

RESULTS OF PILOT TESTING THE CRYSTASULFSM PROCESS

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ABSTRACT

CrystaSulf is a new *nonaqueous* sulfur recovery process that removes hydrogen sulfide (H₂S) from gas streams and converts it into elemental sulfur. CrystaSulf features high sulfur recovery similar to aqueous-iron liquid redox sulfur recovery processes; however, CrystaSulf differs from the aqueous processes in that CrystaSulf controls the location where elemental sulfur particles are formed. As a result, CrystaSulf features solids-free circulating liquor streams, avoiding the operational problems associated with pumping aqueous sulfur slurries. Radian International is the exclusive commercializer of the CrystaSulf process, under license from GRI. GRI holds the patent on the original CrystaSulf concept, and Radian has developed proprietary improvements to the process.

The CrystaSulf pilot unit is located in the Permian Basin of west Texas. The pilot unit processes a slipstream of a 300 psig sour carbon dioxide (CO₂) stream from enhanced oil recovery operations. The pilot unit can process gas at 0.05 to 1.0 MMscfd with sulfur production of 20 to 200 pounds per day. This paper provides a description of the CrystaSulf pilot unit and its operation since initial startup at the end of 1998, and gives results such as sweet gas H₂S content, net sulfur recovery, sulfur purity, and chemical usage. These results are used to describe expected CrystaSulf performance for other direct treat applications such as removing H₂S from high-pressure sour natural gas. In addition, expected performance for using CrystaSulf to treat Claus tail gas is covered.

INTRODUCTION

Radian International developed the CrystaSulfSM process, which uses unique, nonaqueous chemistry to remove H₂S from gas streams without the foaming and sulfur plugging and handling problems that users of aqueous redox processes have experienced. The nonaqueous approach results in solids-free circulation throughout most of the plant. The crystallizer is the only place where solids form and they are large, pure sulfur crystals which are easy to separate and purify. In addition, by using sulfur dioxide (SO₂) as the oxidant rather than air, chemical degradation is reduced, and potential environmental issues associated with the air vent are eliminated. Finally, the process equipment is small, and exotic materials of construction should not be necessary, resulting in low costs and reliable operation.

GRI funded basic research at Radian that led to the development of this new CrystaSulf concept for the small to mid-range sulfur recovery niche in which liquid redox technology is typically used. Radian International acquired an exclusive license for GRI's process. In addition, Radian has funded its own proprietary improvements and moved forward with pilot-scale testing to

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prove the technology and generate data for commercial applications. The first round of pilot testing occurred over a seven-month period starting at the end of 1998. Modifications were then made to improve equipment performance and to allow long-term testing at low pressure. The second round of pilot testing is underway. U.S. patents have been issued for CrystaSulf;¹ international patents and patents on process enhancements are pending.

This paper presents the objectives of the pilot unit testing, describes the pilot unit flow scheme, summarizes the results of the pilot unit tests, discusses process modeling, and discusses the potential commercial applications for the technology.

OBJECTIVES OF PILOT UNIT TESTING

The pilot unit effort is being conducted to meet several objectives, which are listed below and discussed in the text that follows:

- Demonstrate that treated gas H₂S specifications can be met;
- Provide long-term chemical stability and loss data;
- Determine the best method of oxidizing the absorbed sulfur species to elemental sulfur;
- Demonstrate operation without the operating problems common to aqueous-iron redox processes; and
- Develop data to support commercial application of the technology.

Meet H₂S Specifications for Treated Gas. To be marketable, the CrystaSulf process must be able to meet the desired outlet H₂S gas specifications for different applications (i.e., high-pressure natural gas, low-pressure natural gas, Claus tail gas). The host site only requires that the H₂S concentration be less than 100 ppm H₂S in its treated gas. This was the initial target removal requirement for the pilot unit. However, data were also collected to demonstrate that more stringent 4-ppm H₂S specifications seen in direct treat natural gas applications could be met.

Provide Long-term Chemical Stability and Loss Data. Current liquid redox and similar processes are generally believed to fit the range of sulfur recovery between about 0.2 and 25 long tons per day (LTPD) of sulfur produced. This size range is typically above the maximum range of H₂S scavenging processes due to the large chemical costs incurred with once-through processing. Capital costs often make amine/Claus or amine/Claus/tail gas treatment combinations unattractive for this size range. The established iron-based liquid redox processes are touted to fit this niche because they have lower chemical costs than the scavenging processes and lower capital costs than the amine/Claus processes in this size range. However, higher than anticipated chemical usage was experienced in pilot efforts previously conducted using two of these processes.^{2,3} Chemical costs experienced by commercial aqueous-iron liquid redox users were also frequently higher than commonly thought.⁴ As a result, it was important to demonstrate CrystaSulf's low chemical costs at pilot scale.

Determine Best Method for Oxidizing the Absorbed Sulfur Species to Elemental Sulfur. It was also important to determine the best reoxidation scheme for use in the CrystaSulf system. Using oxygen (e.g., from air) as an oxidant has long been observed to result in destruction of the

organic chelates in aqueous-iron systems.^{5,6,7} While lab- and bench-scale testing with CrystaSulf showed relatively low solvent degradation when using oxygen (air) as the oxidant, it was desirable to compare air oxidation with other milder oxidation strategies such as oxidation with sulfur dioxide (SO₂) or combinations of air and SO₂.

Demonstrate Operation Without Problems Typically Reported with Aqueous-Iron Redox Systems. Operating problems resulting from aqueous redox systems producing sulfur solids have frequently been reported.^{2,3,4} It was an important objective to demonstrate CrystaSulf pilot unit operation without the common aqueous-iron liquid redox problems caused by sulfur solids circulating throughout the system, namely contactor foaming, plugging of high-pressure equipment, and difficulty operating with high carbon dioxide (CO₂) partial pressures.

