

# Liquid redox enhances Claus process

Claus units can easily achieve sulphur recovery efficiencies exceeding 99.9+% by employing a liquid redox system such as LO-CAT as a tail gas treating unit. The significantly lower capital cost of this combination compared to conventional amine-based tail gas units offsets its higher operating costs. Further benefits include reduced sensitivity of the Claus unit to changes in feed gas composition and flow rate and excellent turndown capability.

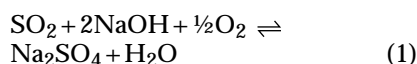
**Gary J. Nagl** of USFilter Gas Technology Products discusses the merits of this process combination.

Throughout the years, the Claus process has undergone a continuous evolution in attempts to increase the sulphur recovery efficiency of the process. In the 1930s, a thermal stage was added to the two catalytic stages, which increased the recovery efficiency from 95% to approximately 97%. In the 1970s, the SCOT process was introduced which added hydrogenation/hydrolysis plus amine separation to treat the tail gas from the Claus process. In 1988, SuperClaus was introduced, which added a selective oxidation reactor to the end of the Claus process, increasing the efficiency to approximately 99%. And just recently, EuroClaus<sup>1</sup> was introduced, which replaced the second Claus reactor in the SuperClaus process with a selective hydrogenation catalyst increasing the efficiency to 99.5%.

It is obvious that the trend is to achieve higher and higher sulphur recovery efficiencies. It is anticipated that in the near future Claus units installed in developed nations will required sulphur recovery efficiencies of 99.5% or better. Coupling a Claus unit and a liquid redox process, such as the LO-CAT<sup>®</sup> either directly or indirectly in combination with a hydrogenation/hydrolysis reactor, however, can reliably achieve 99.9+% sulphur recovery.

## Direct tail gas treatment

When considering liquid redox to treat Claus tail gas without the inclusion of a hydrogenation/hydrolysis reactor, the amount of SO<sub>2</sub> in the tail gas is an important operating parameter. Since liquid redox units operate at alkaline pHs in the range of 8 to 9, any SO<sub>2</sub> in the tail gas will be easily absorbed, and form sulphates in accordance with reaction 1:

