



GOAR, ALLISON & ASSOCIATES, INC.

## ***Sulfur Degasification— The D'GAASS™ Process***

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***By:***

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## **Abstract**

Goar, Allison & Associates, Inc. (GAA) has developed and received a patent for the D'GAASS Sulfur Degasification Process. The process is a simple, low capital cost and low operating cost degassing process that achieves less than 10 ppmw H<sub>2</sub>S equivalent in liquid sulfur.

The unique design features of the D'GAASS Process allow for easy retrofitting to an existing plant or incorporation into grass root plants. The small flow of pressurized gas waste stream can easily be recycled to the SRU main burner, thus eliminating the degassing process as an emission source.

The first D'GAASS unit was retrofitted September 1996 to the 160 LTPD Sulconam Facility located in Montreal, Canada. This 160 LTPD D'GAASS Unit has been tested at various combinations of process parameters with all analytical work performed by Alberta Sulfur Research Ltd. (ASRL) using the state-of-the-art Fourier Transform infrared (FTIR) analytical procedure.

Test results have verified that the D'GAASS Process is capable of degassing liquid sulfur to below 10 ppmw of combined H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub>.

## **Introduction**

Sulfur degasification is a process that removes dissolved H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> vapor from produced liquid sulfur. Undegassed sulfur presents odor and potential toxic hazardous conditions in the storage, loading and transport of liquid sulfur. Also, up to 80% of H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> present in the liquid can be retained on solidification. The gradual release of H<sub>2</sub>S gas from sulfur in the solid form presents odor problems. Also, the gas gives voids and surface imperfections which weakens the solid, and increases "dusting" in handling.

Tests have shown that H<sub>2</sub>S concentrations of greater than 20 ppmw in liquid sulfur can result in closed vapor spaces with H<sub>2</sub>S concentrations greater than the lower explosion limit of 3.5%. Obviously, the explosivity concern is also coupled with the H<sub>2</sub>S toxicity issue. Toxic levels of H<sub>2</sub>S can build up in closed vapor spaces of sulfur pits and transport containers. Also, high levels of H<sub>2</sub>S may accumulate near sulfur pit and sulfur loading areas.

Degasification is clearly the best method of preventing H<sub>2</sub>S release from liquid or solid sulfur, and the associated problems with odor, explosivity and toxicity.

The patented D'GAASS Process reduces combined H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> to 10 ppmw in sulfur product in a simple, low capital and operating cost method without catalyst addition. The process operates at elevated pressure, thus allowing the use of a small, low residence time vessel that is easily retrofitted external to sulfur pits. The elevated operating pressure easily allows for recycling of the overhead vapor stream back to the SRU main burner, thus eliminating sulfur degassing as an emission source.

The first commercial D'GAASS Unit was commissioned in September, 1996 at Sulconam's Montreal Facility. The D'GAASS Process was retrofitted to the existing 160 LTPD SRU at Sulconam. The design and operating results of the D'GAASS Unit at Sulconam are presented in this paper.

## Existing Technologies

The existing major sulfur degassing technologies use a combination of mechanical, catalytic and/or oxidation techniques for the removal of H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> from liquid sulfur<sup>(2)</sup>. Several commercial technologies are capable of achieving the generally accepted residual H<sub>2</sub>S standard of 10 ppmw. The relative capital cost of the existing technologies is approximately equal<sup>(3)</sup>. While the existing technologies are capable of achieving the 10 ppmw specification, some of the limitations of the existing technologies include:

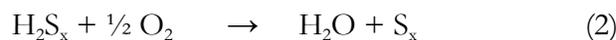
- 1) High capital cost
- 2) Difficult to retrofit to existing SRU
- 3) High operating cost
- 4) Long residence time, thus large footprint
- 5) Catalyst requirement with possible negative impact on (a) sulfur quality (b) salt formation resulting in equipment plugging
- 6) Additional SO<sub>2</sub> emissions because degasification waste stream (containing H<sub>2</sub>S, SO<sub>2</sub> and/or S) is fed to the incinerator.

The D'GAASS Process addresses all these limitations in a simple, low capital and operating cost, zero emission technology that degasses liquid sulfur to less than 10 ppmw combined H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub>.

