

A NEW ERA IN SULFUR DEGASSING – WE HAVE TOUCHDOWN

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ABSTRACT

The modified Claus process is used to convert various sulfur compounds recovered from crude oil and gas into elemental sulfur. A by-product of this process is that H₂S is absorbed into the liquid sulfur. This explosive and poisonous gas makes storage and handling both complicated and dangerous. A new degassing technique uses a solid, packed bed catalyst and a vapor stream to rapidly remove the dissolved H₂S from the liquid sulfur.

The first commercial installation of this technology occurred in gulf coast refinery and started operation in June 2018. This unit has been providing continuous sulfur degassing at a rate of 325 long tons per day.

This ICON™ Degassing System can use a variety of vapor streams for the stripping gas and works at any operating pressure. This flexibility allows the system to be configured in a multitude of arrangements depending on the needs of each specific installation.

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Background

Need for Degassing

Crude oil and gas contain naturally-occurring sulfur compounds. Sulfur in the end-product will cause practical and environmental problems; thus, the bulk of this sulfur must be removed. Various processes are used to convert and/or remove the sulfur compounds, the most common compound being hydrogen sulfide (H_2S). One process, the modified Claus process, is almost universally used to convert H_2S into elemental sulfur. An unintended by-product of the Claus process is incorporation of unreacted H_2S into the elemental sulfur being produced.

Mixtures of H_2S and air have two unfortunate properties; the mixture can be both poisonous and explosive. Control of H_2S is therefore a high priority for refineries and gas plants. Extended exposure to air-born H_2S at concentrations as low as 5 parts per million by volume (ppmv) is likely to cause respiratory irritation and other symptoms. Extended exposure to concentrations as low as 100 ppmv can cause death. Concentrations of 500 ppmv result in death within minutes.

H_2S in sulfur is not stable and will gradually migrate into any available vapor space. This process is relatively slow, thus emission of H_2S from the sulfur remains a concern for all the downstream sulfur storage, handling, and transportation. H_2S is explosive starting at concentrations of roughly 4 percent by volume (%vol). Thus, accumulation of H_2S in the vapor space of storage vessels is also a significant concern.

This combination of H_2S /air mixtures being both poisonous and explosive leaves sulfur facilities with few good choices for safe handling. Storing the sulfur in air-containing vessels, tanks, or concrete pits creates an explosion concern. Venting the storage vessels and transfer points to remove the evolved H_2S creates an exposure concern. The general industry consensus at this time is (1) to aggressively sweep/vent sulfur storage containers to prevent H_2S accumulation and (2) to treat the vent gas via incineration or Claus processing to prevent exposure and environmental damage. But personnel exposure remains a concern throughout the sulfur handling process; fresh air breathing apparatus and aggressive venting are commonly used in areas with potential exposure to sulfur.

Sulfur degassing to remove the H_2S has long been used at various points throughout the various sulfur industries. In the past, degassing was typically performed only as a necessary step for forming and transporting sulfur. But over time, degassing for safety reasons has become more common. Similarly, there is a trend to move the degassing process further upstream so that the safety benefits are provided earlier in the process. For this reason, refineries and gas plants have been adding degassing equipment to their facilities in greater number.

Where degassing is used, the typical target is 10 parts per million by weight (ppmw) H₂S or less in the sulfur. At this level, the equilibrium concentration limit of the vapor space is less than 4%vol H₂S. Thus, it is not physically possible to achieve an explosive H₂S/air mixture in a storage vessel. It should be noted however, that fires are still possible as the sulfur itself is flammable. Also, the H₂S concentration in the vapor space may still exceed lethal levels. So while the concentration of H₂S near and around sulfur handling facilities is greatly reduced, some hazard does still remain.

The ICon™ (In-situ Claus Optimization) degassing technology seeks to bring new degassing capabilities and options to refineries and gas plants. ICon has a unique ability to be installed immediately after the Claus unit sulfur condensers – essentially eliminating the need to store undegassed sulfur. ICon also provides greater configuration flexibility to better accommodate the varying restrictions inherent in retrofit applications.

Development of ICon™ Sulfur Degassing

The development of the ICon degassing system is a joint effort between Phillips 66 and CSI-Ametek. The partnership started in 2013. Phillips 66 has been providing chemistry expertise and a platform for testing at one of their refineries. CSI has been providing process and equipment engineering and fabrication.

Field testing was performed at a Phillips 66 refinery from 2015 to 2017. Testing had to be performed with an active SRU so that all the correct process streams could be used. While the prototype degassing contactor was not full-scale, it was large enough to enable accurate scale-up for full-scale design.

The first commercial ICon degassing system was purchased by a gulf coast refinery and started operation in 2018. More details regarding this installation are provided later in this paper.

Theory of Operation

Description of Chemistry

The H₂S contained within the liquid sulfur exists in two chemical forms: Dissolved H₂S and chemically-bound H₂S.

Dissolved H₂S is simply H₂S molecules mixed in with the liquid sulfur molecules. This form of H₂S can be removed readily by agitation. When liquid sulfur containing dissolved H₂S is exposed to a vapor with a low H₂S concentration, it readily leaves the liquid in favor of the vapor. The rate of removal is driven primarily by the sulfur surface area exposed to the vapor. Spraying the sulfur through a vapor space or sparging the sulfur with a vapor stream are both effective methods of removing dissolved H₂S. All existing degassing technologies use some form of sparging, spraying, or other agitation with vapor.

