



GOAR, ALLISON & ASSOCIATES, INC.

## ***Continued Development of the D'GAASS Sulfur Degasification Process***

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## **ABSTRACT**

Claus unit product sulfur normally contains 250-350 ppmw H<sub>2</sub>S in the form of dissolved H<sub>2</sub>S and chemically bound polysulfides, H<sub>2</sub>S<sub>x</sub>. The H<sub>2</sub>S is slowly released from stored sulfur product as the product is cooled and/or agitated and over time. Storage and handling operations can emit noxious odors and release toxic and explosive mixtures of H<sub>2</sub>S in air. Historically, sulfur has not been degassed to remove H<sub>2</sub>S. There are a few countries that have implemented limits on the residual H<sub>2</sub>S concentration allowed in liquid sulfur shipments, and some companies are implementing sulfur degassing to control odor and improve safety and/or meet customer product specifications.

The Goar, Allison & Associates, Inc. D'GAASS Process was developed to provide an inexpensive, small footprint process for sulfur degassing. The D'GAASS Process has been in service at the Sulconam Plant in Montreal since September 1996. It is particularly well suited for retrofitting to existing plants. The process has received wide acceptance by the sulfur recovery industry over the past two years.

Since the Sulconam Unit start-up, Goar Allison has collected extensive data to confirm and update our design methods. Degassing process performance factors are discussed, and test results from the latest testing are presented in this paper. There have also been improvements in the D'GAASS Process to increase the unit reliability and reduce the total sulfur emissions from the sulfur recovery area.

## **INTRODUCTION**

All product sulfur from modified Claus process sulfur recovery units (SRU's) contains residual H<sub>2</sub>S; some as dissolved H<sub>2</sub>S and some in the form of loosely chemically bound polysulfides, H<sub>2</sub>S<sub>x</sub>. The total residual H<sub>2</sub>S concentration is influenced by the H<sub>2</sub>S vapor concentration (partial pressure) and the temperature at which the sulfur product condensed. As SRU's are pushed to and beyond their design capacities, the H<sub>2</sub>S content of product sulfur increases.<sup>1</sup> Oxygen enrichment also results in higher residual product H<sub>2</sub>S.<sup>2</sup> The average H<sub>2</sub>S concentration in typical SRU product sulfur is 250-350 ppmw. Some H<sub>2</sub>S is released during sulfur storage, handling, and transportation. The released H<sub>2</sub>S results in safety hazards from the toxic H<sub>2</sub>S gas and potentially explosive concentrations of H<sub>2</sub>S and air.<sup>3</sup> Solid sulfur product formed from undegassed liquid sulfur is more friable (prone to fracture and create dust). The release of H<sub>2</sub>S from solid or liquid product results in noxious odors. Undegassed sulfur is also more corrosive. Degasification of liquid sulfur controls most of the above listed problems.

Several factors contribute to the release of H<sub>2</sub>S from liquid product sulfur (degassing). The primary factors that contribute to this release during normal operation are low H<sub>2</sub>S concentration in the gas above the liquid sulfur, mechanical agitation, cooling, and time. The equilibrium ratio of H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> is dependent on temperature; the ratio of H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> is about 1.5 at 155°C (311°F) and 10 at 125°C (257°F).<sup>1,4,5</sup> Over time, dissolved H<sub>2</sub>S will desorb into the gas phase; physical desorption is favored by low H<sub>2</sub>S

gas concentrations. As  $H_2S$  is desorbed, some  $H_2S_x$  is converted to  $H_2S$  to maintain the equilibrium  $H_2S/H_2S_x$  ratio. The conversion of  $H_2S_x$  to  $H_2S$  is relatively slow, and the overall degassing rate is primarily controlled by the rate  $H_2S_x$  is converted to  $H_2S$ .

## **BASIS OF D'GAASS PROCESS**

Earlier commercial degassing processes were designed to strip  $H_2S$  from liquid sulfur at atmospheric pressure by passing stripping gas (normally air) through the sulfur product or passing product sulfur through a stripping gas stream. These processes were designed to promote the physical desorption of  $H_2S$  into the stripping air stream using a combination of mechanical agitation to increase the surface area between the sulfur and air stream and maintaining a low  $H_2S$  concentration in the gas phase by continuous removal and replenishment of the stripping gas stream. The physical desorption of  $H_2S$  is relatively easy and fast. However,  $H_2S_x$  is a high molecular weight compound that is not volatile and therefore is not removed by physical desorption. The commercial processes required from several hours up to a few days sulfur residence time to achieve less than 10 ppmw residual  $H_2S/H_2S_x$ . The primary reason for the long residence time was to allow conversion of  $H_2S_x$  to  $H_2S$  which could then be removed by physical desorption. Some processes utilize a chemical catalyst/additive to aid in the decomposition of  $H_2S_x$  to  $H_2S$  and reduce the required degassing time.

The Shell Process sparges air into the product sulfur using specially designed pit internals. Two of the earlier processes based on passing sulfur through an air stream are the Texas Gulf Sulphur and SNEA Processes. The SNEA process also uses a catalyst. The original Exxon Process was based on chemical catalyst addition and very long residence time to allow the  $H_2S$  to 'weather' off. A more recent Exxon development uses air sparging to reduce the required residence time. These processes are described in more detail in previously published papers.<sup>6,7</sup>

The above described processes all use air as the stripping medium. Several other gas streams have been utilized/tested/proposed. These include gases such as SRU tail gas,  $CO_2$ , and nitrogen. Steam has also been utilized in several locations. Steam sparging systems are typically homemade by the operating company. The results using these stripping alternates have not been as effective as using air. In general, air is preferred; steam is next in effectiveness, and inert gases are least effective.

Research by Alberta Sulphur Research Ltd. (ASRL) has identified the primary advantage of air stripping to be the direct oxidation of some of the  $H_2S/H_2S_x$  directly to sulfur.<sup>1,8</sup> ASRL has also determined the oxidation reaction to be primarily a liquid phase reaction.<sup>9</sup> Steam stripping is thought to be more effective than inert gas stripping because small quantities of the boiler water treating chemicals are carried with the steam and catalytically promote decomposition of  $H_2S_x$  to  $H_2S$ . Many plants that have implemented steam stripping have experienced very significant corrosion in the sulfur pit.

The patented D'GAASS Sulfur Degasification Process<sup>8</sup> was developed by Goar, Allison & Associates, Inc. (GAA) to provide a simple, compact process that maximizes the advantages of air stripping. The other commercial degassing processes operate at or near atmospheric pressure. The D'GAASS Process operates at elevated pressure to increase the partial pressure of oxygen and concentration of dissolved oxygen in the liquid sulfur. The higher oxygen concentration increases the oxidation reaction rate of H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> to sulfur and SO<sub>2</sub>. The SO<sub>2</sub> can then react with H<sub>2</sub>S via the Claus reaction to form additional sulfur.

### **D'GAASS PROCESS DESCRIPTION (Figure 1)**

Degasification is carried out in a vertical vessel in which the undegassed sulfur is contacted with pressurized process air. Air and sulfur flow counter-currently across fixed column internals. The upward flow of air provides both agitation of the sulfur and stripping of H<sub>2</sub>S.

Undegassed sulfur from the sulfur collection pit is pumped to the D'GAASS contactor. The pumping rate is flow controlled at the sulfur production rate. The sulfur feed rate may be controlled using a sulfur pit level controller to provide a cascade set point for the flow controller. The degassed sulfur from the contactor flows to sulfur storage, sulfur forming, or directly to truck or rail car loading. The pressure of the degassed sulfur exiting the process is adequate to transfer the sulfur to the forming unit, a storage tank, or loading rack(s). There is a return line from the bottom of the contactor to the sulfur pit that is used to drain the system and to allow recycling to the pit during start-up or if there are problems with the downstream facilities.

The Claus sulfur product temperature is typically above the optimum temperature for sulfur degassing. Cooling the feed sulfur before it enters the contactor is required to achieve 10 ppmw residual H<sub>2</sub>S in the degassed sulfur. Cooling the sulfur in a shell and tube exchanger using boiler feedwater as a cooling medium has proven to be a good method.

The major unit controls are: (1) temperature control of the feed sulfur; (2) flow control of the sulfur feed rate to the D'GAASS Unit at the SRU sulfur production rate; (3) flow control of the process air based on the maximum rated capacity; (4) level control of the contactor by regulating the flow of degassed sulfur leaving the vessel; and (5) unit pressure control by regulating the overhead vapor effluent flow.