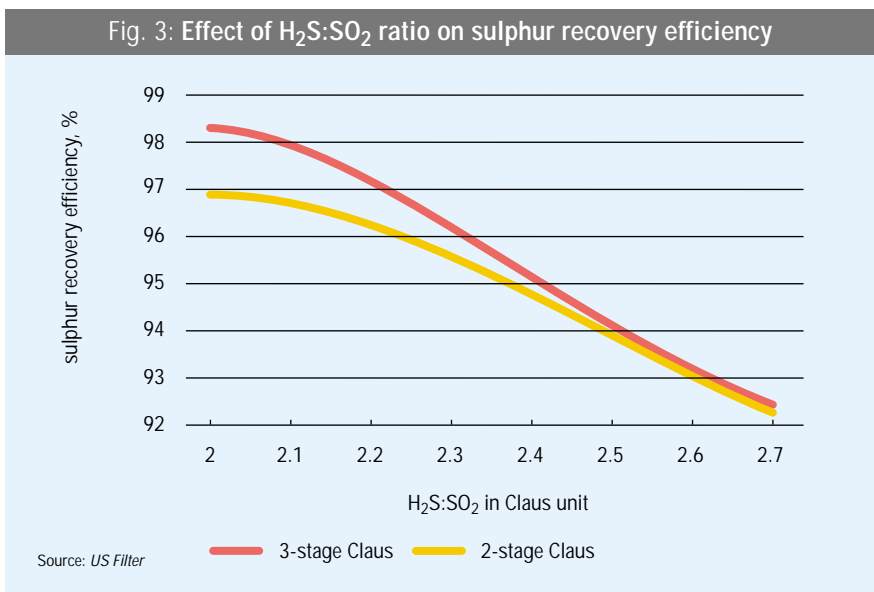
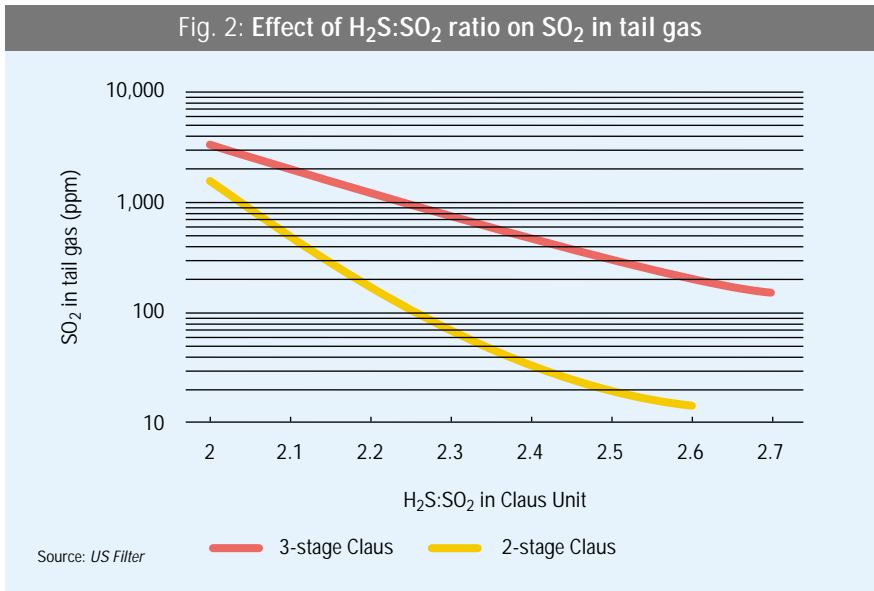
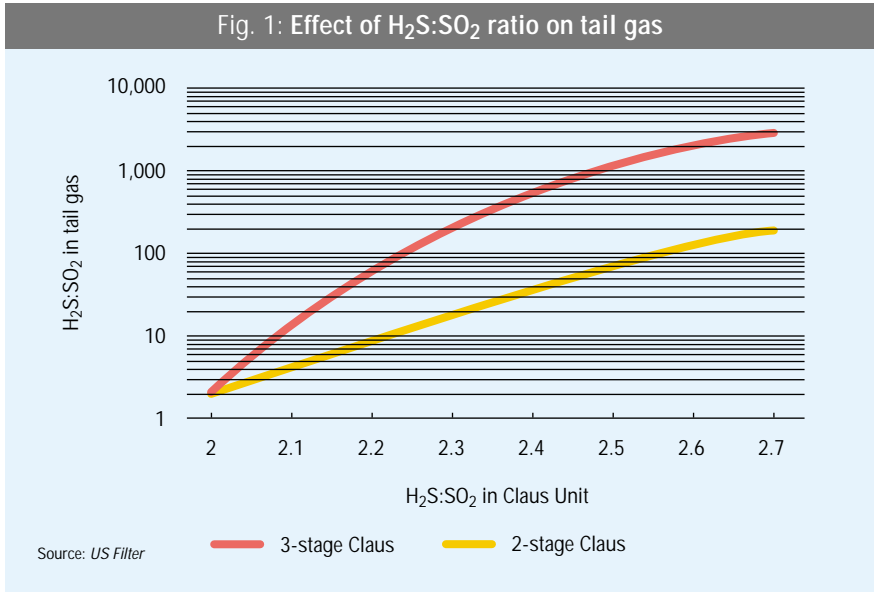


It is important to note that SO<sub>2</sub> does not interfere with the liquid redox chemistry and consequently does not

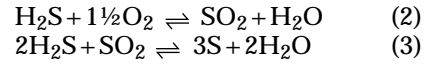
affect the H<sub>2</sub>S removal efficiency of the process. However, reaction 1 does affect the operating cost of the process in two ways. First, two moles of caustic are consumed for each mole of SO<sub>2</sub> absorbed, which increases the operating cost of the unit. Secondly, the resultant sulphate product accumulates in the liquid redox solution, and eventually a blowdown is required resulting in loss of valuable catalyst solution. Replacing lost solution adds further to operating costs. Consequently, if this process configuration is to be employed, it is advantageous to minimise the formation of SO<sub>2</sub> in the Claus unit.



The first LO-CAT unit to treat Claus tail gas was recently installed at the Western Gas/Anadorko Bethel plant in Texas, USA.



The SO<sub>2</sub> formation rate can be minimised by operating the Claus unit with sub-stoichiometric quantities of oxygen, thus increasing the H<sub>2</sub>S:SO<sub>2</sub> ratio in the unit. The effect of this mode of operation can be seen by analysing the Claus reactions.



