

ADVANCES IN THE DEVELOPMENT OF TAIL GAS TREATMENT, LIQUID SULFUR DEGASSING AND TAIL GAS INCINERATION

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Summary

Carbon accounting in the USA and elsewhere continues to drive the search for increasingly efficient refining practice. The sulphur plant, arguably the most important system in the refinery, is no exception with current technology relying on processes, which in some cases, were first developed almost 70 years ago. This paper discusses ongoing R and D which aims to lay the basis for improved tail gas processing, liquid sulphur degassing and tail gas incineration. In each case, the overall objective has been to increase the thermal efficiency of the process so lessening carbon emissions as well as achieve 99.9% sulphur recovery.

For tail gas treatment, a scheme is proposed which involves combustion of all sulphur species to SO₂ and adsorption onto a solid material which functions both as the SO₂ adsorbent and a Claus catalyst. A two bed system is envisaged in which the SO₂-laden bed would be regenerated with process gas. In principle, this approach allows >99.9 % sulphur recovery as well as increased thermal efficiency.

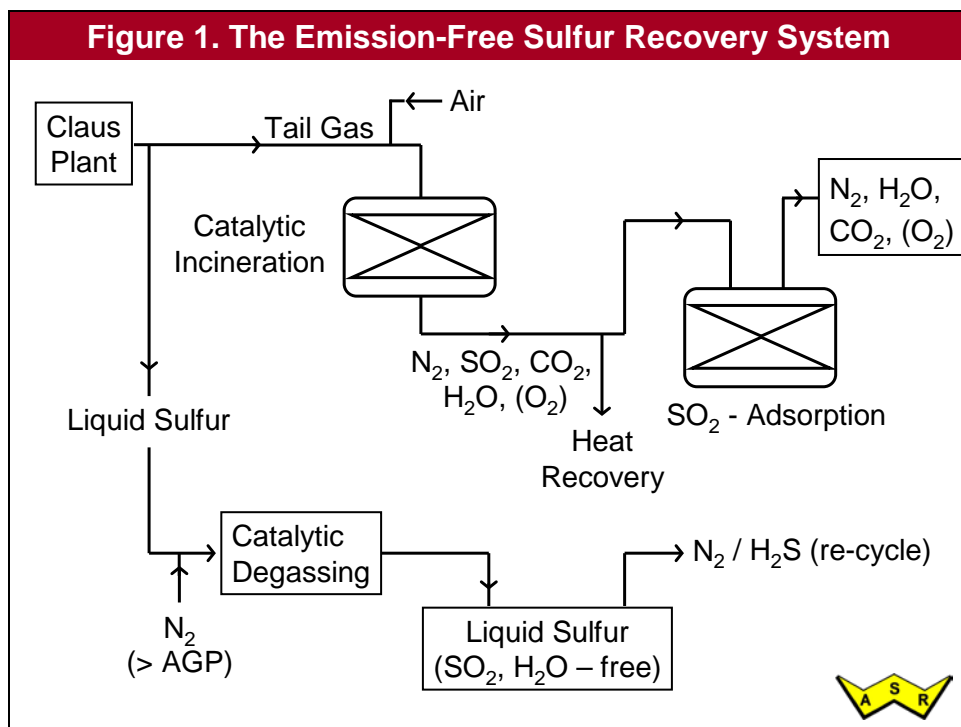
Catalytic decomposition of H₂S_x in liquid sulphur using alumina based materials and an inert gas sparge forms the basis of the degassing developments. The use of an inert gas such as N₂ to remove the H₂S from the sulphur is an important feature as the absence of O₂ will produce dry liquid sulphur free from SO₂. Not only would this degassing methodology produce non-corrosive liquid sulphur, but, also, it should simplify recompression of the off gas back into the plant so eliminating emissions from the degassing unit.

Currently thermal incineration of tail gas requires large quantities of fuel gas to reach temperatures that can convert all species to oxidized forms. CO is particularly intransigent. The application of catalytic incineration has been limited because although commercial catalysts convert all H₂S to SO₂, they do not convert CO or H₂. In this paper, we report novel catalysts which fully oxidize all Claus tail gas species at the anticipated adiabatic temperature for a typical tail gas composition.

Introduction

This paper discusses three potential technologies that could improve the overall efficiency of sulphur recovery: tail gas treatment (TGT) by SO₂ adsorption onto a porous solid, heterogeneous catalyst liquid sulphur degassing and catalytic tail gas incineration. These projects are at the “laboratory” stage and have now reached the point where pilot scale testing is needed. In all cases, the next step requires cooperation with catalyst

manufacturers to formulate products. Overall, it would appear that these potential technologies offer significant energy savings for sulphur recovery and an overall system which could result in zero-emissions sulphur recovery. As may be seen from Figure 1, the catalytic incinerator is placed upstream of the TGT unit and requires no fuel gas for its operation. All sulphur species are converted to SO₂ and other impurities such as CO and H₂ are fully oxidized yielding CO₂ and H₂O. The TGT then consists of removal of SO₂ from the cooled incinerated gas with periodic regeneration of the adsorption bed. A useful feature of the catalytic degassing system is that it produces dry, SO₂-free liquid sulphur with an off-gas that can be readily returned to the main acid gas stream. The following sections provide a detailed discussion of the laboratory research carried out on these potential technologies.

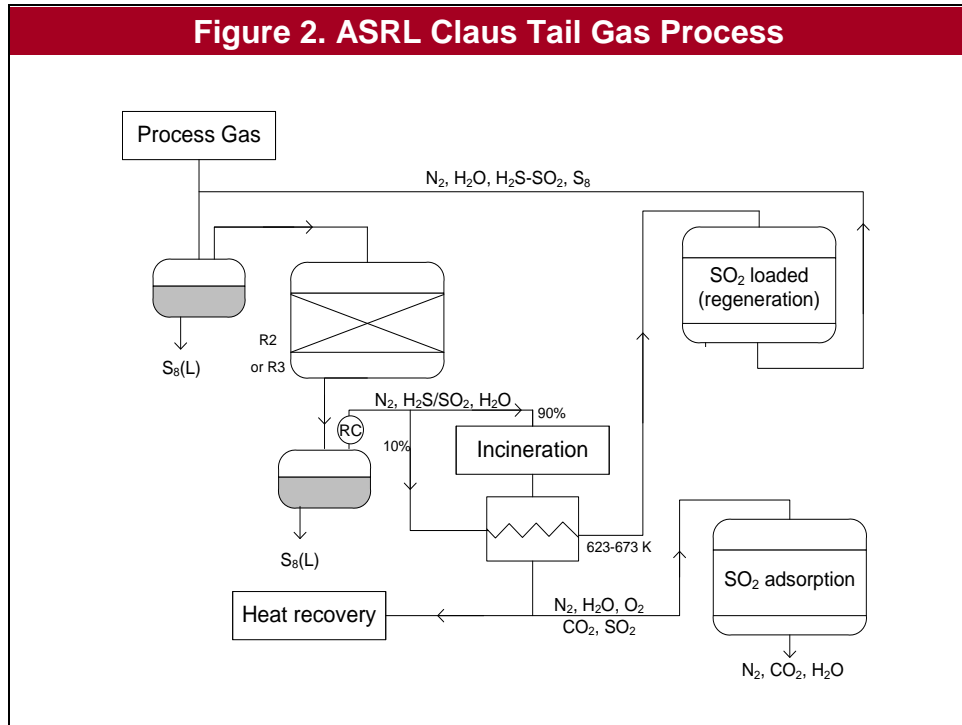


Tail Gas Treatment by SO₂ Adsorption

A classic 2-bed Claus plant can achieve 96 % total sulphur recovery, perhaps 97 % when all units are functioning perfectly, but this total falls well short of the limits set by regulators of the refining and gas processing industry. Amongst existing tail gas treatment processes, only reductive style systems can achieve > 99.9 % total sulphur recovery but this very high figure comes at a cost. In addition to the catalytic reduction unit which transforms all sulphur species to H₂S, a quench unit is required to handle the water-laden gas before the H₂S gas can be captured in a selective amine unit and recycled to the main furnace. This system is expensive to build and operate and, in terms of energy consumption it is said to produce 3 – 4 moles of CO₂ for every mole of SO₂ not emitted to the atmosphere. Other tail gas treatment systems (direct oxidation and sub-