The overhead stream is air with small amounts of H<sub>2</sub>S, SO<sub>2</sub>, and sulfur vapor. The overhead stream can be sent to the incinerator. As an alternate, the elevated D'GAASS operating pressure allows sending the overhead vapor stream to the thermal stage of the SRU or to a tail gas unit burner. The routing of the overhead air stream is discussed in more detail later in the paper.

## **PROCESS PERFORMANCE FACTORS**

There are many factors that influence the performance of the D'GAASS Process, as well as other degassing processes. Included in these factors are feed and product  $H_2S/H_2S_x$  concentration, degassing temperature, degassing pressure, sulfur residence time, and sulfur and air contact time.

The principal degassing performance factors are the concentration of  $H_2S/H_2S_x$  in the undegassed feed and the degassed product. ASRL has shown air degassing to be a pseudo-first order reaction.<sup>1</sup> A simple way to consider the effects of  $H_2S/H_2S_x$  feed and product concentrations is to utilize half-life. This concept should apply to both atmospheric processes and the D'GAASS Process. Using this concept, the time required to reduce the  $H_2S/H_2S_x$  concentration from 300 ppmw to 150 ppmw is the same as the time required to reduce the concentration from 20 ppmw to 10 ppmw.

The importance of temperature in sulfur degassing performance has been known for several years. ASRL presented research data, Figures 2 and 3, indicating the optimum degassing temperature for their laboratory air sparge degassing testing apparatus was between 130 and 140°C (266-284°F).<sup>1</sup> Most sulfur condensers generate 50 psig steam to cool the process gas and condense sulfur. This results in condenser outlet temperature of 160-175°C (320-350°F) for most SRU's. Sulfur pits are usually equipped with steam coils to offset heat losses and maintain the sulfur as a liquid. Normally, 50 psig steam is also used in the coils. The sulfur pit product temperature is typically 150-160°C (300-320°F). Therefore, cooling is normally required for efficient degassing in all processes. The D'GAASS Process utilizes a conventional shell and tube heat exchanger to cool the sulfur feed to the degassing contactor. GAA has found preheating SRU boiler feedwater works very well for the sulfur cooler. The degassing contactor feed temperature is controlled by regulating the boiler feedwater flow through the cooler. This provides very precise control of the temperature at the optimum temperature, which is not possible with the in-pit systems.

The key feature of the D'GAASS Process is the use of pressure to increase the partial pressure of oxygen and therefore the concentration of oxygen dissolved in the liquid sulfur. Applying Henry's Law, the equilibrium concentration of oxygen in sulfur at 90 psig is seven times the concentration at atmospheric pressure. Higher liquid oxygen concentration results in a greater kinetic reaction rate. This feature allows the D'GAASS Process sulfur residence time to be minutes compared to hours for the earlier near atmospheric pressure degassing processes.

The importance of sulfur residence time is probably obvious. As discussed above, ASRL has shown air degassing to be a pseudo-first order reaction. For example, to reduce the residual  $H_2S$  in undegassed sulfur from 300 ppmw to 9.4 ppmw in the degassed product, it requires 5 half-lives. This is equivalent to 5 hours if the half-life time is 60 minutes. If the degassing unit capacity allowed only 4 half-lives, the resulting product residual would be 19 ppmw.

The contact time between air and sulfur may not be as obvious, but it is very important. The effect of pressure on the equilibrium oxygen concentration of oxygen in sulfur was discussed above. However, oxygen does not immediately dissolve in liquid sulfur. The transfer of oxygen to sulfur can be the rate limiting step; equilibrium dissolved oxygen concentration may not be achieved. Mass transfer from a gas phase to a liquid phase has been compared to heat transfer with film resistances to mass transfer similar to heat transfer film resistance. The overall transfer of mass (oxygen) is dependent on the driving force (oxygen partial pressure) and area. Because the system is dynamic, the longer the air and sulfur are in contact the more oxygen will be transferred. Therefore, maximizing the contact time is important.

The D'GAASS process design optimizes the application of the factors discussed above. The feed temperature is controlled at optimum temperature. The operating pressure is maximized within economic limits. The D'GAASS contactor is a relatively tall, slim vessel to improve process air utilization, and the fixed vessel internals are designed to maximize the contact surface between air and sulfur. Correct application of all these factors is necessary for effective, economical degassing.

### **SULCONAM TESTING**

Since the initial start-up of the Sulconam D'GAASS Unit, GAA has done extensive testing to evaluate the effects of pressure, temperature, air rate, sulfur feed rate, etc. on unit performance. Testing has focused on the H<sub>2</sub>S removal performance with sulfur feed and product analyses performed by ASRL using Fourier Transform Infrared (FTIR) spectroscopy. Overhead gas analyses were done using stain tubes (Dräger, GasTec, etc.), which are good for qualitative checks, but very imprecise quantitative devices.

In October 2000, additional testing was done to specifically evaluate degassing performance after some process modifications and to accurately measure the overhead gas composition using gas chromatography. Testing was performed over a 3-day period with varying operating conditions in the D'GAASS Unit. During testing, Sulconam made changes in SRU operation, which resulted in changing the D'GAASS Unit feed sulfur H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> concentration from about 165 ppmw to 215 ppmw and back to 165 ppmw. The results of this testing are summarized in the following discussion.

There were two significant process modifications to the D'GAASS Unit. The original distributor was replaced with an improved design. The unit had operated since start-up with two internal beds, one a special vapor/liquid contacting bed and the other an oxidation catalyst bed. Before the latest testing, the catalyst bed was removed.

A primary objective was to confirm that degassing to a level of less than 10 ppmw residual H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> could be achieved without the catalyst bed. This objective was achieved with several samples below 10 ppmw. The lowest measured residual was 5 ppmw. This is really approaching zero residual since the lower detection limit of the

FTIR analyzer is 2 ppmw each for H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub>. Therefore, 4 ppmw measured total residual could actually be zero.

Another objective was to accurately determine the overhead gas composition from the degassing contactor. Some customers had expressed concerns that the H<sub>2</sub>S concentration in the overhead gas could approach the LEL for H<sub>2</sub>S in air because the D'GAASS process air rates are much lower than for other degassing processes. During the testing period, 28 overhead gas samples were analyzed. The maximum H<sub>2</sub>S concentration measured was 0.27 mol%, which is less than 10% of the normally accepted LEL for H<sub>2</sub>S in air. This maximum concentration occurred at the minimum relative air rate (air flow/sulfur flow).

Of course, the real objective of a degassing unit is to remove H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> from the feed sulfur. The D'GAASS Process is based on increasing/maximizing the oxidation rate of both H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> by increasing the pressure and therefore, the oxygen concentration in the liquid sulfur. This is verified by the fact that degassing is accomplished in minutes compared to at least several hours for most of the other degassing processes. The typical yield of H<sub>2</sub>S to sulfur during the Sulconam testing was about 60%.

### **IMPLEMENTING THE D'GAASS PROCESS**

The D'GAASS Process has several advantages over other commercial degassing processes in its application to commercial units.

- The degassing operation is carried out in a vertical vessel that is external to the sulfur pit. Therefore, an increase in pit capacity and installation of special internals is not required for retrofits.
- The increased oxidation reaction rate allows the degassing residence time to be minutes compared to 4-24 hours for most of the other processes.
- The process does not require continuous injection of a chemical catalyst to promote decomposition of H<sub>2</sub>S<sub>x</sub>.
- The much shorter required residence time allows the degassing contactor to be small. This results in lower contactor cost and small plot requirements.
- Degassing temperature is much easier to control, is more uniform, and is more precise using a conventional heat exchanger than is possible with in-pit degassing systems.
- The sulfur is pumped, and pressurized air is used. This allows the degassing equipment to be located at any convenient location between the sulfur pit and storage/loading facilities.