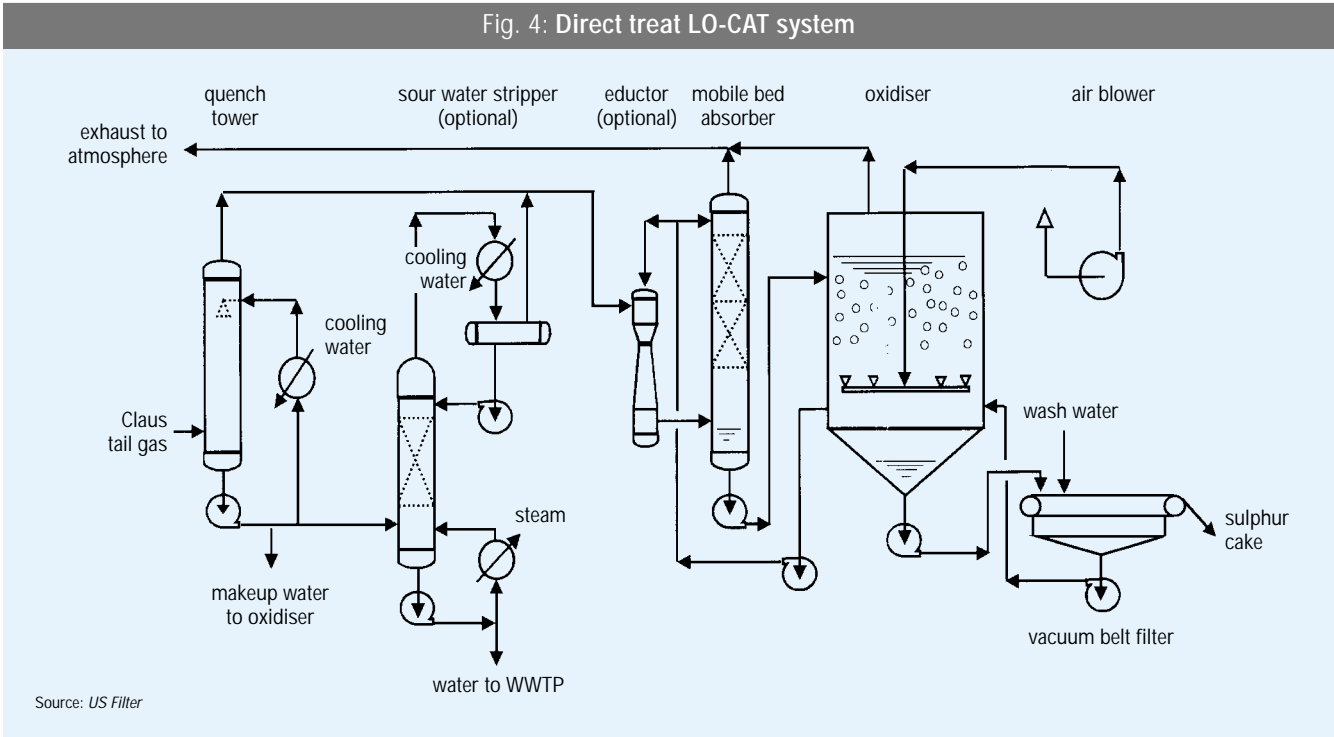
The conventional mode of operation for a Claus unit is to convert one third of the H<sub>2</sub>S to SO<sub>2</sub>, which then reacts with the remaining H<sub>2</sub>S to form elemental sulphur. This is accomplished by carefully controlling the quantity of oxygen entering the system. Due to equilibrium limitations, some of the SO<sub>2</sub> leaves the system with the tail gas.

If the unit is operated in a manner such that there is insufficient oxygen to complete reaction 2, then there will be insufficient SO<sub>2</sub> produced to complete reaction 3, and the H<sub>2</sub>S removal efficiency will be reduced. However, the amount of unreacted SO<sub>2</sub> in the tail gas will also decrease. The effects<sup>2</sup> of H<sub>2</sub>S:SO<sub>2</sub> ratio on the H<sub>2</sub>S and SO<sub>2</sub> contents in the tail gas and the overall removal efficiency are illustrated in *Figs 1-3*.