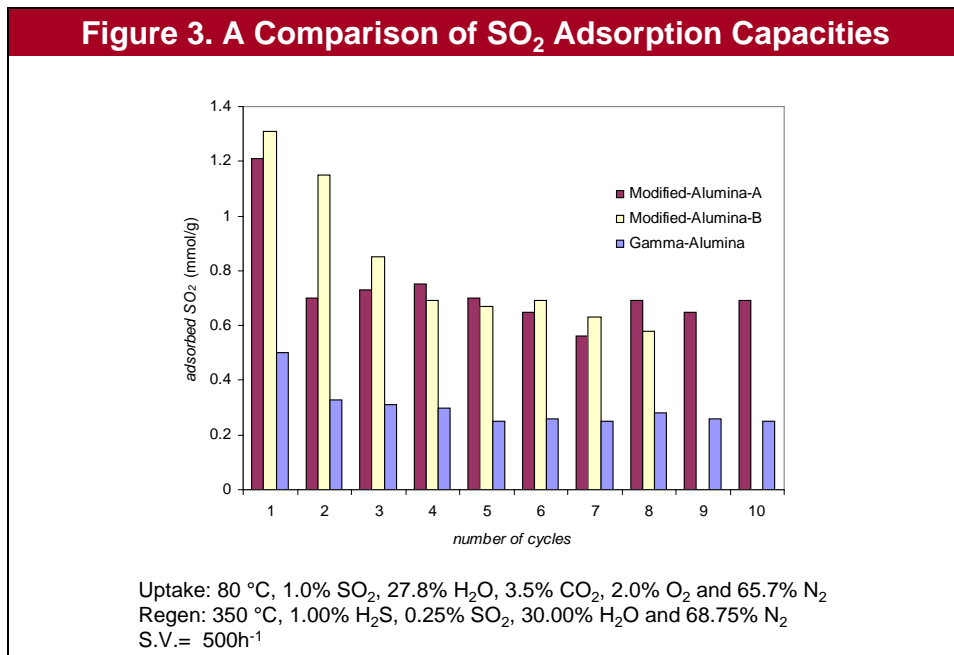
dew point) are able to achieve 99.2 – 99.5 % total sulphur recovery at considerably less cost but these recoveries do not meet all emissions targets.

One of the research objectives in our group has been to examine adsorption of SO_2 onto a solid material which can be regenerated using one of the Claus process gas streams maximizing thermal efficiency for the overall plant. A potential process scheme showing fixed bed operation is shown in Figure 2 although a fluidized bed would further increase thermal efficiency. It is envisaged that the second converter process gas would be incinerated yielding SO_2 as the major sulphur species with heat recovery to bring the incinerated gas to around 120°C . If thermal incineration is employed, it is inevitable that a small amount of SO_3 will be produced during incineration and, because of the high water content of all Claus process streams, the sulphuric acid dew point will be reached as the gas is cooled to 120°C . Thus, the metallurgy will need to be acid resistant for units handling this gas. Quite probably, it will be possible to use catalytic incineration since, as discussed later in this paper, new catalysts for incineration have been developed and it is thought that the advanced catalytic incineration described later will not result in SO_3 formation.



Adsorbents which can remove the SO_2 selectively from the cooled incinerated gas have been identified and shown to work over 10 cycles in laboratory trials (Figure 3). Obviously, such adsorbents must be tested over many more cycles to validate both chemical and physical integrity and will need to be formulated for industrial application. Using flow rate data and the amount of SO_2 produced from the incineration of Claus tail gas from a two converter plant operating at 96% sulphur recovery, it is calculated that the

optimum adsorbent (Figure 3) would allow an uptake cycle of 24 h before breakthrough of SO₂. In the field, an SO₂ detector set to 10 ppmv could be used to initiate bed switching.



The surface chemistry of SO₂ adsorption has been shown to involve physical adsorption of SO₂ as well as formation of thiosulphate and sulphate species (Figure 4). A key feature of this process is the regeneration of the SO₂-laden adsorbent by H₂S using one of the Claus process gas streams. This procedure is necessary as it has been found that alumina-based adsorbents accumulate sulphate-type species which are removed from the adsorbent surface by reduction with H₂S. The presence of H₂S is important as it also consumes any O₂ that remains adsorbed to the catalyst surface (Figure 5). Overall, the SO₂ adsorbent must have the ability to catalyze the variety of reactions shown in Figure 5 as well as act as an SO₂ adsorbent in the regenerated state.

Figure 4. Adsorption of SO₂ onto Alumina – Based Materials

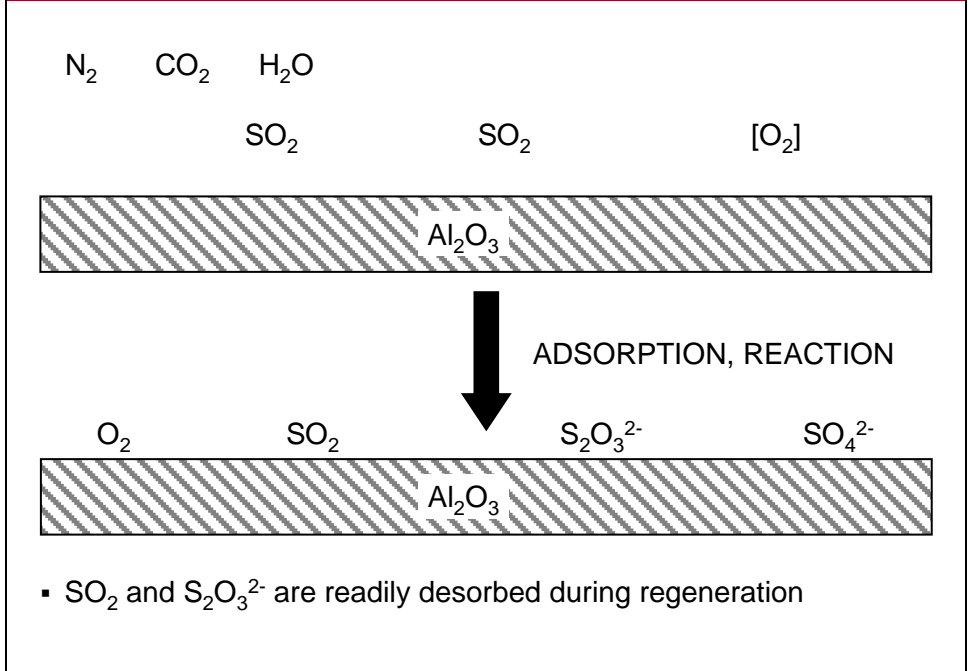
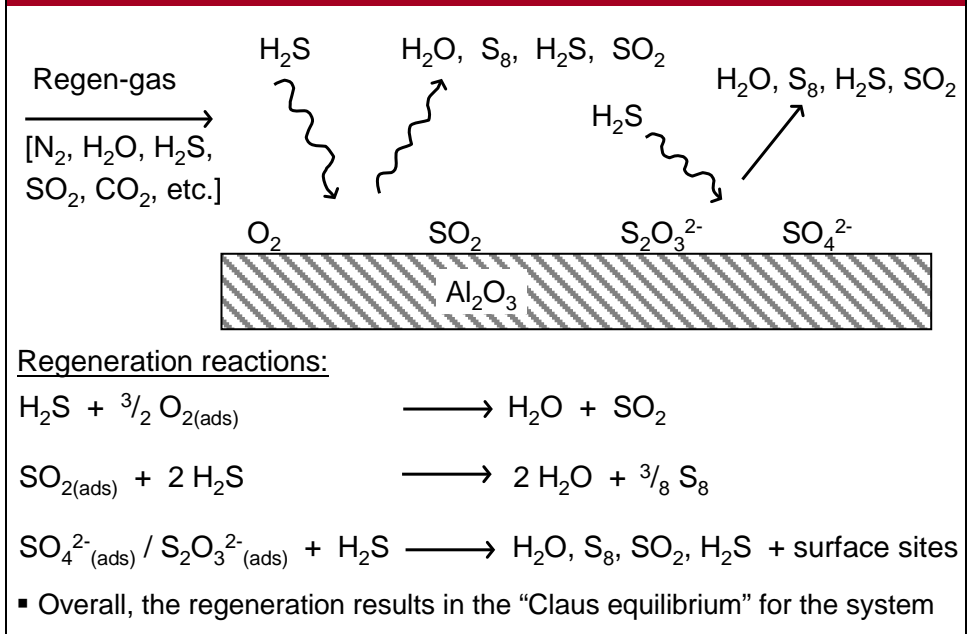
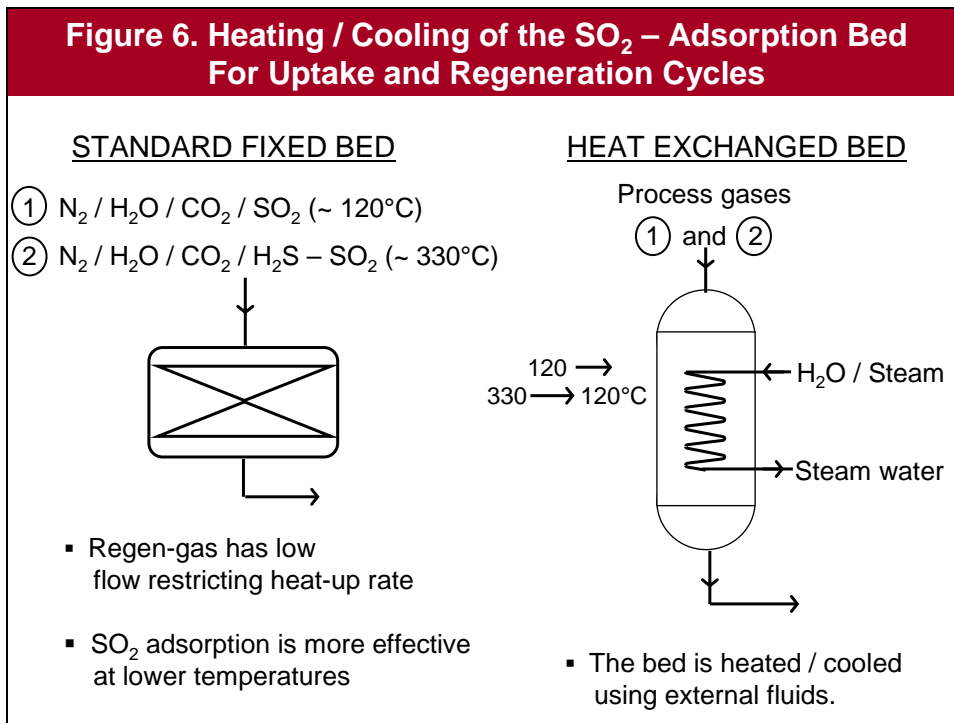