## New Approach – The D'GAASS Process

The D'GAASS Process exploits the favorable thermodynamic equilibrium for the oxidation of H<sub>2</sub>S, while addressing the kinetic limitations of the same reaction. Liquid sulfur produced by the Claus process typically contains 200-250 ppmw H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub>. A major part of the H<sub>2</sub>S is bound to long poly-sulfur molecules, and is called H<sub>2</sub>S<sub>x</sub>. The H<sub>2</sub>S<sub>x</sub> exists in equilibrium with H<sub>2</sub>S dissolved in sulfur. Thus, removal of H<sub>2</sub>S from the liquid results in decomposition of H<sub>2</sub>S<sub>x</sub> to H<sub>2</sub>S, allowing ultimate total H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> degasification to below the targeted 10 ppmw total.

Kinetic experiments have indicated that the rate equation, and hence, the order of the reaction is first order with respect to H<sub>2</sub>S concentration. The overall partial oxidation of H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> to sulfur is given by the elementary reactions:



The D'GAASS Process is designed to operate at elevated pressures to address the kinetic limitations, resulting in a small contactor that achieves the target 10 ppmw H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub>.

### **D'GAASS Design Parameters**

The key to the D'GAASS Process is the elevated operating pressure with the fixed vessel internals. Degasification is carried out in a pressurized vertical vessel, which contacts the undegassed sulfur with pressurized process air (instrument or clean utility air). The undegassed sulfur is pumped to the vessel and intimately contacted with air across special fixed vessel internals. Operating pressures are typically in excess of 60 psig. The elevated pressure improves the kinetics of the oxidation process. Due to the elevated pressure, no catalyst addition is required; the elevated pressure in combination with the fixed internals is sufficient to degas the liquid sulfur to below 10 ppmw H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub>.

The fixed vessel internals are sized based on GAA tower modeling criteria. Commercial data are not available for liquid sulfur/air systems operating at elevated pressures. Effective vapor-liquid contacting with sufficient reaction residence time is necessary for effective degassing. Also, a properly sized wire mesh mist eliminator is utilized to minimize potential sulfur liquid entrainment in the overhead vapor stream.

### **The D'GAASS Process Advantages**

As a result of the improved kinetics due to the elevated pressure with the special fixed internals, the D'GAASS Process has several economic and operating advantages.

a. Size and Capital Cost

Operation at elevated pressure reduces the size and reaction time requirements. The commercial 160 LTPD unit is an 18" O.D. vessel. With a tower height of 30', or less, the D'GAASS contactor requires a small footprint and is easy to retrofit. The carbon steel construction makes this small vessel relatively inexpensive; the fixed internals cost in the range of 20-30% of the vessel cost. Since the process is external of the sulfur pit, downtime for installation, if any, is minimal. The overall size is small and the equipment cost is low.

b. Low Operating Cost

For continuous operation, the improved kinetics results in much lower air requirements than other commercial units. Typical annual operating costs for the sulfur pumping and process air requirements are given below.

SRU Capacity LTPD	Annual Operating Cost <sup>(1)</sup> (\$)
100	2,000
1000	20,000

Note 1. Based on electricity cost of 4¢/kwh and 365 days of continuous on-line operation.

With a single, fixed-internal contactor located external of the sulfur pit, maintenance costs are projected to be very low. Also, due to the simplicity of the process the projected on-line time is expected to be near 100%.

c. Sulfur Degassing with Zero Emissions

The elevated D'GAASS operating pressure allows recycling of the overhead vapor stream back to the front end of the SRU. The waste stream contains less than 0.1% H<sub>2</sub>S and thus is essentially an air stream. Due to the small flow and elevated pressure the stream can be recycled to the front portion of the SRU without metering the stream and without adverse effects to the SRU main burner control.