- The process piping is smaller and less expensive because the sulfur is pumped and pressurized air is used.
- The high pressure sulfur feed pump capacity can be lower than the existing transfer pump since the sulfur feed rate is equal to the production rate. The production rate is normally significantly lower than the truck/rail loading rate or transfer rate to storage. This also allows the sulfur feed piping to be smaller.
- No, or very limited, modifications are required to the existing sulfur pit. This avoids the long SRU downtime necessary to evacuate the pit of all sulfur to make internal pit modifications, and possibly expand the pit.
- The D'GAASS Process lends itself well to modular construction.
- The process is less costly to install and avoids lost production costs associated with long downtime.
- Maintenance requirements are low since the only rotating equipment items are the sulfur pumps and process air compressor, which are both very reliable.
- Operator attention is minimal because the process operation is very stable and process control is simple.
- Operating costs are low. The only utility usages are power for the sulfur feed pump and air compression, low pressure steam for heat tracing, and instrument air. There are no continuous chemical injection costs.
- The degassed sulfur product is available at sufficient pressure to transfer the product to storage, loading, or forming without additional pumping.
- The sulfur collection pit is operated at the lowest practical level. This results in minimum residence time in the pit for undegassed sulfur which minimizes the H<sub>2</sub>S release upstream of the D'GAASS Unit. This reduces the total sulfur emissions from the sulfur complex because all H<sub>2</sub>S released in the pit is routed to the incinerator.
- Operation under pressure allows the overhead air stream to be routed to the main SRU burner, tail gas unit burner, or upstream of a selective oxidation stage such as SUPERCLAUS. Routing to any of these locations results in zero sulfur emissions directly from the degassing unit. The overhead stream can also be routed to the thermal oxidizer.
- For grass roots facilities, the sulfur collection pit can be small (4 hours working volume or less). This reduces the SRU plot requirements and overall cost.



The D'GAASS Process is particularly suited for retrofitting to an existing SRU/sulfur complex. Because there are virtually no modifications required to the existing unit, the process can be installed with minimal or no SRU downtime. These factors can be particularly important if there are future regulations that require degassing in existing sulfur recovery facilities.

- The only required modifications to the normal sulfur pit are installation of higher discharge pressure sulfur feed pumps, routing new sulfur piping from the pump discharge to the D'GAASS Unit, and possibly installation of a return connection to the pit.
- If the existing sulfur pit has dual installed sulfur pumps, one new feed pump and sulfur feed piping can be installed without shutting down the SRU. The second pump can be installed after the D'GAASS Unit start-up, eliminating the requirement to shut down the SRU.
- If a modular type unit is utilized, major equipment (sulfur cooler and air compressors, if required, excluding the contactor vessel), interconnecting piping, and field control instrumentation can be installed on the module, Figure 4. This allows utilization of more efficient shop labor and minimizes field construction time.
- The degassing contactor and other equipment can be located in any convenient location between the sulfur pit and storage or loading facilities. The plot requirements for the modular unit shown in Figure 4, which can process up to 1000 LTPD of sulfur, is only 15 ft. X 40 ft.
- The field construction can take place during normal SRU operation.
- Depending on the routing of the contactor overhead gases, it may be possible to totally install and start-up the D'GAASS Unit without shutting down the SRU. Even if an SRU shutdown is required, the duration can be very short to make final tie-ins.

A listing of licensed D'GAASS Process Units is attached as Table I. There are currently 11 trains licensed with a total processing capacity of over 9700 LTPD. Of the 11 trains, 7 are retrofits and 4 are grass roots units.

## **REDUCING TOTAL SULFUR EMISSIONS**

Emission regulations continue to become more stringent. In the United States, SRU's with sulfur processing capacities of 20 LTPD and greater are required to achieve 99.9% minimum overall sulfur recovery. Most other countries do not require recoveries to be this high, but there is always interest in reducing overall sulfur emissions.

Product sulfur emissions contribute significantly to the total sulfur emissions from the sulfur complex, although these emissions are often not measured. Many plants recover pit sweep air using a steam driven eductor to pull atmospheric air into the vapor space above the liquid sulfur and discharge it to the thermal incinerator. Some plants, but many less, also recover vapors from truck and rail car loading operations using steam driven eductors. However, plants that do not recover H<sub>2</sub>S from pit sweep gas and product loading often resist recovery and routing these streams to the thermal incinerator because it will contribute to the total reported emissions. Of course, if the fugitive H<sub>2</sub>S is not recovered and sent to the incinerator, it is released directly into the atmosphere. Regulatory agencies are now beginning to focus more on emissions from product sulfur, particularly in the recovery of vapors from sulfur loading operations. GAA expects pit sweep air and loading vapor recovery will be required in the U.S. in the future.

An example of typical emissions from a relatively large U.S. refinery sulfur recovery complex is included in APPENDIX A. The example shows that the emissions from product sulfur can range from about 18% of the corresponding typical SRU tail gas unit to almost six times the emissions from an ultra-high recovery tail gas unit achieving 10 ppmv H<sub>2</sub>S in the absorber overhead. This example indicates that plant operators can significantly reduce the sulfur emissions from the SRU area by eliminating emissions from product sulfur.

Eliminating product sulfur emissions can be a challenge. Pit sweep air and recovered vapors from sulfur loading are normally available at very low pressures, and the sulfur compounds are in low concentrations. Earlier sulfur degassing processes may be implemented to slightly reduce the total emissions. ASRL<sup>9</sup> has indicated 30-40% of the feed H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> is converted to sulfur through direct oxidation in their laboratory experiments using a highly agitated, air-sparge apparatus operating at atmospheric pressure. If we assume 40% conversion of the total 300 ppmw H<sub>2</sub>S to sulfur for a typical atmospheric air-sparge type degassing system and 10 ppmw residual H<sub>2</sub>S is retained in the product with no release during loading, the total H<sub>2</sub>S release from degassing will be 191 lb/day. This is a slight reduction from 210 lb/day calculated in the APPENDIX A example.

If the D'GAASS Process, Figure 5, is implemented, sulfur emissions can be reduced further. In discussion of the Sulconam test results above, it was noted that the D'GAASS conversion of H<sub>2</sub>S to sulfur was consistently about 60%. This factor alone could reduce the example emissions by an additional 67 lb/day if the contactor overhead is routed to the incinerator. However, there are other steps mentioned in the previous section that can be utilized to reduce the total emissions. These include routing the overhead stream from the degassing contactor to the SRU main burner and operating the sulfur pit at the minimum level to reduce the natural degassing release of H<sub>2</sub>S into the sweep air, Figure 6.

Goar, Allison has conceived of and applied for a patent<sup>11</sup> for a process that can totally eliminate H<sub>2</sub>S emissions from product sulfur. The process utilizes the pressurized

waste stream from the D'GAASS contactor overhead as the motive fluid for the pit sweep air eductor. The discharge from the eductor can then be routed to the SRU burner. Sulfur compounds contained in the overhead stream and pit sweep air stream are converted to elemental sulfur in the SRU and recovered as additional product sulfur. Depending on the specific plant configuration and operating conditions, the total emission recovery system may be implemented in different process configurations. A few of the many possible configurations are discussed below.

The basic process configuration, Figure 7, utilizes a single stage eductor to induce sweep air flow and discharge to the degassing air and sweep air to the SRU burner. The air flow rates can be incorporated into the SRU combustion air calculations. The SRU combustion air blower requirements are reduced by the degassing and pit sweep air. All degassing air and sweep air piping is steam jacketed. The very low sulfur vapor concentration in the feed to the burner allows mixing directly with the combustion air stream, or it may be fed through a separate nozzle.

If the pressurized degassing air stream flow rate or pressure is too low to provide the total sweep air requirement at the required discharge pressure, it may be supplemented by a parallel compressed air driven eductor, Figure 8. The motive air for the supplemental eductor is supplied from the degassing process air compressor. Incrementally increasing the capacity of the process air compressor is a relatively minor increase in the overall unit cost.

When the SRU burner operating pressure is relatively high, it may be more economical to utilize a two-stage eductor system. The degassing air provides the motive fluid for the first stage, and the second stage is driven using compressed air from the degassing process air compressor, Figure 9.

In addition to the SRU burner, there are several other alternate locations for the combined degassing and sweep air streams. These include:

- The oxidizer step in an SO<sub>2</sub> recovery/recycle type SRU tail gas clean-up unit (Wellman Lord, ClausMaster, etc.). Sulfur compounds are oxidized to SO<sub>2</sub>, which are scrubbed from the resulting gas stream and recycled to the upstream SRU for recovery as liquid sulfur product.
- The oxidizer step in a sodium bisulfite (SBS) SRU tail gas clean-up unit. Sulfur compounds are oxidized to SO<sub>2</sub>, which are removed from the resulting gas stream by reaction with sodium hydroxide and sold to several types of chemical processing industries.
- The final reaction stage of an SRU that employs a direct oxidation process such as the SUPERCLAUS Process. The H<sub>2</sub>S is converted to sulfur and recovered; however, any SO<sub>2</sub> passes through the reactor to incineration.