Figure 5. The Chemistry of SO₂ Desorption and Adsorbent Regeneration

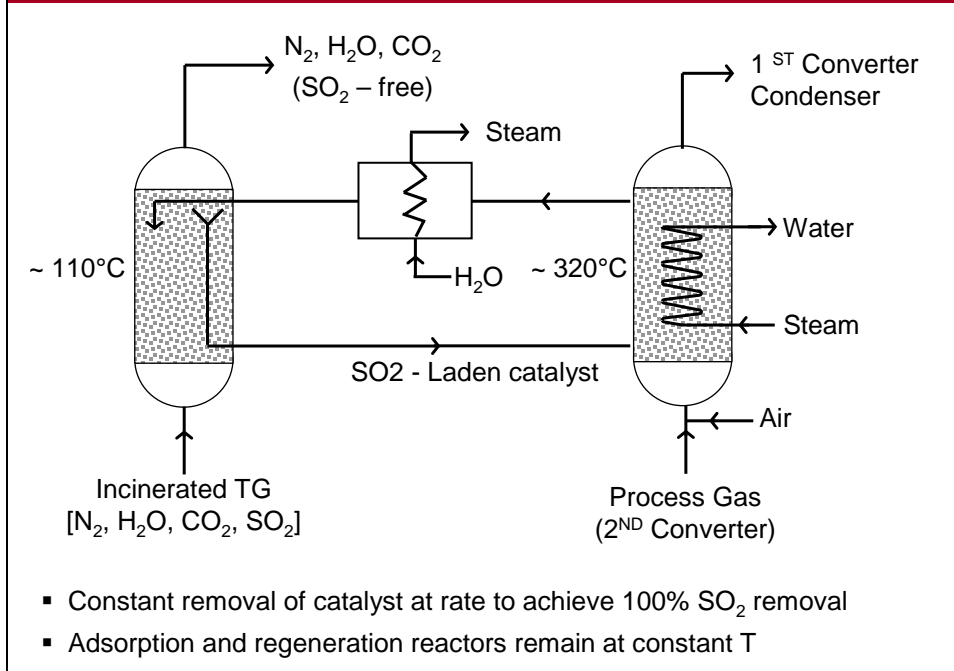


The scheme shown in Figure 2 indicates use of the second converter condenser off-gas for the regeneration. Re-heat of that gas to the regeneration temperature (ca. 320°C) using heat energy from the incineration step should be feasible, but some independent heating may be necessary as the amount of off-gas used is small in comparison to the total tail gas flow, so placing a limit on the rate at which the temperature of the bed undergoing regeneration can be raised. One solution to this problem is to incorporate a heat exchanger in the catalyst bed in order to facilitate both heating and cooling of the bed (Figure 6) (also see later discussion).



Despite the heating – cooling cycle challenge, the overall process has some very interesting features. Firstly, all units use only “gas phase” technology thus avoiding water quench, sour water handling and amine uptake – regeneration cycles of the reductive tail gas treatment processes. Secondly, all major aspects of the TGT involve exothermic processes: incineration, SO₂ adsorption and regeneration with H₂S. This feature presents a significant increase in the thermal efficiency for sulphur recovery coupled to, essentially, a zero emissions process. Lastly, if a fluidized bed system (Figure 7) is incorporated into this approach, yet further increases in thermal efficiency can be envisaged. Studies of fluidized bed systems are underway in our laboratories.