Chemically-bound H₂S is more challenging to remove. Above 159°C (318°F) sulfur rings will open up due to homolytic bond scission to form a chain of sulfur atoms with radicals at both ends. During the Claus process, these radicals react with the available H₂S to form hydrogen polysulfide

(H_2S_x). These polysulfides likely exist in a variety of sulfur chain lengths and quite possibly as $HS_x\cdot$ radicals. Below $159^\circ C$ ($318^\circ F$), these chains are unstable and will slowly break down into elemental sulfur and H_2S . But this process is very slow and is equilibrium-limited by the surrounding dissolved H_2S .

The ICon™ degassing approach accelerates the breakdown of the hydrogen polysulfides by simultaneously using a catalyst and a sparge vapor. The catalyst accelerates the decomposition of the hydrogen polysulfides; the sparge vapor removes dissolved H_2S . While these steps are distinct, they occur in parallel. The decomposition of the hydrogen polysulfides appears to be limited by the presence of dissolved H_2S in the sulfur. Thus, continual removal of dissolved H_2S is needed to facilitate the decomposition reaction. This ‘1-2-punch’ approach fully degasses the sulfur with less than 5 minutes residence time.

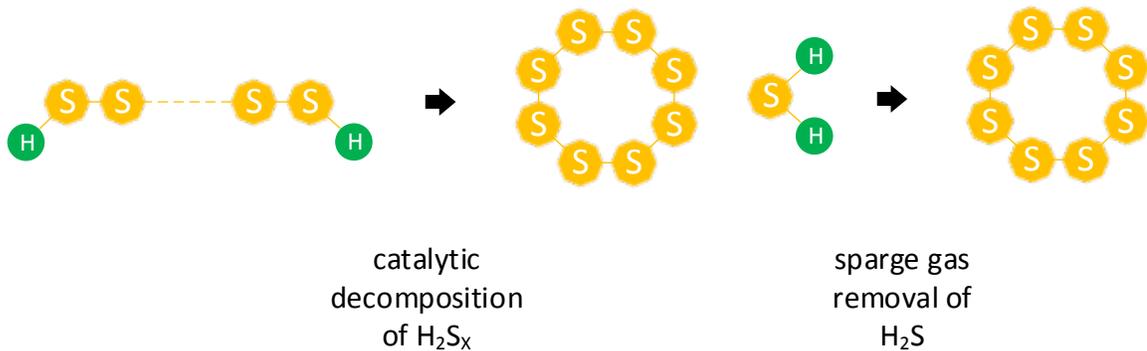


Figure 1 – Degassing Chemical Reaction

Impact of Temperature

Sulfur freezes at $120^\circ C$ ($248^\circ F$). Liquid sulfur above this temperature nominally takes on a molecular form analogous to the shape of an octagon comprised of eight sulfur atoms. But at temperatures above $159^\circ C$ ($318^\circ F$), these octagons open up into diradical chains, which combine to form polymer chains. The ‘friction’ between these polymer chains accounts for the sharp rise in viscosity that takes place at $159^\circ C$.

Liquid sulfur begins to form in the sulfur condenser following either the thermal or catalytic conversion stages. Most of the sulfur condenses at a temperature well above the transition point described above. Thus, diradical sulfur chains will form as condensed sulfur rings open up. Hydrogen sulfide reacts with these open diradical polymer chains forming hydrogen polysulfides. This is significant for a couple reasons. First, it creates the need for degassing as discussed above. Second, the ‘capped’ chains are prevented from combining into longer chains; this effectively dampens the viscosity spike observed in elemental sulfur. The magnitude of the spike is reduced, and the peak of the spike occurs at a hotter temperature. This is significant for SRU design as sulfur from the first several condensers in a typical Claus unit is hotter than $159^\circ C$, and yet readily flows through the run-down lines to the pit.

This is also significant for degassing as hydrogen polysulfides above $159^\circ C$ will not readily break down into elemental sulfur and H_2S . At these higher temperatures the sulfur ring scissions cause

diradical chain formation to occur readily. Removing H₂S from the sulfur under these conditions will result in immediate joining (polymerization) of the newly formed diradical sulfur chains into highly viscous sulfur. Any rings that remain 'open' will also eagerly re-join with an H₂S molecule. Only at temperatures below 159°C will the sulfur resume its stable ring structure eliminating the reactive diradicals. Thus, degassing is best accomplished at temperatures below 159°C.

Design of the Contactor

The degassing reaction described above occurs in the ICon degassing contactor. To support the reaction, the contactor must be configured based on the following key criteria:

- The sulfur must be sparged in the presence of the catalyst so that the H₂S is removed as it is formed.
- The sparge vapor rate must be high enough to provide adequate 'mixing' to promote the interaction of sulfur, vapor, and catalyst.
- The sparge vapor must contain a sufficiently low concentration of H₂S to enable degassing to below 10 ppm H₂S content in the sulfur.
- The sulfur must be provided at a temperature below 159°C.
- The sulfur must have adequate residence time in the contactor.

To achieve the above criteria, the ICon contactor uses a packed-bed catalyst configuration. The liquid sulfur moves through the catalyst in a horizontal direction. The 'sides' of the catalyst zone adjoin an inlet and an outlet plenum that provide even distribution of sulfur flow through the catalyst. The sulfur leaves the contactor by overflowing out of the outlet nozzle; the liquid level is set by the outlet nozzle elevation.