The discharge from the eductor may also be routed to the thermal incinerator. This does not eliminate SO<sub>2</sub> emissions, but it does reduce the fuel requirement for the incinerator by the amount of energy required to heat the previously used motive steam to an exit temperature of over 1000°F. Reducing the incinerator fuel requirement lowers operating costs and reduces CO<sub>2</sub> emissions.

The above described eductors could be driven totally using compressed air from the process air compressor, but this would increase the total compressor capacity, would increase the compressor power, and would increase the total external air flow added to the above listed processes.

The major advantages of implementing the D'GAASS contactor overhead air stream as the motive fluid for the pit sweep eductor are:

1. Eliminating H<sub>2</sub>S emissions from product sulfur reduces total plant sulfur emissions.
2. Power consumption is minimized by eliminating the requirement for all, or a large portion, of compressed air from an external source for eductor motive fluid.
3. SRU combustion air blower power is reduced by supplying a portion of the required combustion air from pit sweep air and degassing overhead air stream.
4. Incinerator fuel requirement is reduced by the amount of energy required to heat the pit sweep eductor motive steam from about 300°F to 1100-1200°F exit temperature.
5. Emissions of CO<sub>2</sub> are reduced by reducing incinerator fuel usage.
6. Usage of treated water is reduced by eliminating the use of steam as motive fluid for the pit sweep eductor, which is discharged to the incinerator.
7. Operation of the system is simple.

The economics of implementing the above described D'GAASS contactor overhead air driven eductor for recovery of sulfur pit sweep air must be evaluated using local site factors. However, the reduction in sulfur and CO<sub>2</sub> emissions and potential fuel and steam utility savings can make the process very attractive to some plants.

## **SUMMARY**

1. The D'GAASS Process can successfully degas SRU liquid product sulfur to less than 10 ppmw residual H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> without using an internal bed of oxidation catalyst.

2. The maximum measured H<sub>2</sub>S concentration in the overhead air stream from the Sulconam D'GAASS Unit was less than 10% of the lower explosive limit of H<sub>2</sub>S in air during the October 2000 testing.
3. The yield of H<sub>2</sub>S/H<sub>2</sub>S<sub>x</sub> to sulfur in the D'GAASS Process is about 60% for the Sulconam operating conditions.
4. The D'GAASS Process is particularly well suited for retrofitting to existing SRU's since modifications to the existing sulfur pit are minimal, if any, and down time to install the process is very limited.
5. Total sulfur emissions can be reduced by utilizing the D'GAASS Process pressurized air waste stream as the motive fluid for a pit sweep eductor with the eductor discharge routed to the SRU burner or other processing that recovers the sulfur components.
6. Incinerator fuel usage is reduced if compressed air is used as the motive fluid for the pit sweep air eductor.

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8. Clark, P.D., McDonald, T.L., Lesage, K.L., "Studies on the Release of H<sub>2</sub>S from Liquid Sulfur". Proceedings of the 1992 GRI Liquid Redox Sulfur Recovery Conference, Austin, Texas, USA, October 4-6, 1992.
9. Clark, P.D., "Liquid Sulfur Degassing". *Sulphur*, No. 273, March/April 2001, p. 29.
10. "Process for the High-Pressure Degassing of Hydrogen Sulfide from Liquid Sulfur". US Patent No. 5,632,967.
11. "Process for the Reduction of Emissions from a Low-Pressure Process Waste Stream Using Another High-Pressure Waste Stream". U.S. Patent Application.

## APPENDIX A

### Case Basis:

- 500 LTPD recovered sulfur product
- Overall sulfur recovery is 99.9% (SCOT type tail gas unit)
- Sulfur product contains 300 ppmw H<sub>2</sub>S as produced
- Average sulfur rundown pit residence time, 1 day

Assumptions on emissions from sulfur product:

- Natural degassing in the sulfur pit is one half-life in 24 hours (ASRL<sup>1</sup>)
- Degassing during truck/rail car loading, severe agitation/splashing is ½ of one half-life

Calculations:

1. Sulfur emission from the tail gas unit is 1120 lb/day as sulfur (0.1% of 500 LT), which is equivalent to 1190 lb/day of H<sub>2</sub>S.
2. Total H<sub>2</sub>S in sulfur product is 336 lb/day (300 ppmw of 500 LT)
3. Natural degassing in pit releases 168 lb/day of H<sub>2</sub>S (½ of 336 lb/day)
4. Loading releases 42 lb/day of H<sub>2</sub>S (½ x ½ of 168 lb/day)
5. Total H<sub>2</sub>S emissions from sulfur product 210 lb/day
6. Sulfur product emissions are about 18% of the SRU tail gas unit emission

### Alternate Case:

- Goar, Allison design for Stretford type tail gas unit replacement with an amine unit designed for 10 ppmv maximum H<sub>2</sub>S overhead.
- Common amine unit for two upstream SRU's using moderate oxygen enrichment, total sulfur recovery 180 LTPD.

Calculations:

1. Design material balance overhead H<sub>2</sub>S from absorber (10 ppmv) is 0.0155 lb-mol/day (12.7 lb/day)
2. Equivalent H<sub>2</sub>S for 500 LTPD is 35.3 lb/day
3. Sulfur product emissions are about 6 times the SRU tail gas unit emission

### Note:

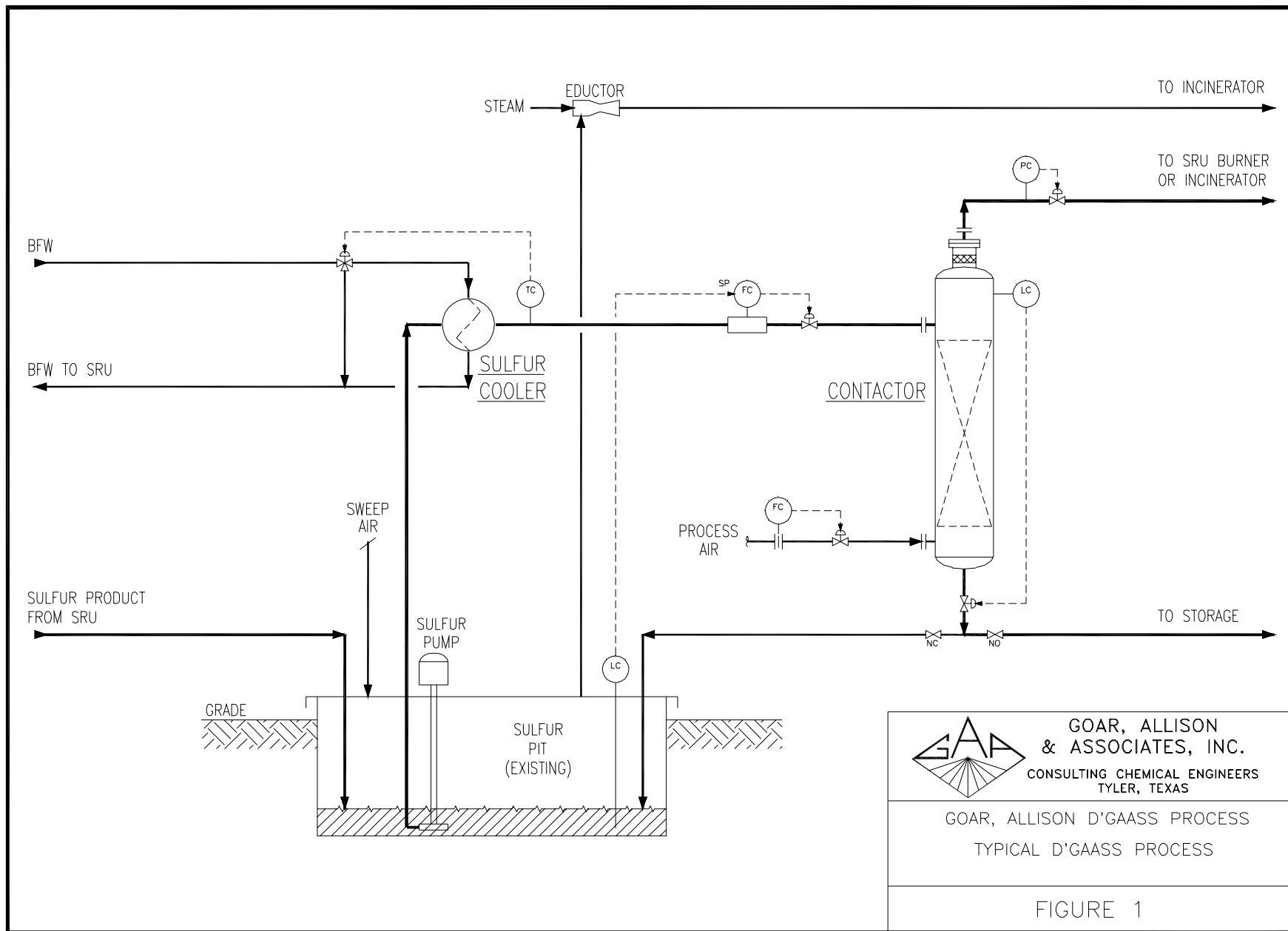
The above calculations are based only on H<sub>2</sub>S emissions. Sulfur vapor emissions from the sulfur product are ignored even though sulfur vapors are definitely emitted.