Figure 7. Application of a Fluidized Bed for SO₂ Adsorption

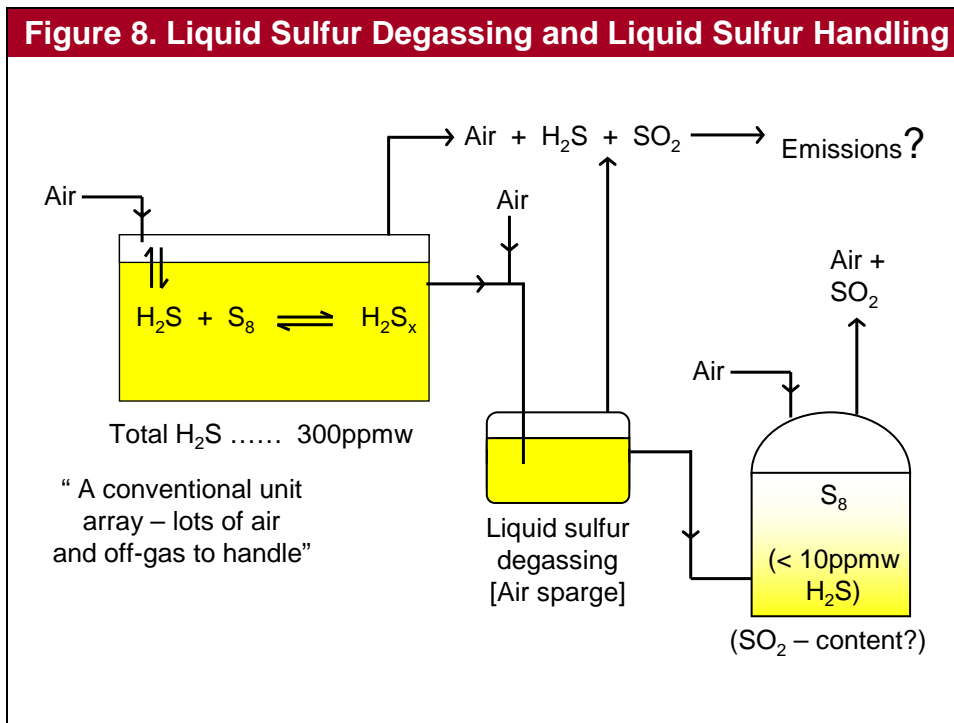


It is useful to consider the regeneration process in more detail, particularly with respect to process control of the overall plant. It is suggested that the Claus furnace and first converter should operate at an H₂S/SO₂ ratio > 2 in order that a reducing atmosphere is available for reduction of the thiosulphate and sulphate species that accumulate on the adsorbent surface. Laboratory studies have shown that simply elevating the temperature of the loaded adsorbent causes loss of the physically adsorbed SO₂ and decomposition of some of the thiosulphate but excess H₂S is required to reduce the surface sulphate. If the regeneration gas ratio was at the optimum value of 2, SO₂ leaving the bed which is recycled to the second converter, would lower the sulphur recovery possible in that unit by reducing the H₂S/SO₂ ratio < 2. Also, the low ratio was cause sulphate to build in the catalyst, possibly impeding the Claus reactions. Thus, operation of the plant at a ratio > 2 provides the conditions necessary for regeneration and, with addition of some SO₂ back to the second converter, a ratio could be attained which would provide decent sulphur production in that unit. A potentially nice feature of a plant operating with an SO₂ TGT system would be that precise ratio control is not required but, placement of the ratio controller after the second condenser set to a value slightly above 2 should result in the overall plant operating at close to maximum sulphur recovery for two converters.

Solid Catalyst Liquid Sulphur Degassing

The potential hazard of handling liquid sulphur from Claus plants has been recognized for many years with strict limits (usually < 10 ppmw) being set for the total residual H₂S allowed in product leaving the plant. The major concern is accumulation of H₂S in the headspace of storage tanks and run down pits to levels which are not only lethal but

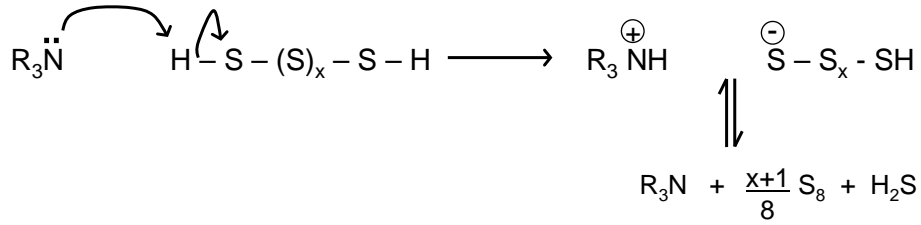
which can also exceed the LEL for H₂S in air. Several degassing technologies have been invented and the various types are in operation in gas plants and refineries World-wide. Most are based on bubbling air through liquid sulphur, using various devices to engender efficient liquid-gas mass transfer (Figure 8). In some technologies, homogeneous or heterogeneous catalysts are used to aid the decomposition of H₂S_x, a chemically combined form of H₂S.



As shown in Figure 9, homogeneous catalysts provide basic sites and these sites aid degassing by abstraction of the proton from H₂S_x which then causes the sulphur chain to decompose to S₈ molecules, releasing H₂S. The alumina catalyst used in the “Amoco” process may also work in the same way providing basic sites to initiate decomposition of the H₂S_x polymer (Figure 9). The use of air in liquid sulphur degassing results in the production of SO₂ by reaction of O₂ with sulphur and/or with H₂S (Figure 10), which in the case of the “Amoco” process can then react with H₂S at the alumina surface (Figure 11). However, as discussed later in this paper, it appears that the dominant function of the alumina is to initiate decomposition of H₂S_x (Figure 9).

Figure 9. Decomposition of H₂S_x

Amine Decomposition



Surface Decomposition

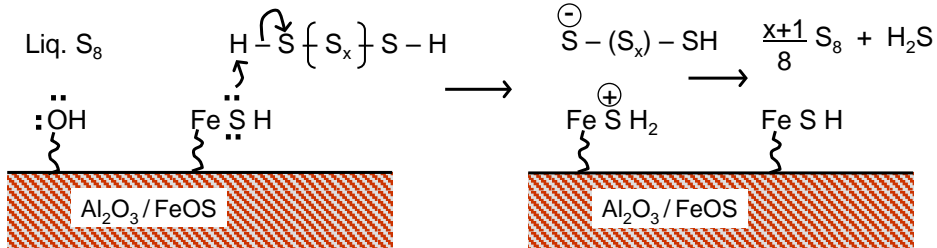
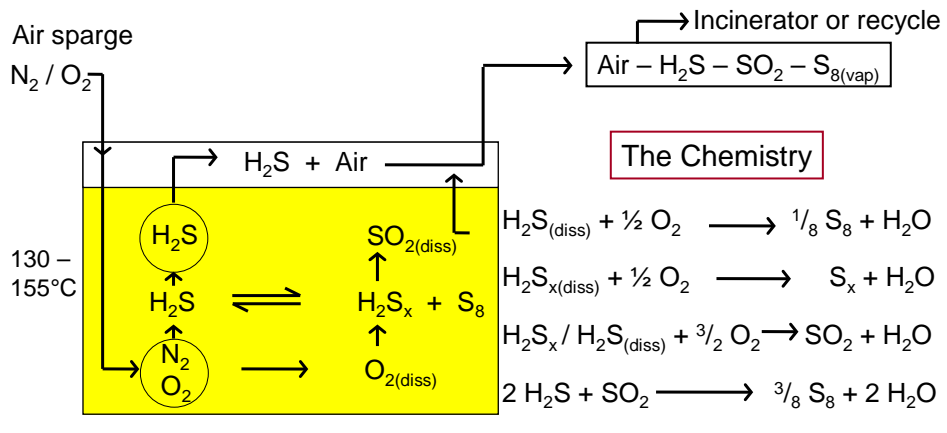


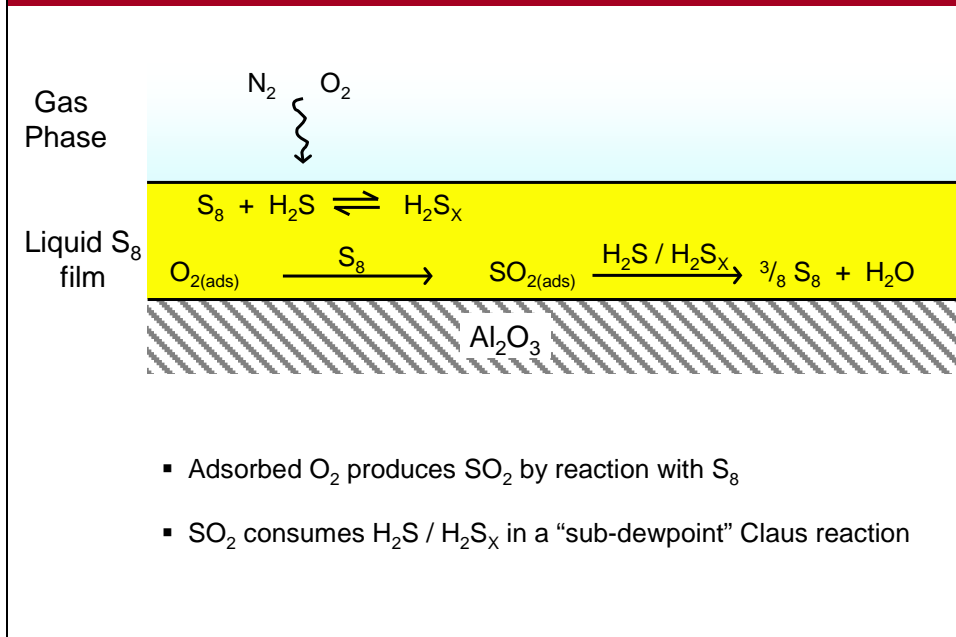
Figure 10. The Chemistry of Air Degassing