A flow diagram of a typical LO-CAT liquid redox unit for treating Claus tail gas directly is shown in *Fig. 4*. Since the liquid redox system is aqueous-based, elevated temperatures will cause water balance problems; consequently, the tail gas is first passed through a cooler where the gas temperature is reduced from approximately 135°C to 50°C. The cooled gas then enters a knockout pot where any condensate is separated. Depending on the amount of condensate and sulphur tonnage, this sour condensate may be employed as make-up water to the liquid redox process. If it cannot all be used as make-up water, the remaining sour water will need to be processed through a sour water stripper with the sour gas being directed back to the liquid redox unit.

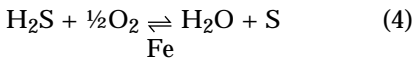
For direct treatment of Claus tail gas, the LO-CAT process would employ a proprietary Mobile Bed Absorber (MBA) because of its low, inherent pressure drop (approximately 500 mm of WC). For contacting media, the MBA uses hollow, ping-pong-like spheres which, when fluidised, are

Fig. 4: Direct treat LO-CAT system



Source: US Filter

self-cleaning. Within the MBA, the H<sub>2</sub>S and the SO<sub>2</sub> are absorbed into the circulating solution, and the sulphide ions are converted to elemental sulphur in accordance with the Reaction 4 while the SO<sub>2</sub> is converted to sulphate as indicated by reaction 1.



As indicated in Reaction 4, the reaction is catalysed by a proprietary chelated-iron catalyst.

MBA's are normally designed to reduce the H<sub>2</sub>S concentration in a gas to approximately 10 ppm. For tail gas applications with H<sub>2</sub>S:SO<sub>2</sub> ratios of greater than 2.0, this would result in overall removal efficiencies of 99.99%. Even if the ratio were maintained at 2.0, the removal efficiency would be 99.7%; however, the caustic consumption would be much higher as indicated in Figure 3.

The solution exiting the MBA is directed to an Oxidiser where air is injected to regenerate the iron catalyst. If there is insufficient pressure available for moving the tail gas through the MBA, a blower can be supplied or an eductor may be installed as shown in Fig. 4.

LO-CAT systems are designed with very ample liquid inventories. Although this increases the capital

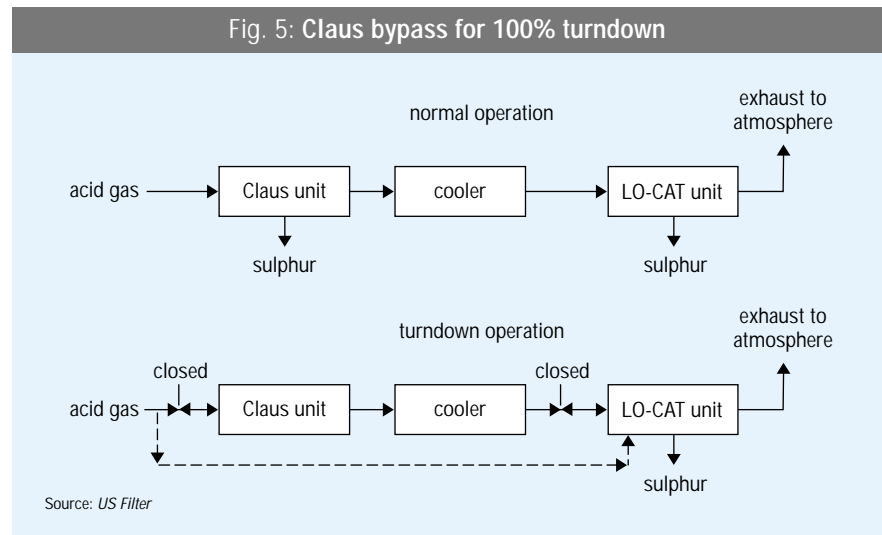
cost slightly, there is sufficient capacitance in these systems to render them very insensitive to sudden changes in feed conditions. Thus, fluctuations in the H<sub>2</sub>S:SO<sub>2</sub> ratio in the Claus unit will essentially have no effect on the overall removal efficiencies of the system as long as the Claus unit continues to run. In the event that the Claus unit is unable to operate due to turn-down requirements beyond its capabilities, the system can be designed to bypass the Claus unit entirely and route the acid gas directly into the LO-CAT unit. This mode of operation (Fig. 5) will still yield H<sub>2</sub>S

removal efficiencies of 99.99+%. The versatility of the liquid redox system will ensure that the overall system will achieve 99.9+% removal efficiencies at all times. This inherent feature of the system is well accepted by regulators. In addition, the effluent from the liquid redox unit will not require incineration since it will only contain a very small amount of H<sub>2</sub>S and essentially no SO<sub>2</sub>.