**Table I**  
**Licensed D'GAASS Process Units**

<b>COMPANY</b>	<b>Location</b>	<b>No. Trains</b>	<b>Train Capacity, LTPD</b>	<b>Start-up Date</b>	<b>Project Type</b>
Sulconam Inc.	Montreal East, Quebec	1	100	Sept. 1996	Retrofit
Suncor Energy Inc.	Ft. McMurray, Alberta	2	600	3 <sup>rd</sup> Qtr. 2001	1-Retrofit 1-Grass Roots
Tengizchevroil LLP	Tengiz, Kazakhstan	4	1340	3 <sup>rd</sup> Qtr. 2001	Retrofit
Shell Canada Limited	Ft. Saskatchewan, Alberta	1	1150	2002	Grass Roots
Syncrude Canada Ltd.	Ft. McMurray, Alberta	1	1700	2002	Grass Roots
NMPRC	Yokohama City, Japan	1	110	2004	Grass Roots
Jupiter Sulphur, LLC	Ponca City, Oklahoma	1	165	4 <sup>th</sup> Qtr. 2001	Retrofit

Total degassing capacity >9700 LTPD.

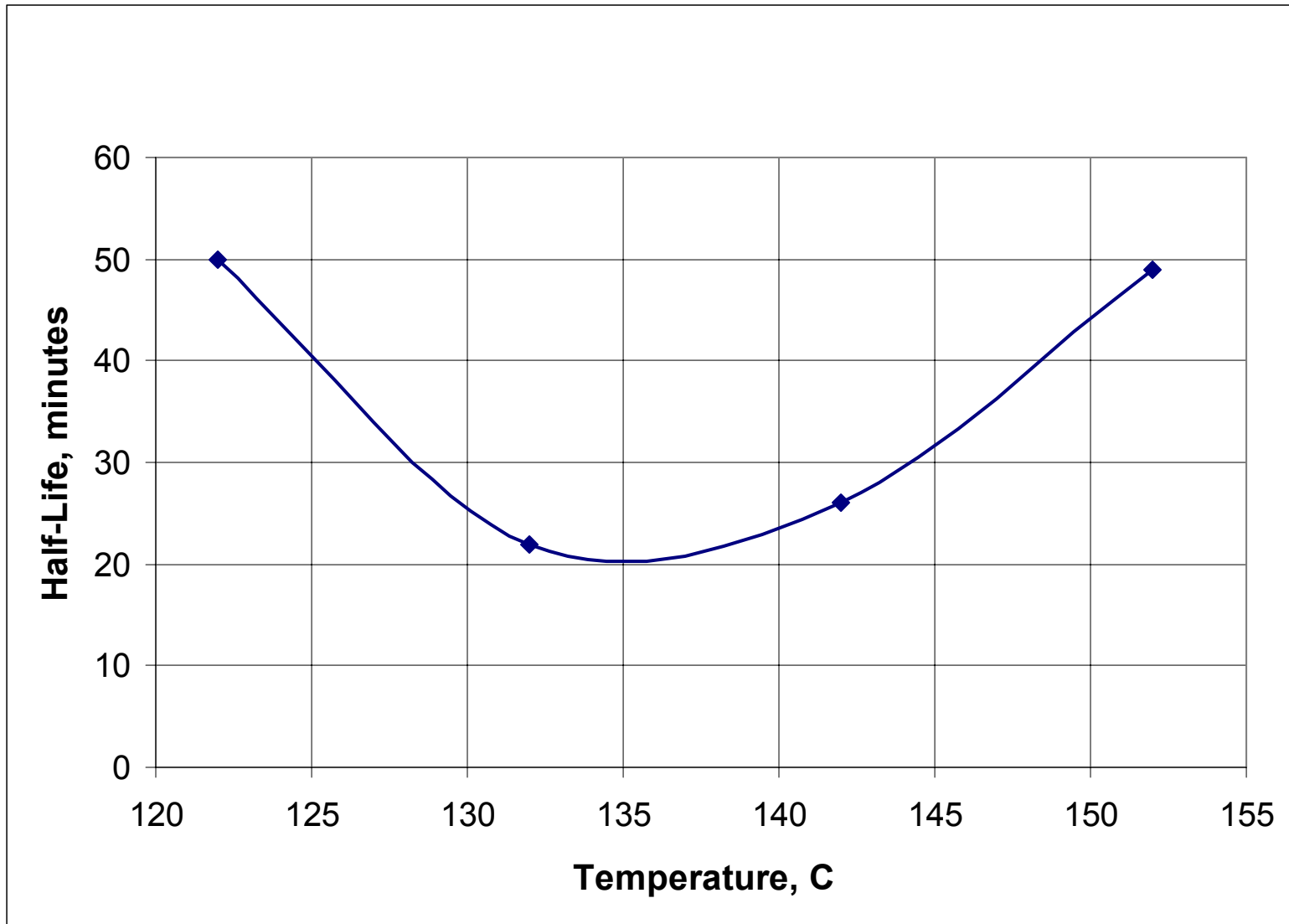




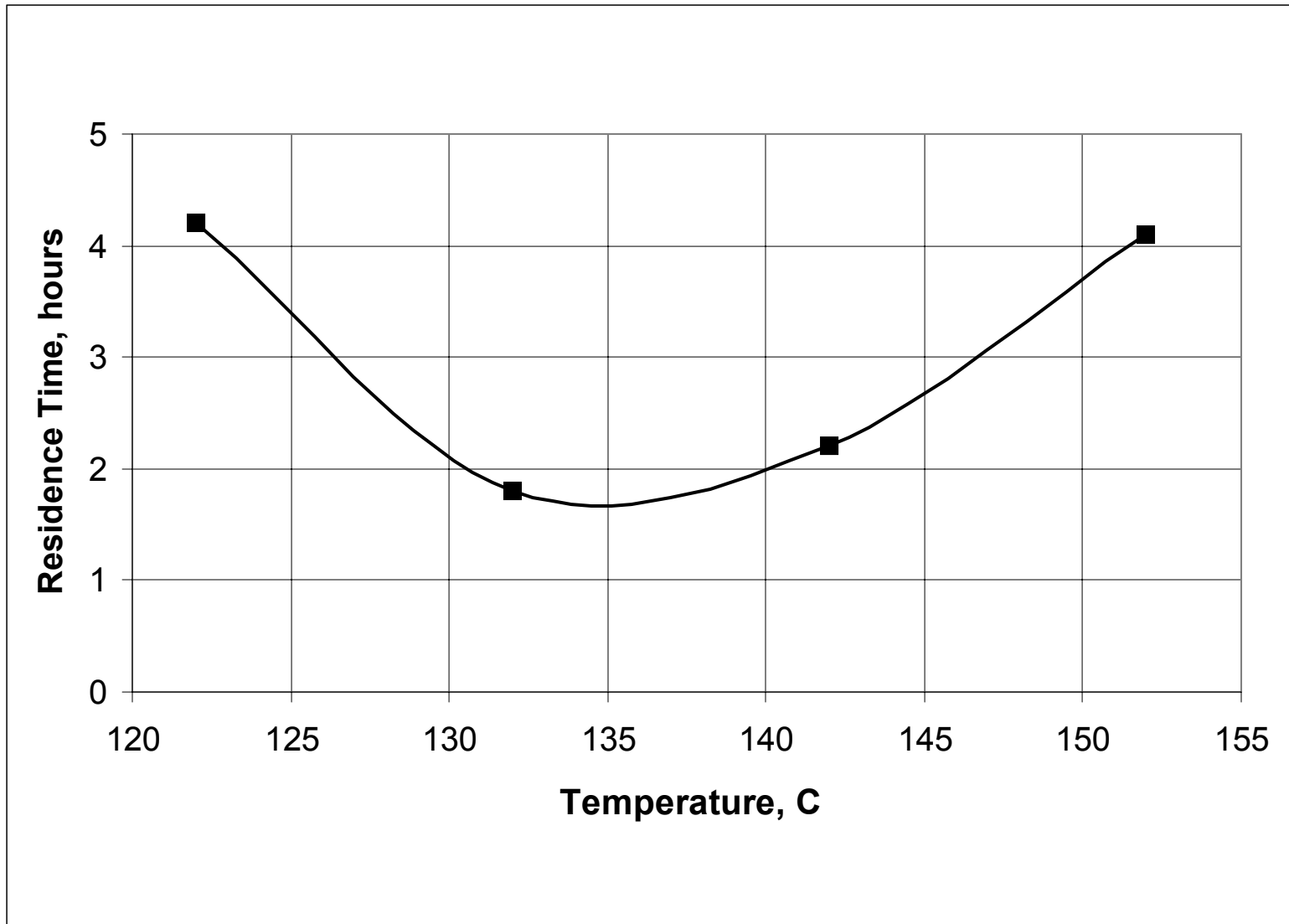
GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS  
TYPICAL D'GAASS PROCESS

