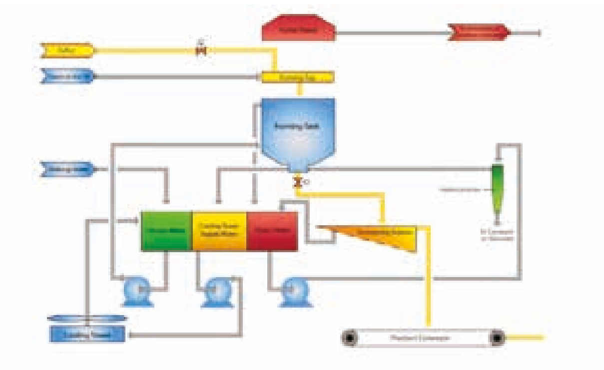


Figure 6. Devco II flow diagram.

smooth surfaced prills producing a premium grade product (GB/T 2449-2006 China National Standard, sulfur for Iindustrial use) by the time they reach the conical bottom of the forming tank. Water flow in the forming tank is countercurrent to the descending droplets, allowing cooler water entering the tank to slowly anneal the prills, which is critical to the formation of hard surfaced prills, making them more resistant to abrasion and crushing in future handling. The water level is maintained by overflow weirs. The formed prills collect in the conical bottom of the forming tank where the level of prills is maintained by a level control valve located at the discharge of the forming tank

Prills exiting in the forming tank are accompanied by some water, which is separated by the dewatering screens to produce a moisture enhanced product. Prills flow from the dewatering screens onto a product belt conveyor that transports them to storage.

The water side of the process includes two loops for the clarification and cooling of the process water. The first loop pumps warm water from the tank that collects the water from the dewatering screens and the overflow weirs to hydrocylones where the sulfur fines are removed before the water flows to a clarified water tank. In the second loop water from the clarified water tank is pumped to a cooling water tower and from there to the clean cool water tank where it is now ready for reuse. This clean cool water is then pumped back to the forming tank with makeup water to compensate for the water in the formed sulfur product and evaporation losses.

Operation of Devco's forming unit is free of sulfur dust, but when the hot feedstock is distributed on the forming trays, any gases inherent in the feedstock will be partially released along with a small quantity of sulfur vapour. These gases are collected by an enclosed granulated unit fume hood fitted over the distribution system on the top of the forming tank and discharged by a fume blower to atmosphere.

Key advantages of the Devco II forming process include:

- Lowest capital cost among all forming technologies. Also, very good economics of scale as 2 – 6 trains of alternate technologies are required to match the capacity of a 2000+ tpd Devco system.
- Lowest operation, utility and maintenance cost because of gravity driven process flow and least number of moving parts.
- Safest technology in the industry due to optimal moisture content leading to no dust or fires during conveying, storage, loading and unloading in any climate. More information is provided below on this vital feature.
- Proven marketability with 30+ years of operation and product that meets the specification of the world's largest sulfur market.
- Smallest footprint.

Optimal moisture content in formed sulfur

A key distinguishing feature of Devco's prilling process over pastillation and granulation based forming technologies is the moisture content in the formed sulfur. The Devco II formed process produces a formed product with an optimal moisture content of 1.5 - 2 % as opposed to a dry product produced by the other technologies. This leads to a product that is extremely safe for conveying, storage, loading, transport and unloading without the inherent risks of fire and explosions that occur due to sulfur dust from dry sulfur processes across the long supply chain. Figure 7 shows a Devco II plant which has been operating for decades in one of the most stringent emission controlled regions of the world.

This section dispels some of the myths and concerns about the Devco product versus dry formed sulfur from pastillation and granulation processes so as to provide end users as well as EPCs the benefit of considering all technologies when evaluating their forming options.

Dry sulfur is not really dry

Alternate technologies produce a 'dry' product but since this product poses a very big safety risk because of the sulfur dust generated, the sulfur formed by these technologies is routinely doused with water/dust suppressant at various stages of conveying, storage and loading. The irony is that this product can end up with 3 - 5% moisture by the time it is loaded with the attendant problems of truck, rail and ship corrosion. The Devco product on the other hand is dry to the touch while still generating virtually no dust.

In instances where the seller has not watered the 'dry' product there are very often complaints from the end user because of dust and risks of fire at the unloading and ultimate end use site. There are instances of customers refusing to accept 'dry' sulfur because of the hazards involved.

Marketability

Today, in excess of 5 million tpy of sulfur is formed and marketed all over the world using the Devco II forming technology without any problem whatsoever. The optimal moisture content is actually a virtue because of the safe atmosphere for operators and safe transport.

Devco units operate or are in the process of being commissioned in most of the dominant and emerging sulfur producing regions of the world including the Middle East, North America, China and Central Asia.

Some very important and growing markets that are particularly relevant such as China have developed their own standards, which incorporate higher moisture content to ensure safety. In fact, Devco's second largest plant (8640 tpd) is in China.

Sulfuric acid production represents the largest market for sulfur and typically most of the producers allow for 2 - 3% moisture content in their sulfur melting operations. So the moisture content difference between the various forming processes is a non-issue from an operational perspective.

Over the next five years recovered sulfur production is expected to increase by approximately 25%. Large new projects that will each generate 1 – 3 million tpy of sulfur are currently under various stages of development in the Middle East and Central Asia. As the power shifts towards the buyer, there will be an increased demand for premium safe product as produced by the Devco technology and 'dry' product that is more dangerous to handle will be the one that will be more difficult to market.

Figure 7. Devco II plant, Long Beach, California, USA.

Conclusion

A significant sulfur surplus is expected in the coming years. As a buyer's market emerges for sulfur it will be all the more important for sulfur producers to adopt technologies for new and retrofit projects that are as cost effective, safe and reliable as possible and that produce a final product with the desirable attributes for the marketplace.