For SRU's with tail gas cleanup units that achieve 99.9% + SRU recovery, conventional degassing systems that vent the vapor stream to the incinerator can be a significant emissions source. Emissions from the degassing systems can be equal to the SRU/TGCU emissions. The D'GAASS Process reacts 90% plus of the H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> feed and the overhead stream can be recycled to the SRU, resulting in zero emissions attributable to the degassing system.

d. Operating Flexibility

The D'GAASS Process can be operated in several different modes:

- I) Continuous Operation (Figure 1)
- II) Batch Operation (Figure 2)
- III) Continuous Recycle with purge (Figure 3)

The continuous operation is based on degassing at the rate of sulfur production. Undegassed sulfur is pumped to the vessel from the collection or sulfur pit at the rate of sulfur production and intimately contacted with air. The degassed sulfur flows from the contactor to a separate sulfur production pit or tank. The pressurized vapor flow containing a small amount of H<sub>2</sub>S flows from the degassing section to either the SRU main burner (not an emission source) or the to the incinerator (small emission source).

In batch operation, the sulfur is pumped from the sulfur pit to the vessel at a flow rate equal to the transfer or loading rate and intimately contacted with air. The degassed sulfur flows from the contactor to the transfer destination

or loading facility. The pressurized vapor flow containing a small amount of released H<sub>2</sub>S flows from the degassing section to either the SRU Main Burner (not an emission source) or to the incinerator (small emission source).

For continuous recycle operation with purge, the sulfur is pumped from the sulfur pit to the vessel at preferably a greater flow rate than the sulfur production rate and intimately contacted with air. The degassed sulfur flows from the contactor back to the sulfur production pit. The pit geometry can sometimes be used directionally to create separate zones of degassed sulfur and undegassed sulfur. Some improvement in product quality can be obtained by locating the degassing feed pump at the end of the pit nearest the raw sulfur inlet(s), while locating the degassed sulfur return line and sulfur loading pump at the opposite end of the pit. Creation of separate zones in the pit can be enhanced by operating the D'GAASS Process at rates significantly higher than the sulfur production rate of the SRU. The pressurized vapor flow containing a small amount of released H<sub>2</sub>S flows from the degassing section to either the SRU Main Burner (not an emission source) or to the incinerator (small emission source).

Advantages of the D'GAASS Process advantages can be summarized as:

- 1) Low capital cost
- 2) Low operating cost
- 3) Small footprint
- 4) Easy to retrofit
- 5) Zero emission sulfur degassing
- 6) Option to operate in continuous, batch or recycle-purge mode
- 7) Not intrusive to the sulfur pit.

## Operating Results

The D'GAASS Process was retrofitted to the 160 LTPD SRU at the Sulconam Treating Facility, Montreal, Quebec in September, 1996. The commercial (pilot) unit was built with facilities to allow measurement of:

- 1) pressure, temperature and flow of feed streams
- 2) sample connections of feed streams, product streams and contactor intermediate profile.

All analytical measurements were performed by Alberta Sulfur Research Ltd. (ASRL) at site. Measurement of residual H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> in the liquid sulfur feed and product streams was performed using ASRL's Fourier Transform Infrared (FTIR) spectroscopy method. Traditionally, wet chemical methods have been used but wet chemical methods are laborious and inaccurate unless done carefully. The FTIR method allows for accurate and repeatable testing of a large number of samples. The effluent gas composition was determined by an ASRL pH methodology and Draeger tubes.

The degassed sulfur contains 10 ppmw  $H_2S / H_2S_x$  without the requirement of catalyst addition. The mechanical strength of sulfur is related to the amount of polymeric material in the sulfur <sup>(4)</sup>. Air-degassed sulfur contains significant quantities of polymers and as a result has a high compressive strength. In contrast sulfur degassed with catalysts contains no polymeric sulfur and thus has low compressive strength. High compressive strength is desirable for sulfur forming; lower compressive strength can result in higher dust emissions.

Analysis of the overhead vapor stream and material balance calculations indicate that over 90% of the  $H_2S$  and  $H_2S_x$  are reacted.

## **Conclusions**

The D'GAASS Process is a sulfur degasification process that can achieve 10 ppmw residual  $H_2S / H_2S_x$  in sulfur without the use of a catalyst. Over 90% of the  $H_2S / H_2S_x$  fed is oxidized.

Operation at elevated pressure results in low capital cost, low operating cost and facilitates degassing operation with zero emissions.

Due to the elevated operating pressure, the D'GAASS contactor is small in size. Location of the D'GAASS vessel external of the pit in combination with the small size makes the D'GAASS process easy to retrofit to an existing facility or incorporate in a grass root design.

## References:

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