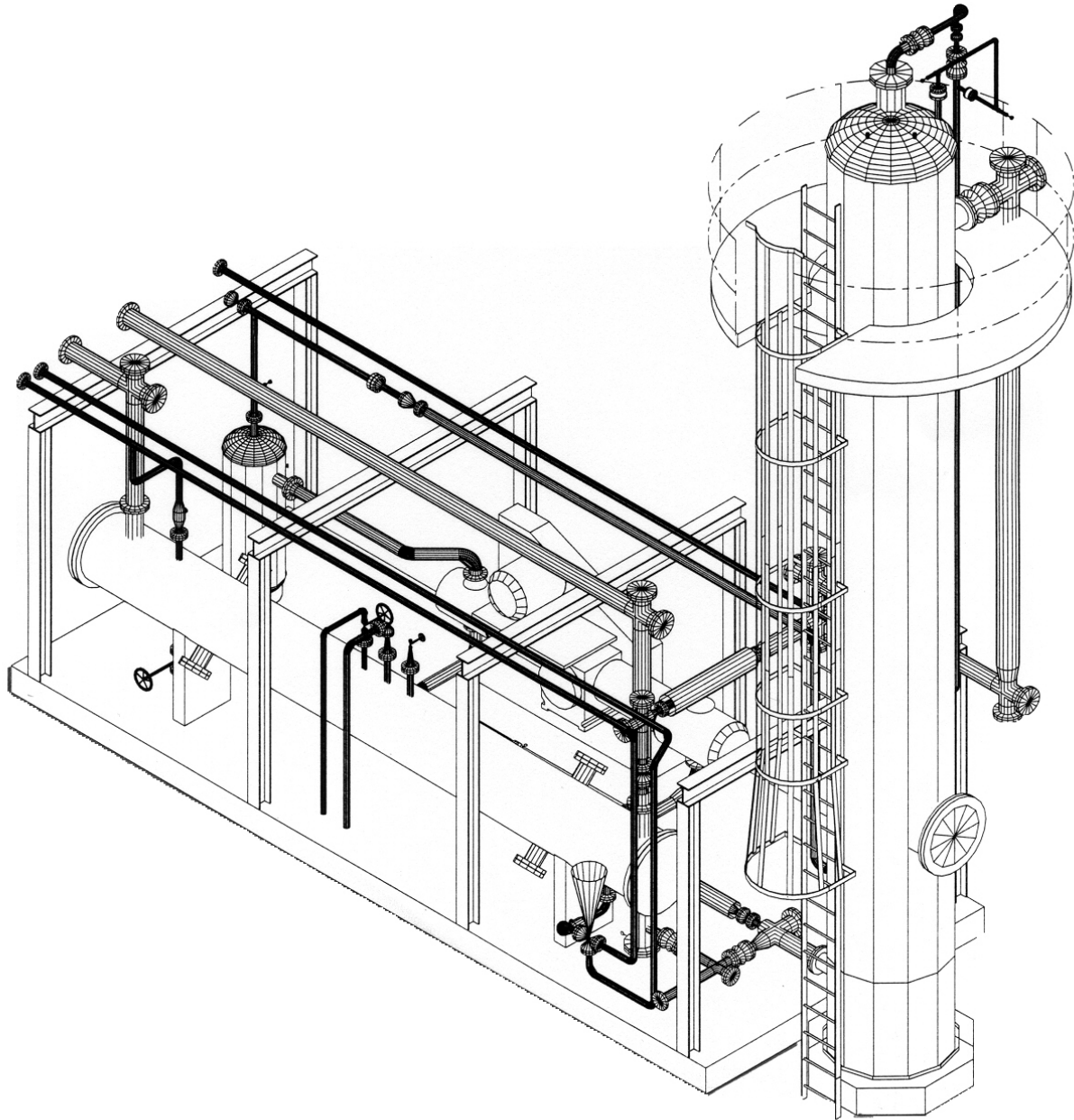
FIGURE 1



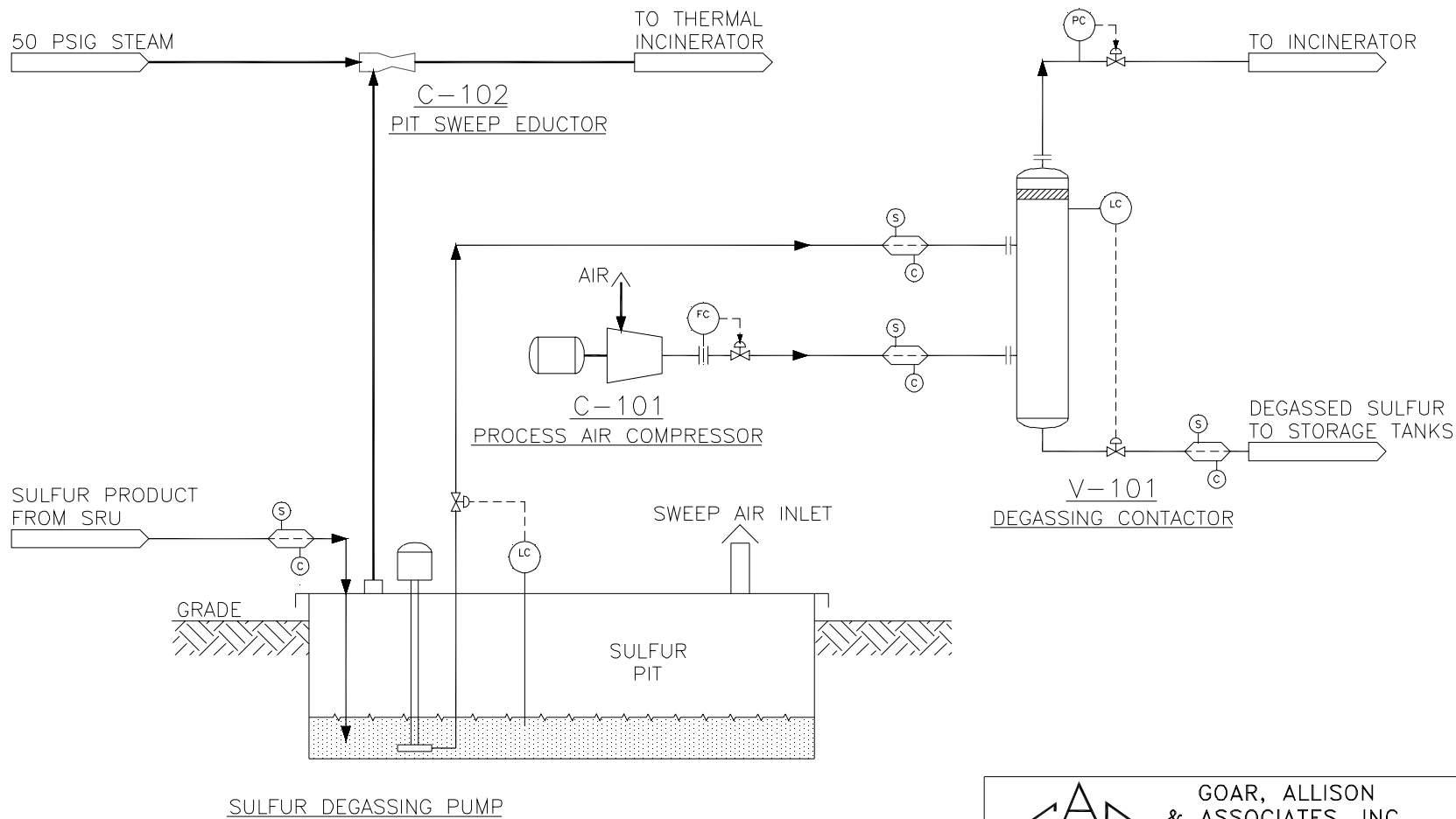
**Figure 2, Effect of Temperature on Sulfur Degassing Half-Life**