### Indirect tail gas treating

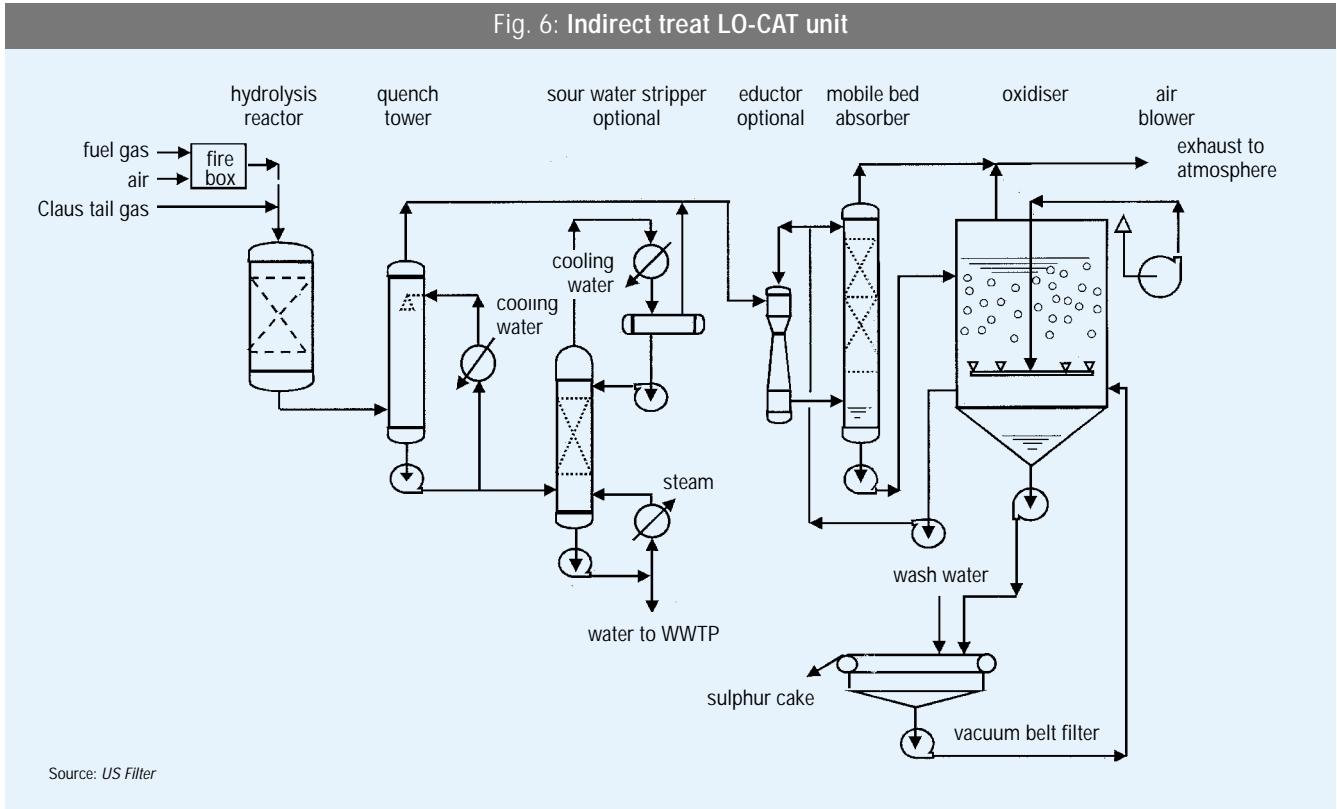
In this processing scheme (Fig. 6) all sulphur compounds in a Claus tail gas

Fig. 5: Claus bypass for 100% turndown

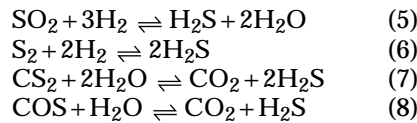


Source: US Filter

Fig. 6: Indirect treat LO-CAT unit

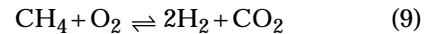


are converted to H<sub>2</sub>S by passing the tail gas through a hydrogenation/hydrolysis, catalytic reactor at elevated temperatures. Reactions 5 and 6 (hydrogenation) and reactions 7 and 8 (hydrolysis) represent the major reactions, which occur in the reactor.