The sparge vapor moves up through the catalyst in the vertical direction. The bottom of the catalyst zone uses a sparge plate to create a uniform vapor flux through the catalyst. The sparge vapor rate and the sparge plate must be configured such that the upward flow of vapor through the orifices prevents sulfur from leaking into the vapor pocket below the plate. Any sulfur that entered the vapor pocket would not be fully degassed and may interfere with the vapor distribution. Vapor leaves the contactor through an outlet nozzle at the top of the vessel above the catalyst.

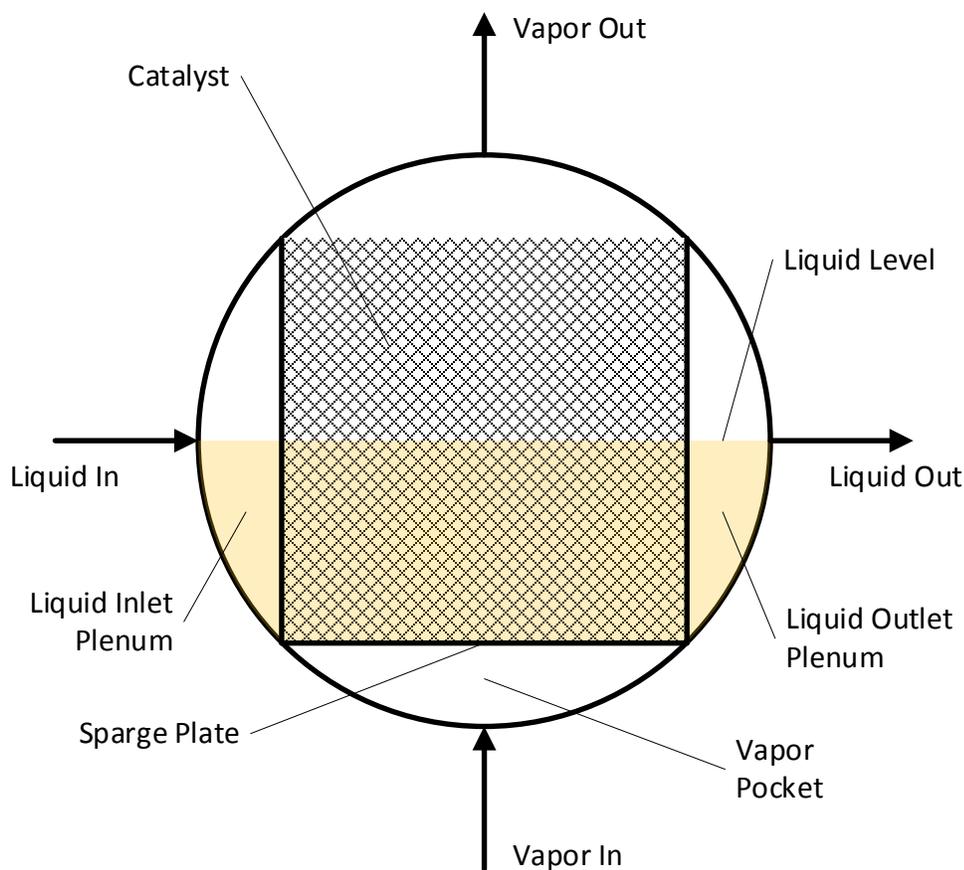


Figure 2 – ICon degassing contactor cross-section

First Commercial Unit

Technology Selection

In 2017 a major gulf coast refinery chose to install an ICon™ degassing system on a 325 long ton per day (LTPD) SRU. The refinery wanted to employ sulfur degassing for three reasons:

First was concerns about the environmental impact of H₂S emissions from sulfur storage. Some of this emission was being captured and processed. But some emission was thought to be unintentionally escaping due to lack of sophisticated recovery equipment.

Second was concerns about operator exposure during sulfur handling, particularly at sulfur loading. The refinery was very attentive to operator protection measures and was employing those measures successfully. Nevertheless, reducing the available H₂S was considered more reliable than PPE as a protection measure.

Third was concerns about the pit sweep air system reliability. Pit sweep air systems are vulnerable to several failure modes: Plugging with solid sulfur, corrosion of the piping due to the sulfur/water mixture in the process, and failure to create adequate draft due to poor

pit lid seals are all common problems. The refinery had wrestled with these issues in multiple sulfur pits and was eager to find a more reliable solution.

The ICon degassing system was chosen because it provided an advantage in a few key areas:

Pre-Pit: ICon was the only viable technology that provided the option of degassing the sulfur prior to the sulfur pit. Converting all or a portion of the pit to degassed sulfur storage was the most effective way of addressing the pit sweep system reliability concerns.

Installation: This particular Claus unit already had the necessary tie-points installed in the process piping. Thus, the ICon degassing system could be installed and tied-in without disrupting operation of the SRU.

Cost: The ICon degassing system was the lowest cost solution. This was especially true when considering the cost of future pit sweep system upgrades and maintenance – a cost that is greatly reduced when degassing prior to the pit.

Performance

The degassing system started operation in June 2018 and has been operating continuously as of the writing of this paper (December 2018). The sulfur is being continually degassed from an inlet concentration range of 350 to 365 ppmw to an outlet concentration of less than 10 ppmw H₂S. Figure 3 shows the H₂S concentration of the degassed sulfur exiting the degassing contactor over time. The data shown includes sulfur flow rates ranging from 250 to 400 LTPD as well as some variation in the vapor sparge rate and other operating parameters.