**Figure 3, Residence time Required to Reduce H<sub>2</sub>S from 100 ppmw to 6.25 ppmw**



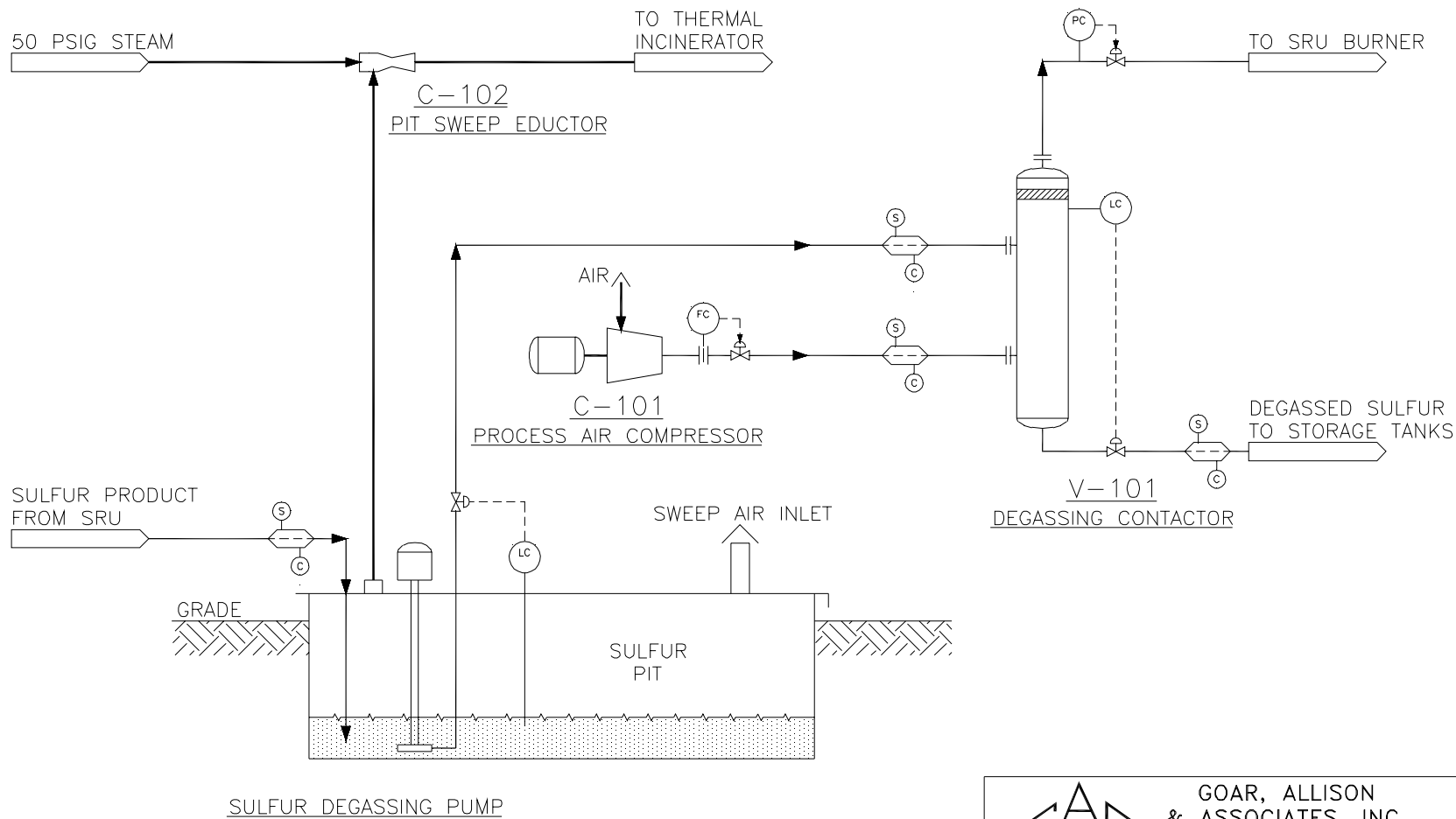
**FIGURE 4, MODULAR D'GAASS SULFUR DEGASIFICATION  
UNIT**



GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS  
TYPICAL D'GAASS PROCESS  
CONFIGURATION