Key Points

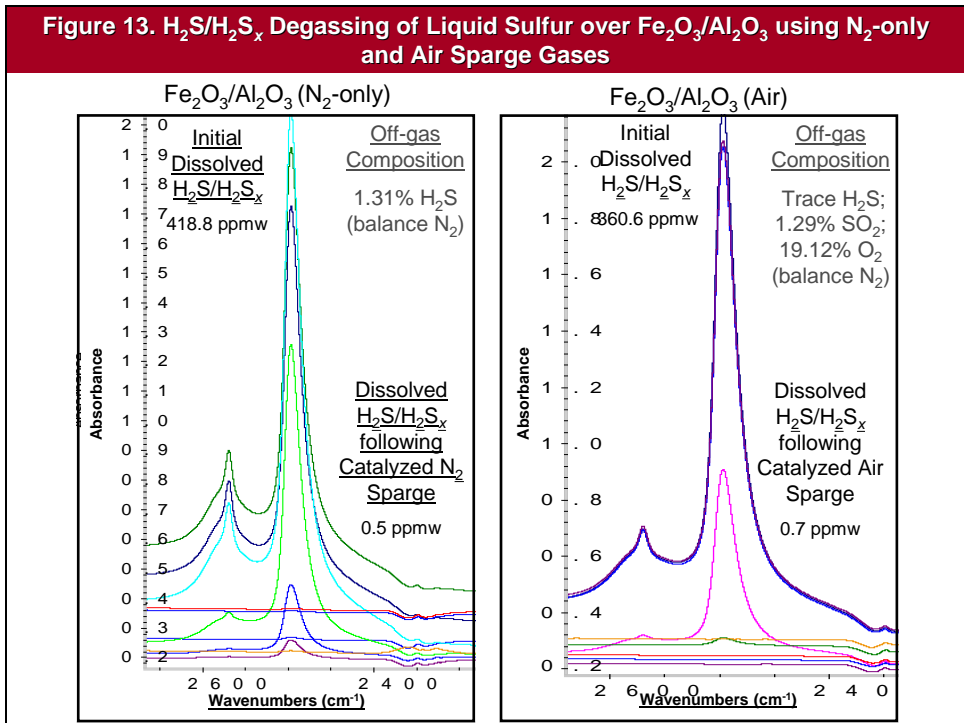
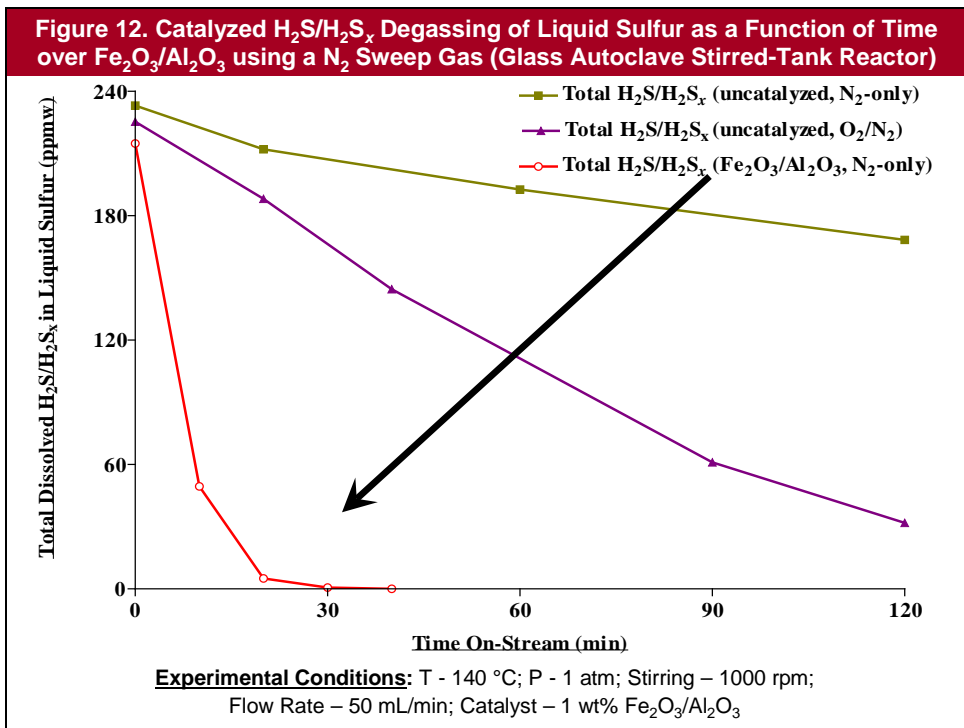
- H₂S_x must decompose to H₂S before H₂S can partition to the gas phase
- O₂ must dissolve in liquid sulfur before it can react with H₂S and H₂S_x. O₂ may also react with liquid sulfur producing SO₂

Figure 11. Possible Chemistry Occurring in the “Amoco” Process



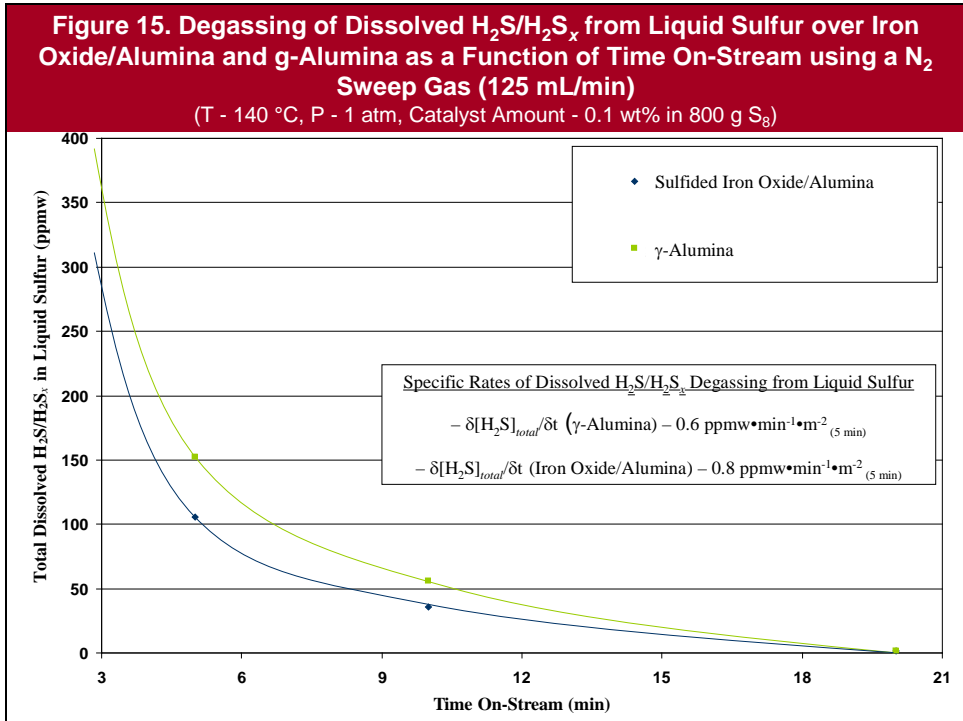
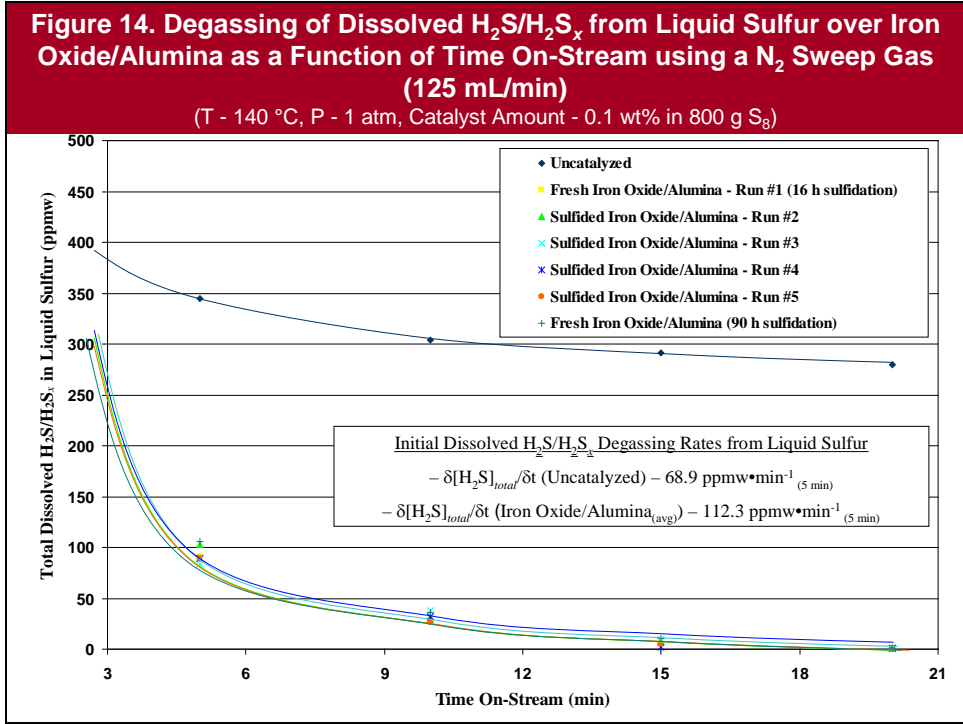
Overall, when air degassing is pushed to achieve very low residual H_2S levels (< 5 ppmw), one consequence is to produce sulphur which contains dissolved SO_2 and which can be corrosive because of the combined presence of water and SO_2 . Another feature of air degassing is that large volumes of air containing SO_2 , H_2S and sulphur vapour must be compressed back into the front end furnace to prevent increased sulphur emissions if this off gas was to be routed to the incinerator.