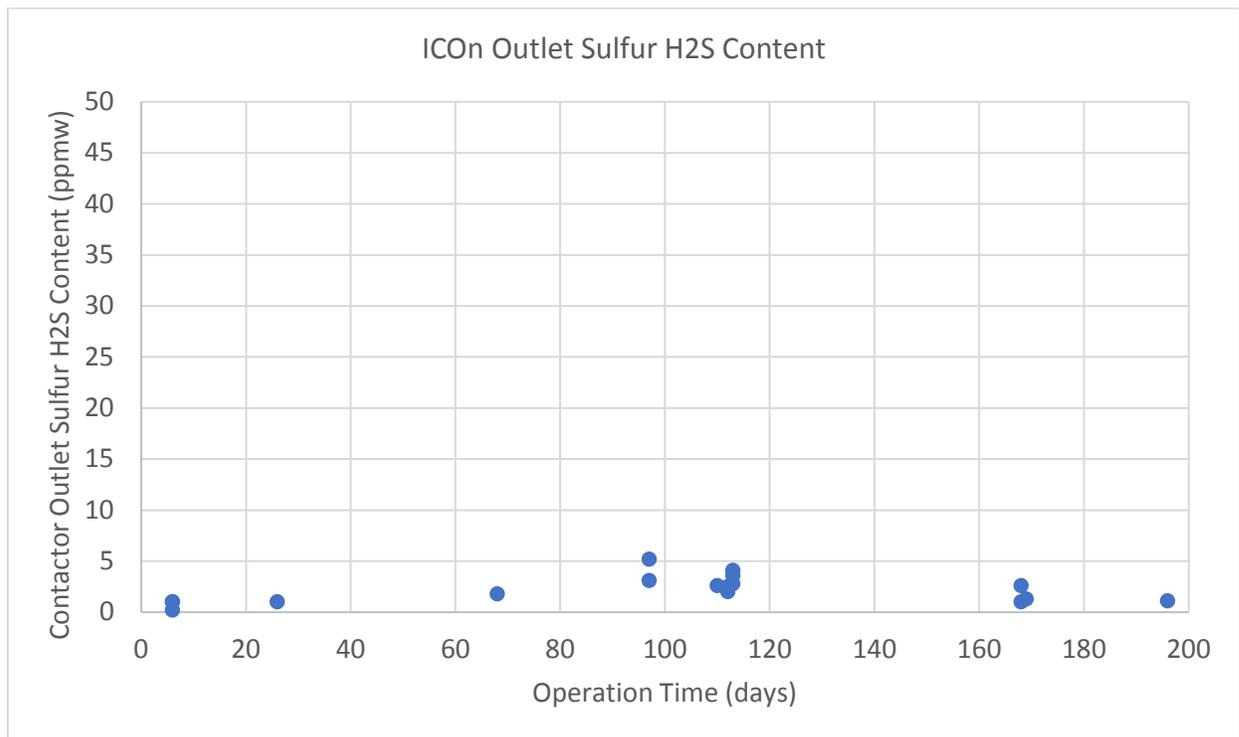


Figure 3 – Commercial Unit Performance Over Time

The degassing contactor was fitted with intermediate sample points so that the rate of degassing could be tracked as the sulfur flows through the contactor. The reaction rate closely follows a first-order chemical reaction. Figure 4 shows the H₂S content of the molten sulfur versus the equivalent residence time associated with the various sample points.