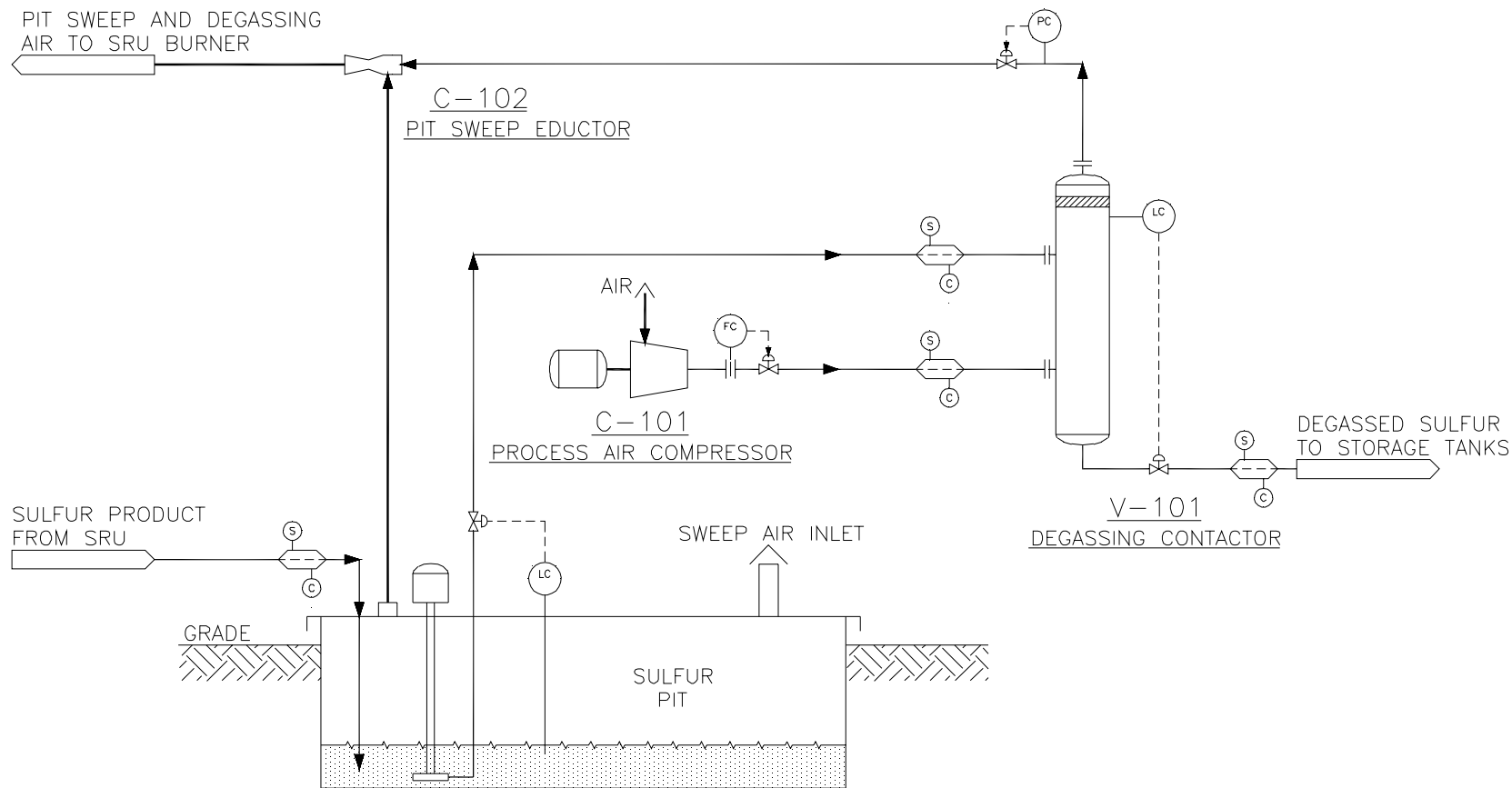
FIGURE 5



GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS  
ALTERNATE D'GAASS PROCESS  
CONFIGURATION

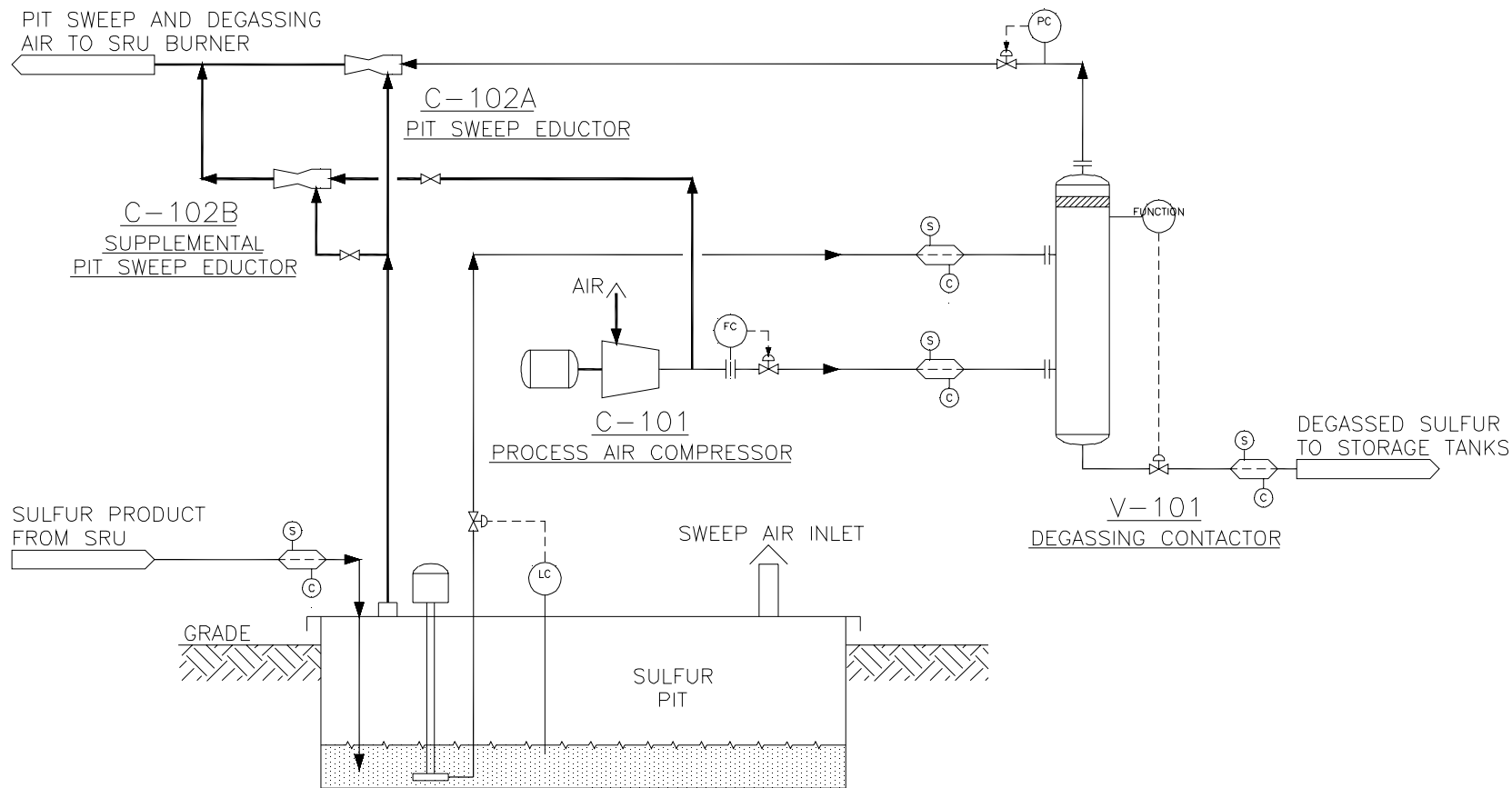
FIGURE 6



GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS  
WITH SINGLE STAGE  
PITSWEEP EDUCTOR

FIGURE 7



SULFUR DEGASSING PUMP

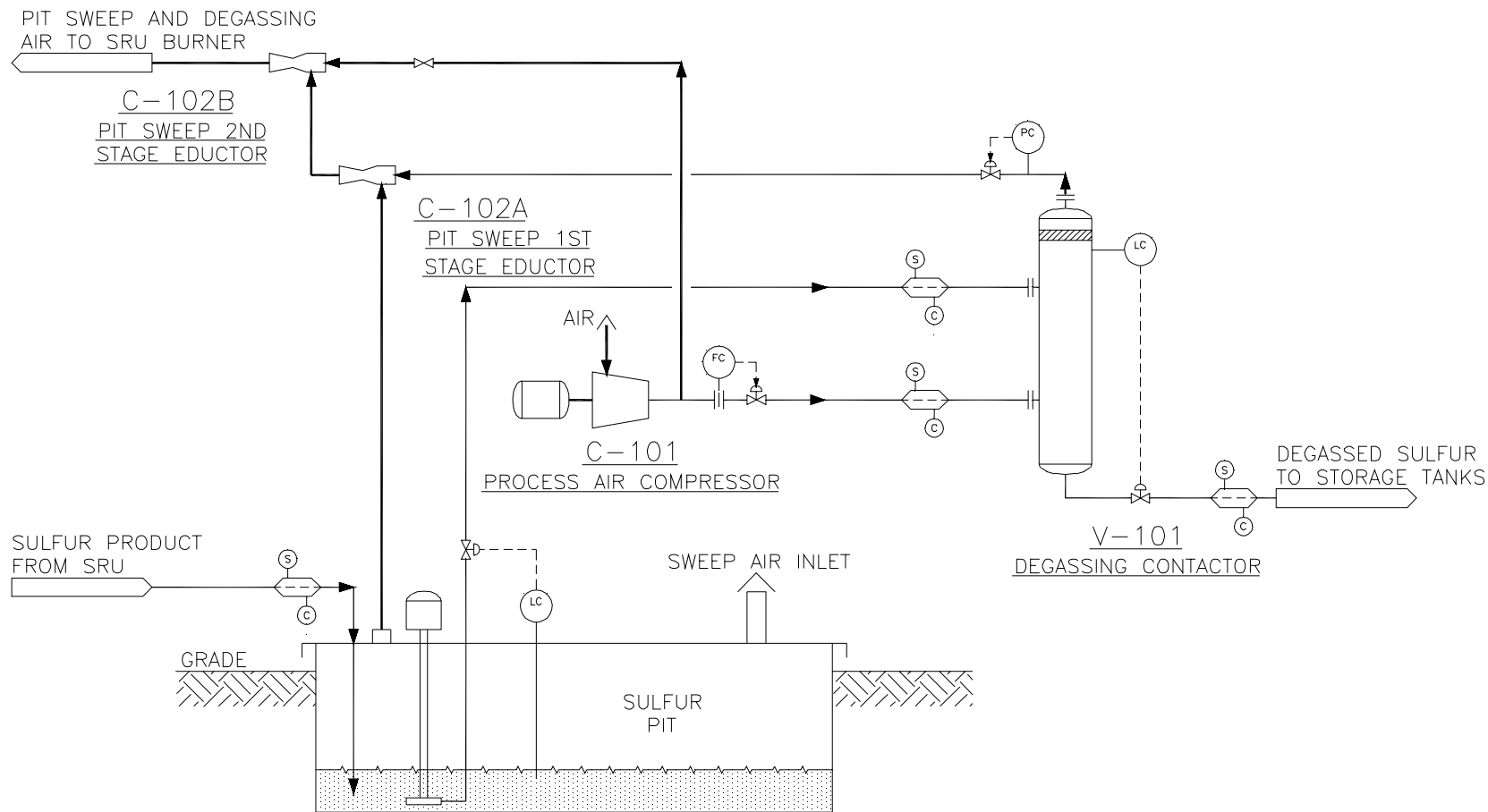


GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS  
WITH SINGLE STAGE PIT SWEEP EDUCTOR  
AND PARALLEL SUPPLEMENTAL EDUCTOR

FIGURE 8





SULFUR DEGASSING PUMP



GOAR, ALLISON  
& ASSOCIATES, INC.  
CONSULTING CHEMICAL ENGINEERS  
TYLER, TEXAS

GOAR, ALLISON D'GAASS PROCESS

WITH TWO STAGE  
PIT SWEEP EDUCTOR

FIGURE 9