In this processing scheme, a fuel gas is subjected to partial oxidation, which not only generates sufficient

heat to raise the tail gas to reaction temperatures but also generates sufficient hydrogen (reaction 9 shown below) to satisfy the requirement of reactions 5 and 6.

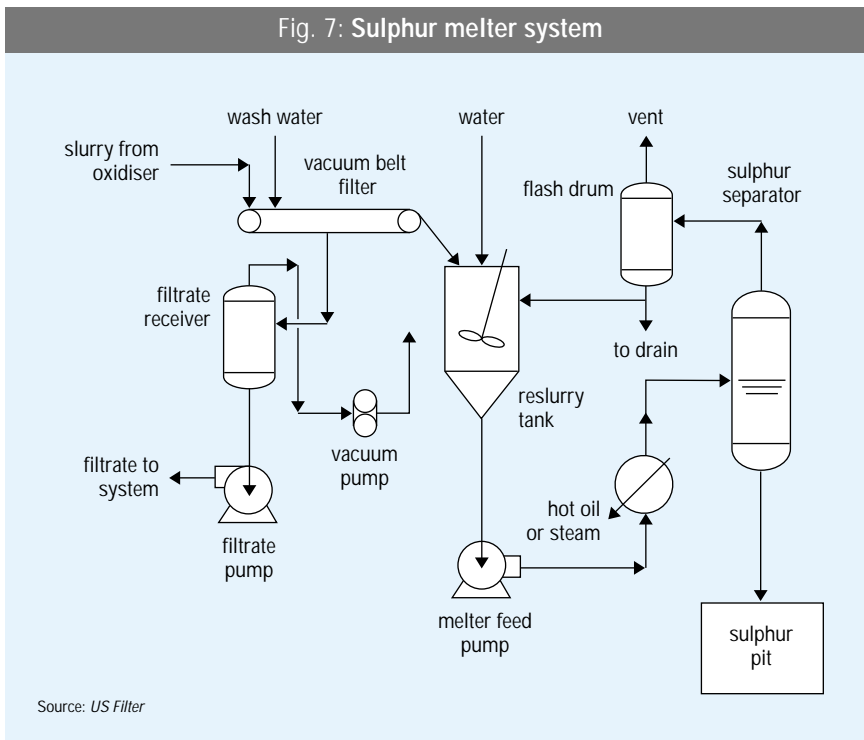


After passing through the reactor, the effluent gas must be cooled to approximately 50°C. This can be accomplished by employing a direct contact condenser as shown in *Figure 6*. Alternatively, an indirect condenser can be employed.

In either case, sour cooling water or sour condensate will be generated. Again a portion of the sour condensate or water may be used as makeup water for the liquid redox unit; however, some of it will need to be sent to a sour water stripper with the vapor being routed back to the liquid redox unit.

This processing scheme will be even more forgiving to changes in the operations of the upstream Claus unit, since the hydrogenation/hydrolysis unit will act to muffle any compositional changes from the Claus unit. Consequently, the amount of SO<sub>2</sub> entering the liquid redox unit will remain fairly constant, and the operating cost of the system will remain constant.