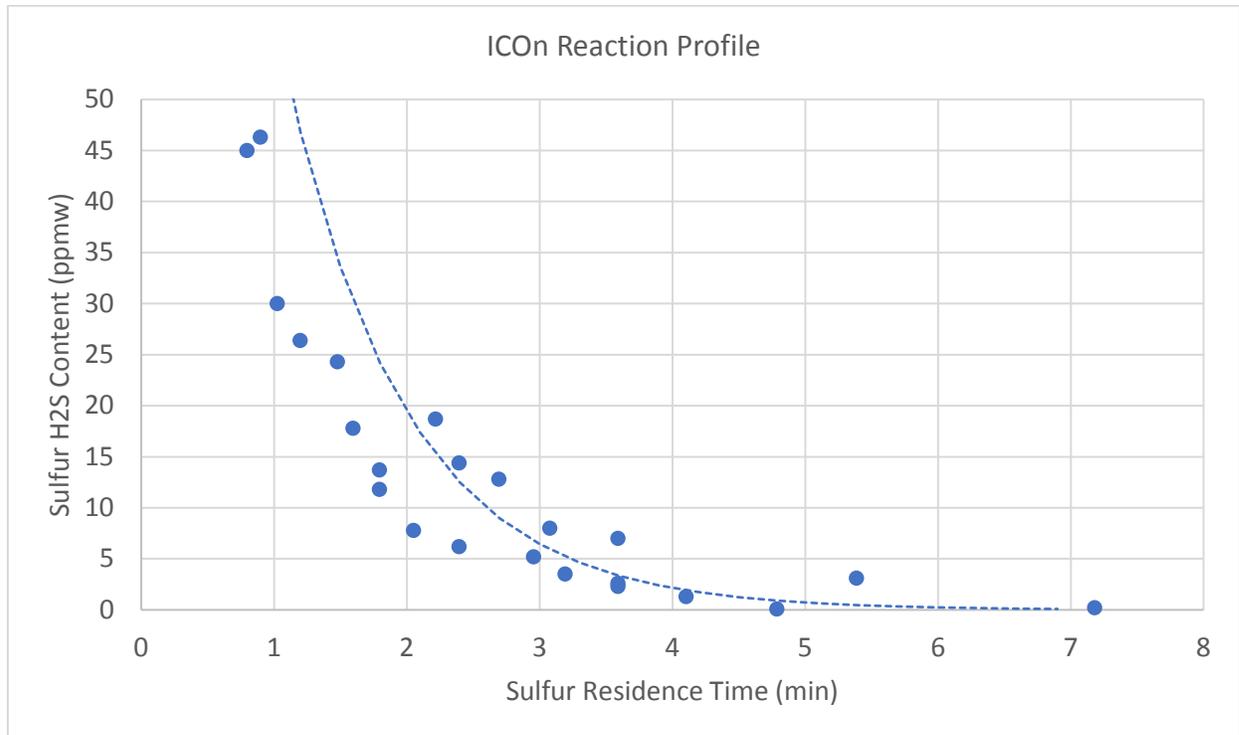


Figure 4 – Commercial Unit Reaction Profile

Configuration

The ICOOn degassing system can be arranged in many different configurations depending on the needs of the specific plant. These configuration options will be discussed in detail later. The configuration used for the gulf coast refinery installation is summarized in figure 5.

On the liquid-side, the existing sulfur pit already contained weirs and functioning pumps. Rather than tie into the existing run-down lines, the end user chose to tie into the outlet of an existing pit sulfur pump. This configuration provided the benefits of greater simplicity and lower cost. The disadvantage was that the pit would still contain some un-degassed liquid sulfur, but the volume of un-degassed sulfur was greatly reduced from prior to installation of the ICOOn system.

On the vapor side, 150 psig steam sparge gas is being let down to the contactor operating pressure of roughly 5 psig. The vapor returns to a tie-in located near the process gas inlet of the 4th condenser. This was a convenient, pre-existing tie-in location; alternate locations may have some process advantages as will be discussed later.

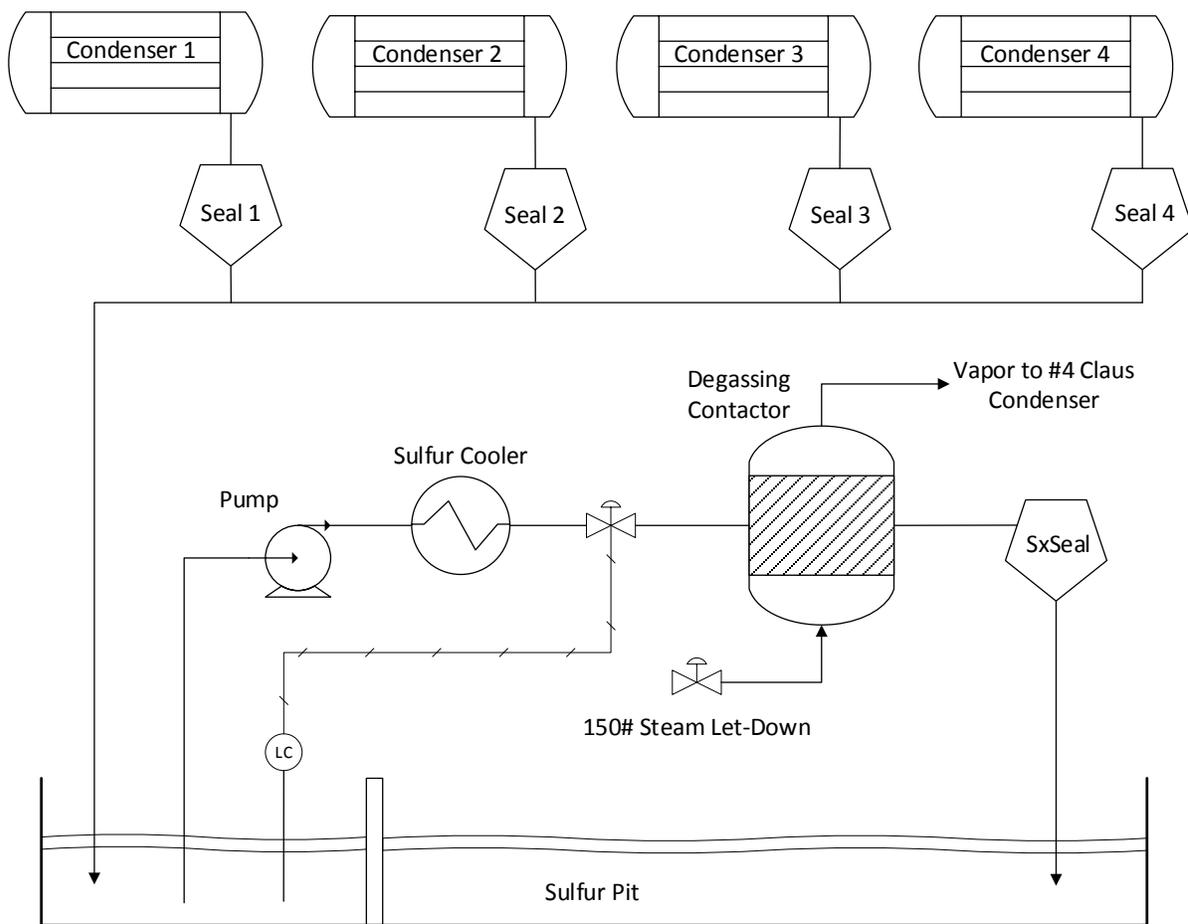


Figure 5 – Commercial Unit PFD

With the sulfur being pumped to the contactor as illustrated above, it is possible to feed a single ICOn contactor with sulfur from multiple Claus trains. This is a configuration that the refinery expects to utilize on future Claus units. This, first ICOn installation was restricted to a single Claus unit. This was done so that the technology could be evaluated and refined on a more isolated installation. Future installations may also replace the pits on some Claus units with collection headers to further reduce pit emissions potential. On the vapor side, it is expected that the same steam sparge configuration will continue to be used.