Recent work in our laboratories has shown that by simply contacting liquid sulphur with alumina or a promoted alumina catalyst, rapid degassing occurs even if no air is present (Figure 12). Some sweep gas is still needed to remove the H_2S as it is released but if this gas is N_2 or another inert gas, very pure liquid sulphur can be produced (< 5 ppmw residual H_2S) which contains no SO_2 or water. If the sweep gas is compressed N_2 , then the off-gas is readily returned to the main acid gas stream as it contains only H_2S (Figure 13). In contrast, when air sparge is used in combination with catalyst degassing, a large amount of SO_2 is observed in the off-gas (Figure 13), some of which also contaminates the liquid sulphur.

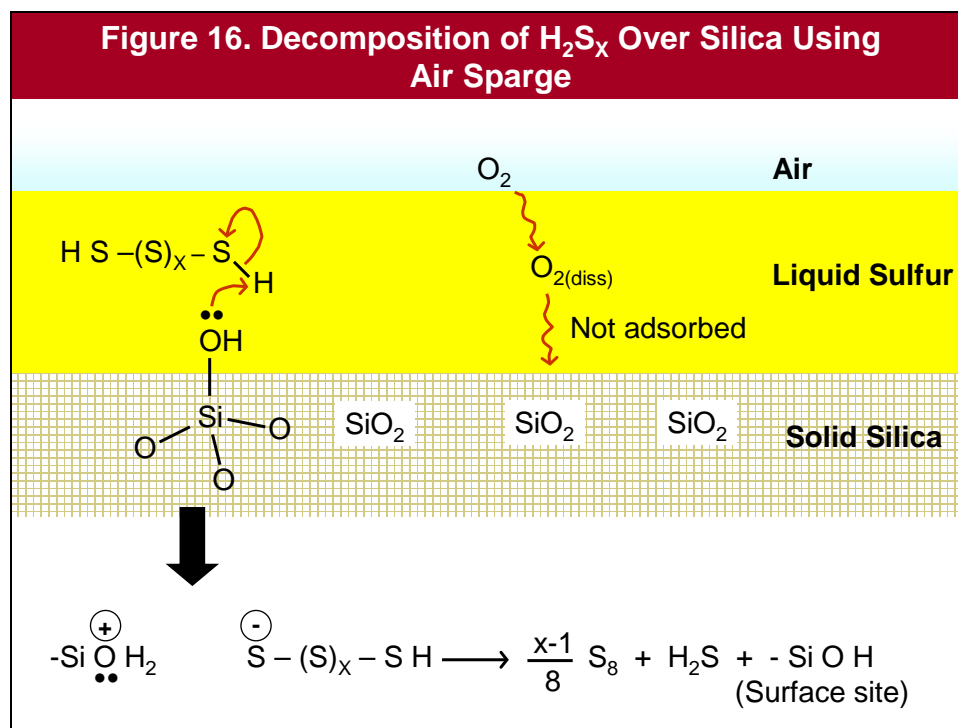


Rates of degassing have been produced for both iron oxide promoted alumina and for alumina (Figures 14 and 15). Overall, the data show that the iron oxide promoted catalyst is more efficient and that it works reproducibly regardless of its exposure to H_2S

and sulphur. Thus, as depicted in Figure 9, basic sites presented by both iron and aluminium species catalyze the decomposition of H_2S_x with the iron species being more active as the specific rates are significantly higher for the iron catalyst (Figure 15).



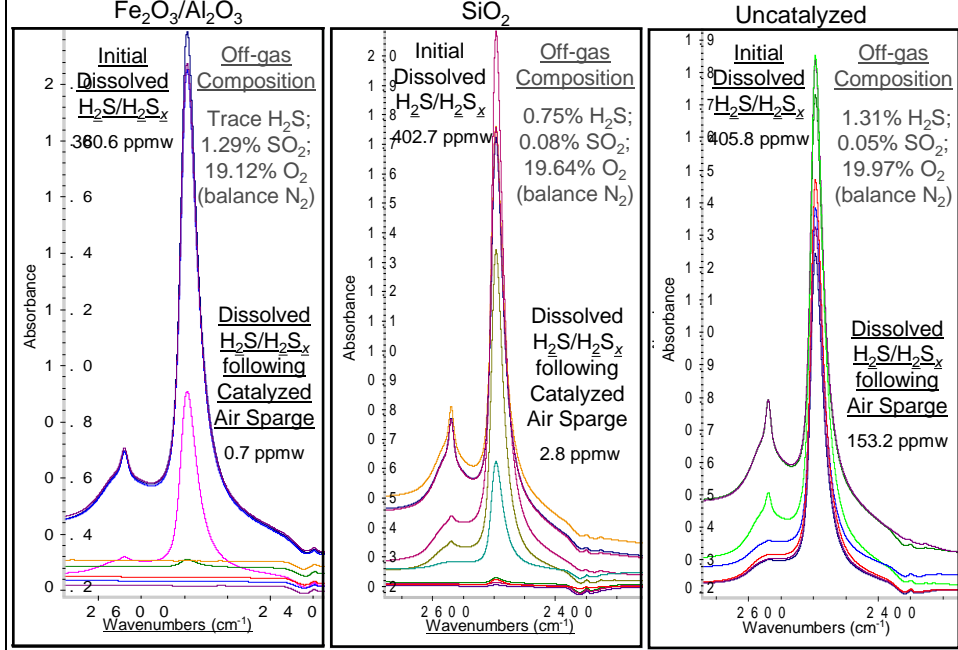
It is projected that silica would also work as a solid degassing catalyst because, like alumina-based materials, it also has basic sites which will initiate the decomposition of H_2S_x (Figure 16). However, since silica does not catalyze oxidation reactions, it should be possible to use it with an air sparge without producing large quantities of SO_2 . Overall, the experimental data obtained with silica confirm these projections as very efficient degassing is obtained but only small quantities of SO_2 were observed in the off-gas compared with iron oxide – alumina when air was used as the sparge gas (Figure 17).



Catalytic Tail Gas Incineration

Thermal incineration has been practiced widely because it enables complete conversion of all sulphur species to SO_2 and conversion of CO and H_2 to CO_2 and water respectively. But, it has the disadvantage of using large quantities of fuel gas to achieve the high temperature. Moreover, because of these high temperatures, some SO_3 may be formed which is often visible as a plume of sulphuric acid mist just down wind of the stack top. Catalytic incineration has been used commercially in several plants but the catalysts employed to date, although very efficient for conversion of H_2S , are unable to oxidize CO and H_2 so restricting introduction of the technology more widely. In addition, operators have been unable to control the temperature rise in the catalyst under conditions in which higher than normal levels of H_2S reach the catalytic incinerator.

Figure 17. H₂S/H₂S_x Degassing of Liquid Sulfur over Fe₂O₃/Al₂O₃ and SiO₂ using an Air Sparge Gas



A generic tail composition (Figure 18) illustrates the complex nature of Claus tail gas although there will be a wide variation of the quantities of the individual components depending on the composition of the inlet acid gas and the units within the plant. In particular, high CO concentrations will be found in plants processing high CO₂ content acid gas. The amount of fuel gas required to attain temperatures high enough for CO oxidation are significant and will count against refineries which have to report CO₂ emissions (Figure 19). In addition, higher incineration temperatures lead to increased SO₃ formation and a higher probability of plume formation.