Fig. 7: Sulphur melter system



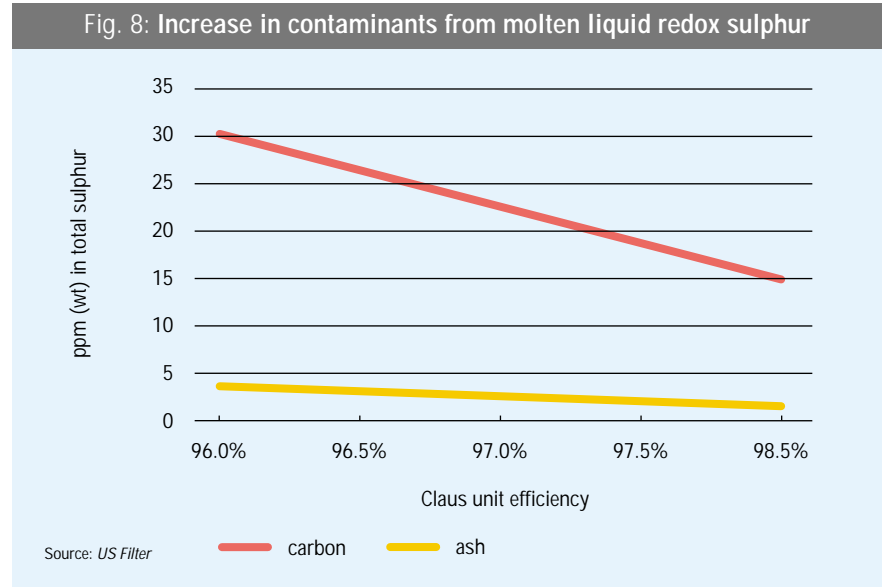
## Sulphur disposal

Because of its poor quality, sulphur produced from liquid redox processes has a bad reputation, which in some cases is well earned. However, due to the relatively small quantities of sulphur produced in liquid redox installations, most liquid redox sulphur has been either landfilled or disposed of as solid, agricultural sulphur; hence, not a lot of effort has been exerted to improve its quality. However, great progress has been made in improving the quality of sulphur produced in LO-CAT units.<sup>3</sup>

Sulphur is produced as a solid in a liquid redox unit. Since the reactions are not gas phase, there is no dissolved H<sub>2</sub>S in liquid redox sulphur; thus sulphur degassing is never required. The sulphur is normally filtered and washed to produce a filter cake, which is 65% to 85% sulphur depending on the type of filter used, with the remainder being water and dissolved salts. It is not possible to simply dump this cake into the Claus sulphur pit, since there is insufficient heat in the pit to evaporate the water and to melt the sulphur. And even if the moisture is removed prior to dumping the sulphur in the pit, the solid particles have a tendency to float on top of the molten sulphur thus making heat transfer and consequently melting very difficult. Due to these problems, the sulphur from the liquid redox system must be disposed of as a solid<sup>3</sup> or melted prior to being introduced into the sulphur pit.

Melting of liquid redox sulphur can be accomplished in either batch type melters or continuous melters. As a rule of thumb, sulphur production rates of greater than 5 tons per day (TPD) warrant continuous melting while rates less than 5 TPD generally require batch melting due to economics. However, continuous melters can be installed on any LO-CAT system regardless of size. A typical melter system for a LO-CAT system is shown in Fig. 7.

The change in quality of the Claus sulphur due to the addition of molten, liquid redox sulphur will be as indicated in Figure 8. As a matter of comparison, specifications for sulphuric acid plant grade sulphur are less than 1000 ppm carbon and less than 250