Lessons Learned

Not shown in the PFD above is a steam ejector that was part of the original design. The original design used Claus tail gas as the sparge vapor and an ejector to pull the vapor through the contactor. When operating in this configuration, accumulation of liquid sulfur in the tail gas analyzer was observed. It was found that sulfur droplets picked up in the contactor were being atomized by the ejector. The resulting sulfur ‘mist’ was very fine; it did not condense out in the Claus condenser and was not captured by the condenser’s demister. This sulfur ‘mist’ passed through the Claus unit and increased the load on the tail gas treating unit.

Switching to steam sparge gas eliminated the need for the ejector which eliminated the formation of sulfur ‘mist’. Several other configurations could be used to avoid the sulfur mist issue including

vapor return upstream of a Claus re-heater or the use of a demister pad prior to the steam ejector. For this application, switching to steam sparge was the most expedient and least costly solution.

Process Impact

The switch from process sparge to steam sparge provided a unique opportunity to evaluate the Claus unit performance for both configurations. Both were simulated using commercial process simulation software ProTreat®. The simulation was a risk evaluation measure to address the concern that the additional water vapor may negatively impact the Claus reaction equilibrium.

In both cases, simulations did not show a significant impact on overall recovery due to increased water vapor. Brimstone Sulfur Testing Services was employed post-installation to confirm the effect of the additional water vapor added to the system. The effect on overall Claus recovery, as predicted by the ProTreat model, is shown in figure 6.

Configuration	% S Recovery w/o degassing	% Recovery w/degassing
Steam sparge	97.282	97.225
Tail gas sparge with ejector	97.210	97.160

Figure 6 – Impact of Degassing System on Recovery

Considerations for Future Installations

The ICon™ degassing system is unprecedented in its flexibility. It can accept/deliver both the gas stream and the liquid stream from/to a large variety of locations. As shown in figure 7 and described below, there are several viable options for each stream:

Vapor Source: The degassing contactor can use nearly any sparge vapor source provided it does not contain too much H₂S. It is expected that steam, nitrogen, Claus process gas, and air will be the common vapor source choices.

Vapor Destination: The vapor can be sent to a variety of locations including an incinerator, the Claus furnace, a mid-point in the Claus plant, or a tail gas treating unit. Of course, the composition of the vapor must be considered; air sparge, for example, could not be sent to a mid-point in the Claus plant without upsetting the Claus reaction. Also important to consider is the operating pressure of the vapor destination. The contactor operating pressure will generally need to be slightly higher than that of the destination. Depending on the sulfur source, a lower contactor pressure may be advantageous (see next paragraph). An ejector can be used to lower the contactor pressure by several psi if needed.

Liquid Source: The un-degassed sulfur can be pumped into the contactor or, if coming from an elevated pressure source, can be delivered without a pump. Common sources utilizing a pump are expected to be the sulfur pit or sulfur storage. As the Claus condensers operate at elevated pressure (typically between 2 and 8 psig), sulfur can be pushed from the condensers to the contactor via gravity and the natural pressure differences between the equipment. This ‘natural flow’

configuration requires careful hydraulic design of the run-down area and may not work with all SRUs depending on the operating pressures and equipment elevation.

Liquid Destination: Degassed sulfur overflows out of the contactor outlet. Thus, draining from the contactor to low-elevation sulfur storage, such as a pit, is very simple. If the degassed sulfur needs to be directed to elevated sulfur storage, a pump will likely be required at the exit of the contactor.