Figure 18. Catalytic Tail Gas Treatment – Increasing Thermal Efficiency

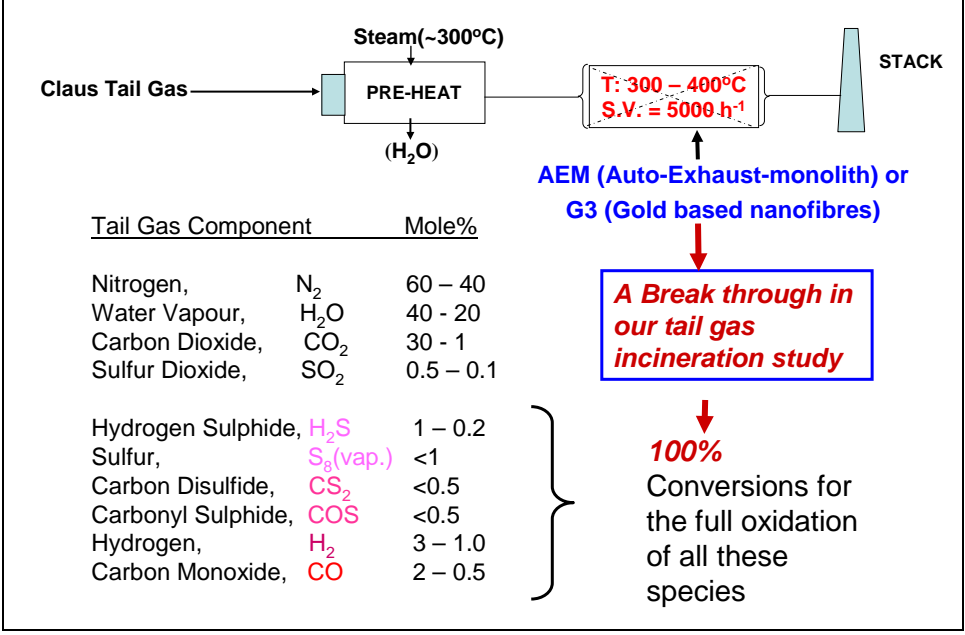
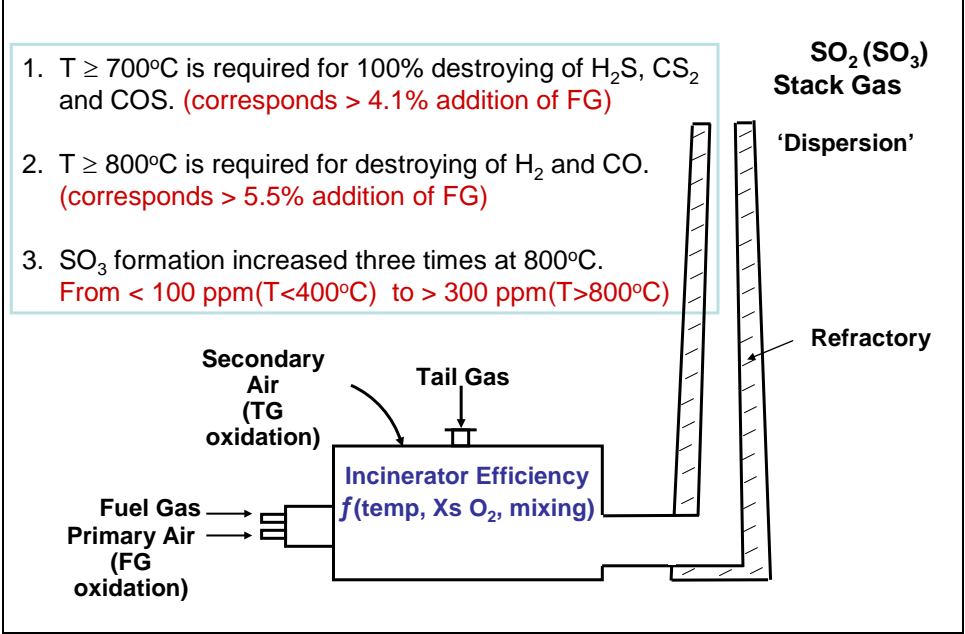


Figure 19. Fuel Gas Requirements and SO₃ Production for Thermal Incineration



Previous studies in our laboratories have deduced the kinetics for oxidation of typical Claus tail gas species (Figure 20) illustrating the high energy of activation for oxidation of both CO and H₂ and, also, has shown that if these species could be oxidized catalytically, no fuel gas would be required so, potentially, saving refinery and gas plant operators penalties for CO₂ emissions. Indeed, the adiabatic temperature obtained for full oxidation of all species in a typical tail gas (around 500°C) is beginning to approach the temperature for stable catalyst design. Numerous catalysts were prepared and tested in our laboratories over the last 5 years, all showing excellent activity for oxidation of H₂S but only stabilized gold dispersed as nano-particles on titania have shown complete oxidation of all Claus tail gas species, including CO and H₂ (Figures 21 – 23). Immediately, let us answer the objections that gold is too expensive! Gold is approximately half the cost of platinum, the metal used in catalytic reforming catalyst which, in many cases is only leased to the refiner to keep the cost to a reasonable level. Of course, platinum is also found the automotive catalytic unit.

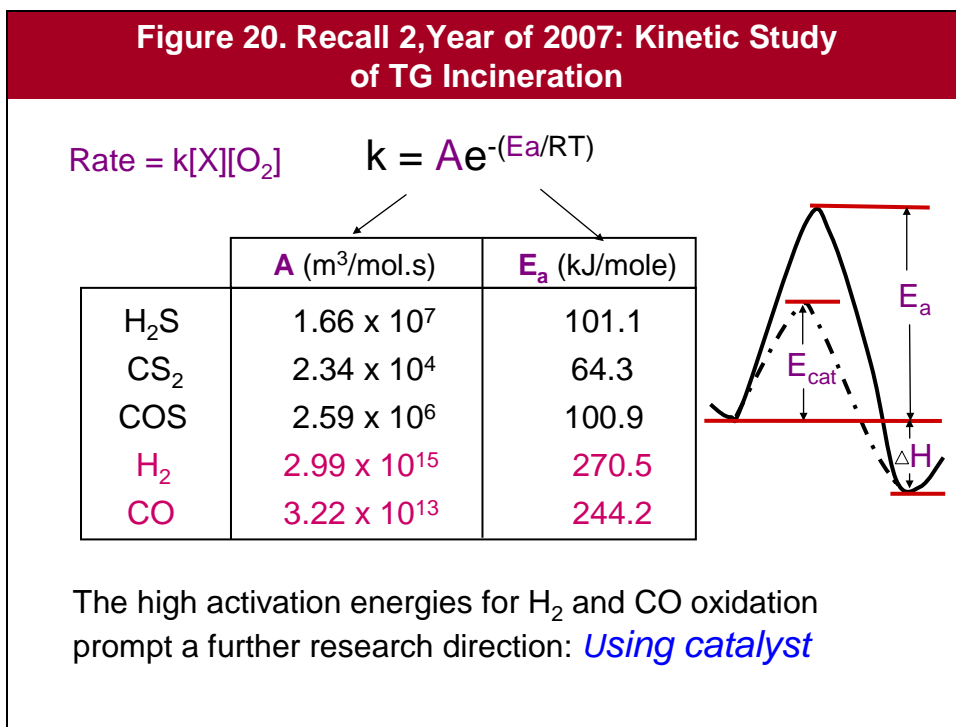


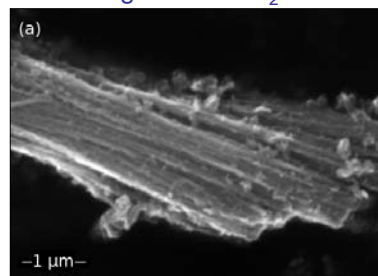
Figure 21. Claus Tail Gas Oxidation Over Au on TiO₂

Results encouraging at 400°C in the presence of S compounds :

H ₂ S	}	100% conversion
COS		
CS ₂		
H ₂		
CO		~96% conversion

However, performance is not stable at 400 – 600°C, which prompts a further direction of research: **addition of stabilizers such as La₂O₃ on catalyst.**