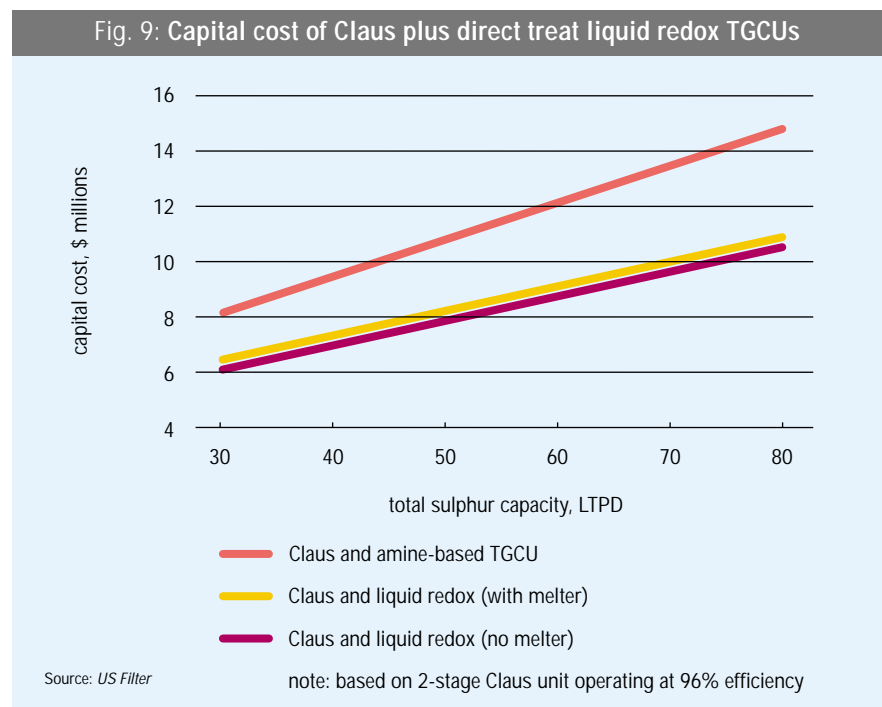


ppm ash. This suggests that adding molten, liquid redox sulphur to a Claus sulphur pit can be done without degrading the Claus sulphur to any great degree. However, the overall quality of the sulphur mix can be further improved by processing the liquid redox sulphur through a diatomaceous earth filter prior to directing it to the sulphur pit.

## Costs

Budgetary capital costs of direct-treat, liquid redox, tail gas units complete with coolers and sour water strippers

are contained in Fig. 9. For comparison purposes, the capital costs<sup>4</sup> of amine-based, tail gas cleanup units (TGCU) are also contained in Fig. 9. It is obvious that considerable capital cost savings can be realized by utilizing liquid redox systems as tail gas treating units. With regard to operating costs, the liquid redox system will increase the operating cost of the Claus unit by approximately \$14 per long ton of sulphur entering the Claus unit. For an amine-based TGCU this figure will be approximately \$8 per long ton. Consequently, each application needs to be analysed to see if the



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savings in operating cost of the amine-based system justifies the higher capital cost.

### Field experience

The direct contact, tail gas treating scheme described above has never been demonstrated commercially; however, the two processes comprising the scheme are commercially proven. The HCR<sup>2</sup> process, which is a Claus unit operating with sub-stoichiometric oxygen, is well proven while the LO-CAT liquid redox process has been in commercial operation for over 20 years with 150 licensed units. In addition, approximately 50 of these units are treating acid gas streams (CO<sub>2</sub> and H<sub>2</sub>S). Consequently, there is no reason to believe that the proposed arrangement would not operate satisfactorily.

Variations of the indirect, tail gas treating scheme employing an intermediate hydrogenation/hydrolysis step have been in commercial operation since the early 1970s when the Beavon Sulphur Removal Process was introduced. This process consisted of a hydrogenation/hydrolysis reactor followed by a Stretford unit. Approximately 30 of these units were installed. The process fell out of favour due to the potential toxicity problem with the vanadium catalyst employed in the Stretford process. Due to this problem, iron-based, liquid redox processes such as the LO-CAT process has since replaced the Stretford process.

Recently, Western Gas installed the first LO-CAT unit in a Claus tail gas application at their natural gas production field in Palestine, Texas, USA. Initially, the LO-CAT unit was treating amine acid gas; however, as the processing and the sulphur capacities of the facility increased, a 2-stage Claus unit and a hydrogenation/hydrolysis reactor were installed, and the LO-CAT unit treated the reactor effluent. This system is yielding over 99.9+% sulphur removal.

### Conclusions

Claus units can easily achieve hydrogen sulfide removal efficiencies exceeding 99.9+% by employing a liquid redox system such as LO-CAT as a tail gas treating unit. The combination of Claus and liquid redox has a significantly lower capital cost than conventional amine-based tail gas units which offsets its higher operating costs. In addition, the liquid redox unit will significantly reduce the inherent sensitivity of the Claus unit to changes in feed gas composition and flow rate. And if designed properly, the turndown capability of a system employing a Claus unit with a LO-CAT tail gas unit can be approximately 100%. **S**

### References

1. "Jacobs Comprimo Introduces EuroClaus", *Sulphur* No. 270, p. 65 (Sep/Oct 2000).
2. Villa, Sergio and Ramshaw, D.E., "The HCR Modified Claus Process Combined with LO-CAT II," **Sulphur '91 Conference**, New Orleans, LA (Nov 1991).
3. Nagl, G., "Emerging Markets for Liquid Redox Sulphur," **Sulphur '97 Conference**, Vienna, Austria (Nov 1997).
4. Tannerhill, C., "Budget Estimate Capital Cost Curves for Gas Conditioning and Processing," **GPA Annual Convention**, Atlanta Georgia (Mar 2000).