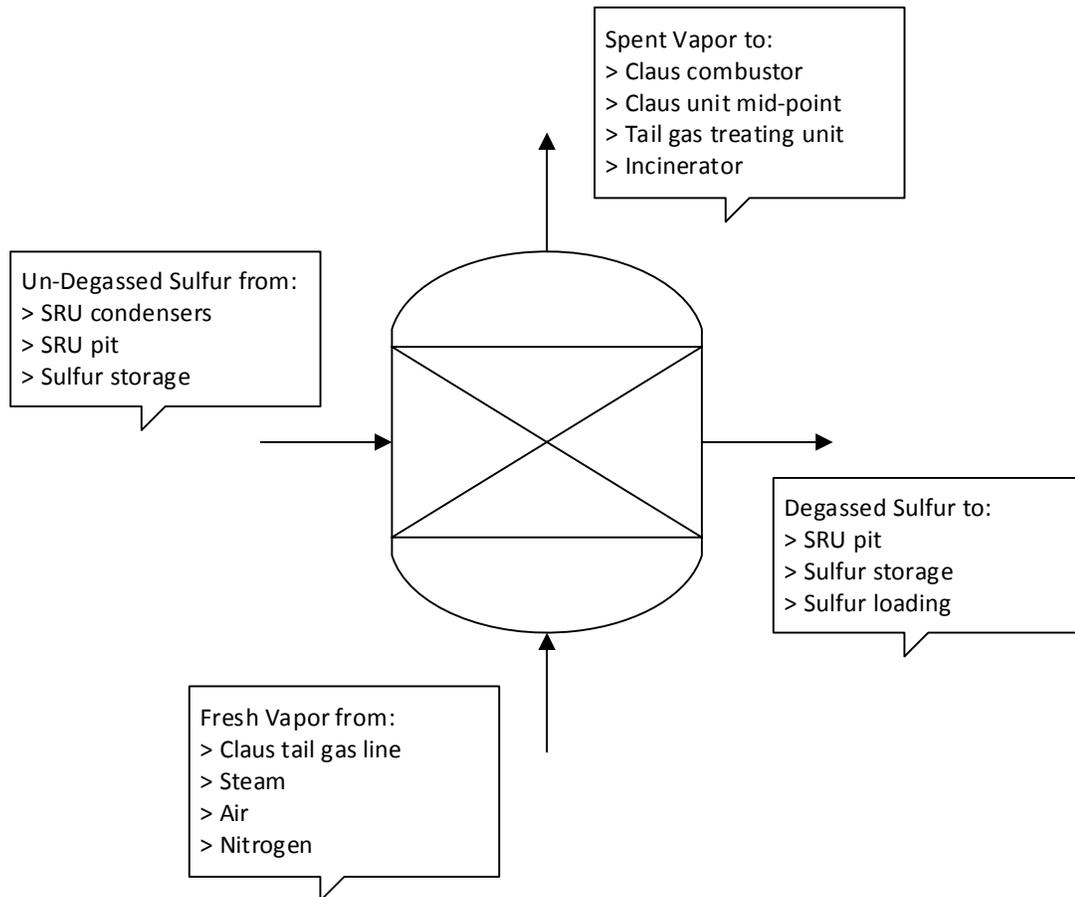


Figure 7 – Vapor and Liquid Stream Options

Example configurations

A myriad of different configurations are possible. The following process flow diagrams illustrate some of the more unique configurations available. Many other configurations beyond these are possible.

Figure 8 shows a configuration in which the degassing contactor is installed in-line with the sulfur run-down lines. No pump is required, and the sulfur is degassed before draining into the pit. The sulfur cooler is a kettle style cooler with the sulfur in the shell-side and the boiling water in the tube-side. Heat transfer with the sulfur is achieved via natural convection of the sulfur around the tubes which results in near-zero pressure drop across the cooler. With this arrangement, the cooler and contactor must be installed near the condensers, and the available elevation drop must

to the furnace. The vapor rate required for degassing is considerably smaller than that required for the Claus unit; it is expected that the addition of ICon will not affect the size or control scheme of the furnace blower.