SEM image of Au/TiO₂ nanofibres



EDS analysis

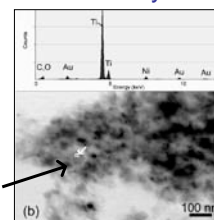


Figure 22. Final Solution: G3 and AEM



G3

1 wt% Au supported on La-Ti (La/Ti=0.035) mixed oxide nanofibres



AEM

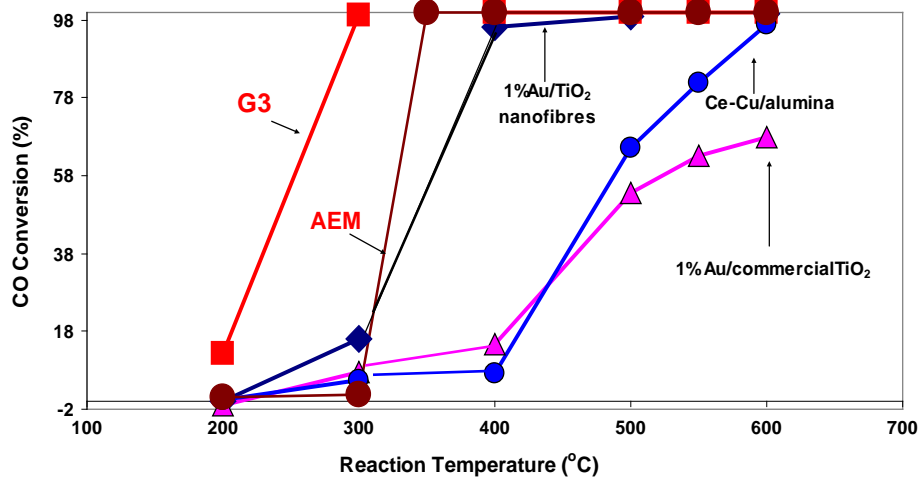
Pt, Rh, Pd plus mixed oxides of Zr, Ni, Cu, Ce loaded on monolith

Figure 23. Comparison of TG Incineration Catalysts

(The conversion of other TG species always reaches 100% before CO)

CO oxidation in TG over different catalysts: S.V. = 5000 h⁻¹

Feed: 1.6%CO, 1.5%H₂, 13.2%CO₂, 22.0%H₂O, 4.1%O₂, 1%H₂S, 0.2%SO₂, 0.05%COS, 0.02%CS₂, balance of N₂



In comparison to the automotive tail pipe catalysts (Figure 22) which were designed for CO oxidation in a low sulphur compound atmosphere, the gold catalysts prepared in our laboratories have as good or better activity and both catalysts are much more efficient than formulations based on copper (Figure 23). Although testing has only been extended out to 32 hours, the gold nano-fibre catalyst shows 100 % conversion of CO, and of all other tail gas species, over this time-frame (Figure 24) and appears to be more active at lower temperatures (Figure 25). This observation is quite important as it suggests that start-up of a catalytic incinerator based on the gold catalyst could be accomplished by preheating the catalytic unit to only a relative low temperature (150 – 200°C). The age of catalytic incineration may well be upon us and could be integrated nicely with the SO₂ adsorption TGT discussed in this paper. Clearly, commercial formulation and long term testing of the gold nano-fibre catalyst is required.

Figure 24. Comparison in Stabilities of TG Incineration Catalysts

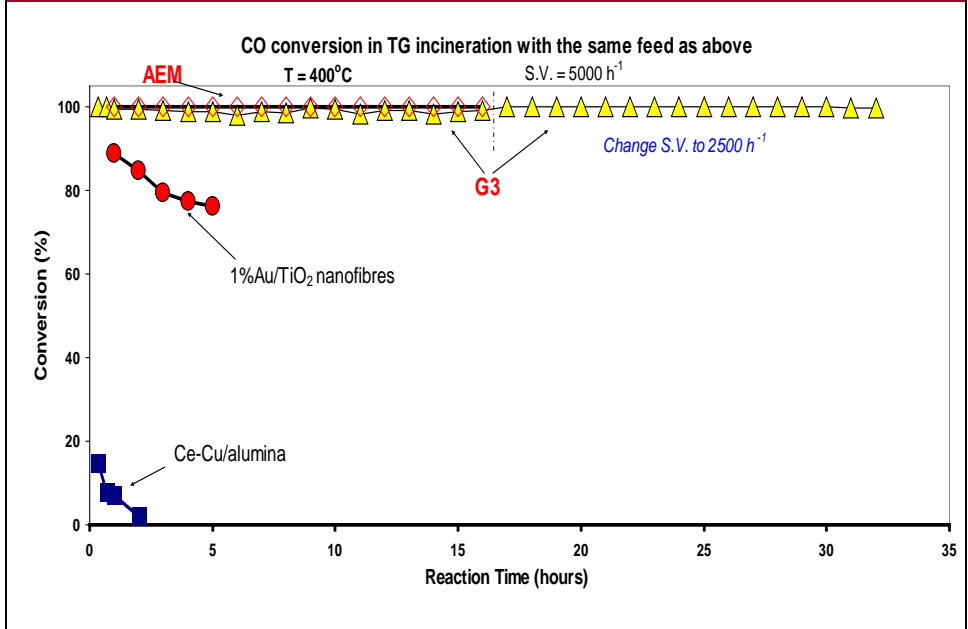
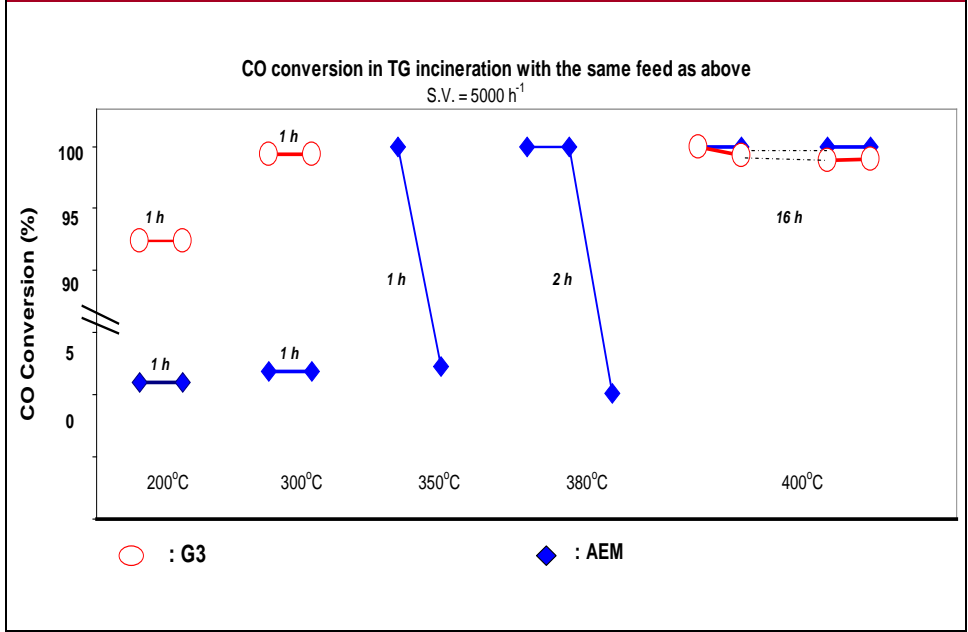


Figure 25. Comparison of G3 and AEM in CO Oxidation Activity



Concluding Comments

The research described in this paper presents the possibility of designing a zero-emissions sulphur recovery plant with much improved thermal efficiency. The key advantages of the process scheme illustrated in Figure 1 have already been discussed but, in summary, they include no fuel gas use for incineration, 100% recovery of all sulphur species in the TGT unit and production of a clean liquid sulphur product which should facilitate downstream storage negating emissions and corrosion concerns. Subsequent distribution of liquid sulphur or production of solid should also be simpler and safer. The remarkable feature of these integrated processes is that all steps are built on process chemistry which liberates energy which could be collected in the form of steam from most of the units. Of course, the drawback is that some organization has to invest time and money to develop the technologies.

Other process features worthy of note are that tight process control in terms of ratio control may not be necessary and, because catalytic incineration is introduced upstream of the TGT, the need to convert CS₂ in the first converter disappears.

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