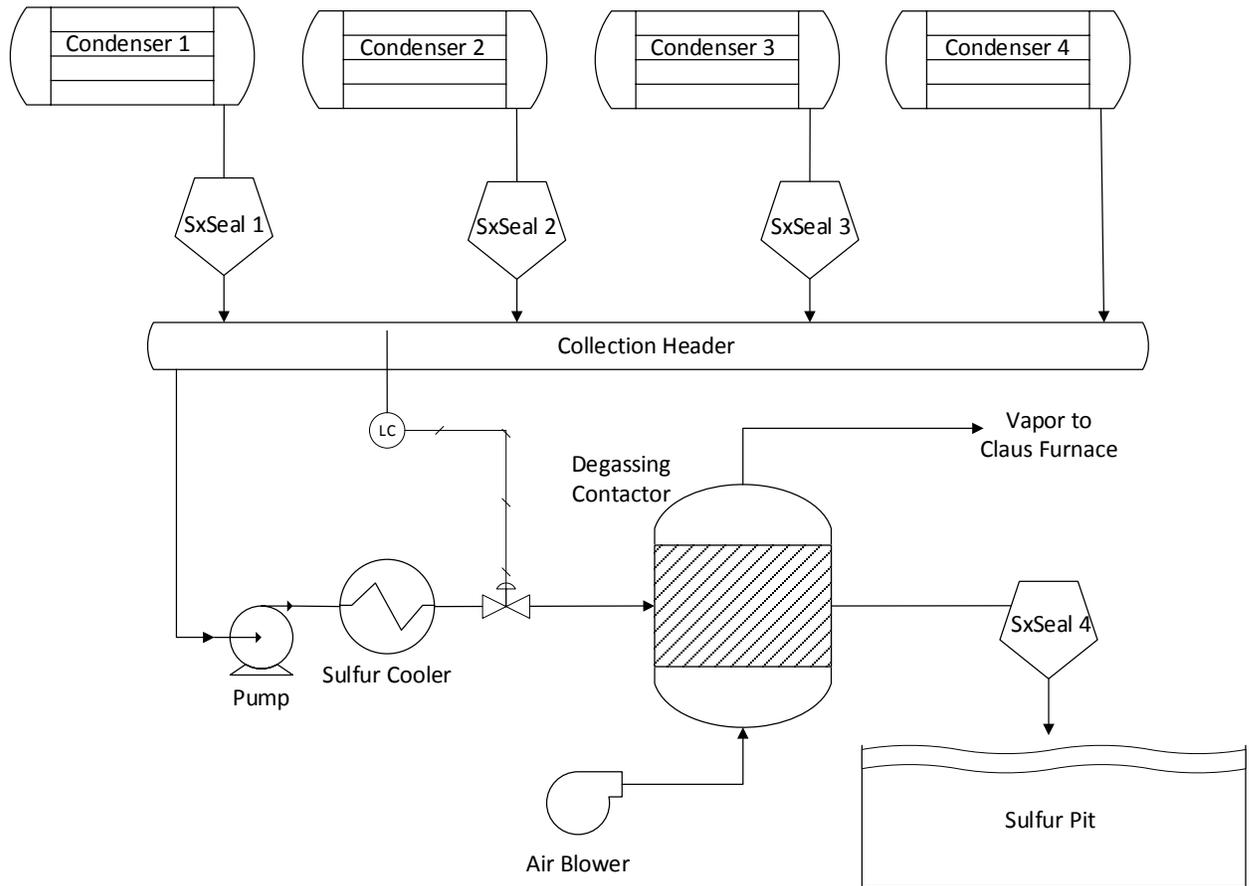


Figure 9 – Example PFD, Sulfur from Collection Header, Air Sparge to Claus Furnace

When using a pump for the sulfur supply, it is possible to combine the sulfur streams from multiple Claus units into a single degassing contactor. In this configuration, connecting the sparge gas to multiple return points would keep the degassing contactor on-line even if one of the Claus units is down.

Operation and Maintenance

Operation: Once started, the ICon degassing system will operate continuously with minimal attention from operations. Instrumentation on the contactor will alert operations if there is a problem. Key parameters that should be monitored are vapor flow, liquid flow, liquid level, and operating pressure/temperature. When sulfur is pumped to the contactor, the sulfur flow rate must be actively controlled to match the rate of sulfur production. This is the only item that requires active controls, everything else uses a ‘set and forget’ configuration.

Maintenance: The catalyst is not consumed or deactivated by normal operation; it is expected to last many years. The contactor is designed with extra catalyst capacity so that some level of catalyst degradation or attrition will not impact performance. At a scheduled turn-around, the catalyst can

be changed, or it can simply be ‘topped off’ if there are no concerns with its ongoing performance. Changing catalyst involves drying it with a hot vapor blow-down, vacuuming out the old material, inspecting the interior of the vessel, and loading in the new material. Most other maintenance activities are those common to other SRU equipment.

CSI provides a yearly maintenance service. Each year, CSI will inspect the degassing system including the steam heating components, review operational data, and measure the sulfur H₂S levels to confirm performance. This service is designed to assure continued smooth operation and identify problems before they affect operation.

Benefits of ICon™

H₂S Exposure: The benefits of having degassed sulfur are primarily related to safety and environmental. The risk of H₂S exposure is greatly reduced for all subsequent sulfur handling points; this includes sulfur storage, loading, transportation, forming and processing. Sulfur storage in the pit area and sulfur loading are the two areas in a refinery that typically provide the most opportunity for operator exposure to H₂S. Reducing the H₂S level in the liquid sulfur greatly reduces the risk of exposure to dangerous levels of H₂S.

H₂S Emissions: Release of H₂S or SO₂ creates an environmental concern. The H₂S emissions from each sulfur storage point should be considered for environmental impact. Degassing the sulfur greatly reduces this H₂S emissions. This has the added benefit of potentially eliminating the need for sophisticated vapor recovery systems. Processing the H₂S vapor stream from sulfur storage often comes with its own set of challenges as there is rarely a convenient way to tie this vapor back into the processing unit. This vapor is often sent directly to an incinerator where the H₂S is oxidized to SO₂.

Sulfur Pit: ICon can be configured between the condensers and the sulfur pit so that only degassed sulfur is sent to the pit. This brings the safety and environmental benefits of degassing to the pit area. This is a benefit that does not exist in any of the existing degassing technologies. Today, refineries employ sophisticated pit sweep systems and cumbersome safety procedures to maintain safe pit environments. Despite these efforts, sulfur pit fires and occasional explosions are still experienced; and sulfur pits remain a large source of H₂S/SO₂ emissions. Degassing prior to the pit greatly reduces the safety and environmental concerns normally associated with this area of the refinery.

Flexibility: The more practical benefits of an ICon degassing system will vary somewhat depending on how the system is configured. But the flexibility of the system itself is a universal benefit. ICon can be configured to accept and deliver the liquid and vapor stream in an unprecedented number of combinations. This benefits retrofit applications in particular. With many different options, a configuration that provides the right cost/benefit balance is more likely to be found.

Waste Stream Treatment: Degassing with an oxygen-free vapor source greatly increases the available treatment options. More conventional air degassing limits the waste stream destination to the Claus furnace or an incinerator. These are not always favorable options as the furnace is at an elevated pressure and the incinerator creates additional SO₂ emissions. But the oxygen-free

waste stream can also be returned to a mid-point in the Claus unit or the tail gas treating unit. This flexibility makes it easier and cheaper to safely treat the degassing waste stream.

Equipment Simplicity: Some configurations provide greater simplicity than others. The extent of the ancillary equipment, such as a sulfur cooler, a pump, or an ejector, can be minimized or adjusted to use only the equipment that is expected to be the most reliable. The use of active controls is also minimized; most of the equipment is of a 'set and forget' nature and only needs adjusted during initial start-up. And finally, with a fixed bed catalyst, the system is expected to last many years, from turn-around to turn-around, without any need to maintenance.

References

1. Al Keller, Brian Groves, Brandon Forbes, Thomas Willingham (2016), "New Pre-Pit Sulfur Degassing Technology", presented at Laurance Reid Gas Conditioning Conference, Norman, Oklahoma