Develop Data to Support Commercial Applications. A final and very important objective of the pilot unit effort was to develop data to support the commercial application of CrystaSulf technology. Data were needed to allow scale-up to larger sizes. Demonstration of acceptable operation under conditions simulating direct treat and other conditions simulating Claus tail gas treating was necessary. And, it was desired to have the pilot unit available for testing in support of specific commercial applications as they arise.

DESCRIPTION OF THE PILOT UNIT

Host Site and Process Stream

The CrystaSulf pilot plant is located at a west Texas gas plant. The plant processes gas recovered from its nearby enhanced oil recovery (EOR) CO₂ flood operations. A large volume (approximately 280 MMscfd) of high-CO₂ gas is recovered from these operations at low pressure along with produced oil. This gas is compressed to approximately 300 psig, treated with an aqueous-iron based liquid redox process to remove H₂S, and then processed for recovery of natural gas liquids. The recovered CO₂ is then reused in the EOR operations.

The CrystaSulf pilot unit takes a small slipstream (up to 1 MMscfd) of sour gas (1800 ppmv H₂S) at line pressure (300 psig) as feed to the unit. The gas contains approximately 85% CO₂ and 10% methane, with the remainder being heavier hydrocarbons. The inlet gas is saturated with water at 80 to 110°F. After passing through the pilot unit, the sweet gas is reduced in pressure and returned to the low-pressure side of the host site's sour gas compression unit.

General Process Overview

Figure 1 shows a simplified schematic of the CrystaSulf pilot unit in the configuration used to develop the results discussed here. In this configuration, sour gas entering the pilot plant from the host site first passes through an inlet gas heater followed by a coalescing filter to remove condensate from the gas.

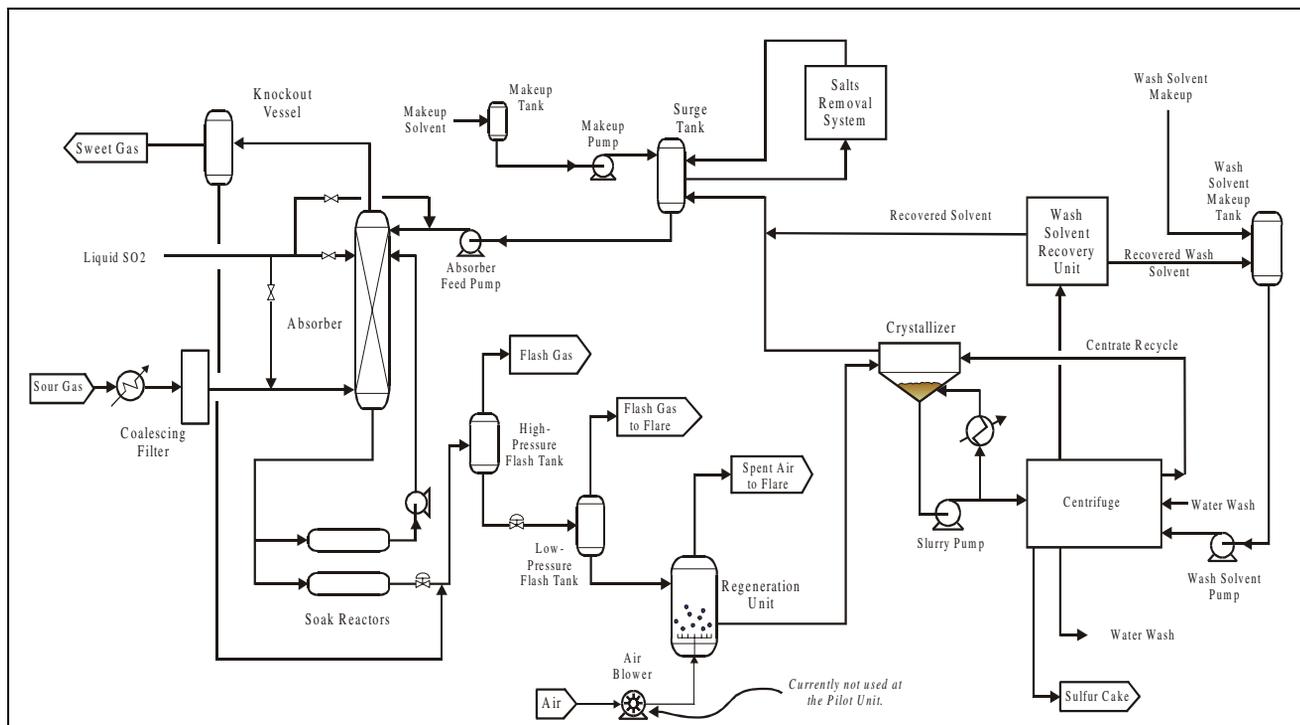


Figure 1. CrystaSulf Pilot Unit

Gas exiting the coalescing filter enters the bottom of the absorber where H₂S is removed. The absorber is a countercurrent tower with 10 trays and 2 bubble caps per tray. As the gas passes upward through the liquid, almost all of the H₂S and small portions of the CO₂ and hydrocarbons are absorbed into the circulating solvent. Gas exiting the absorber is sent to a knockout vessel. Any entrained liquids that carry over from the absorber collect in this separator and can be returned to the system. The sweet gas overhead from the knockout vessel is flashed across a control valve and returned to the suction of the host site compressor.

Lean CrystaSulf solution is pumped to the top of the absorber from the solvent surge tank by a high-pressure, diaphragm pump. Liquid SO₂ is pumped from a pressurized cylinder to one of three places: directly into the absorber, into the lean solvent stream, or into the inlet gas. Make-up chemicals from separate chemical injection systems may be added to the solvent feed stream upstream of the high-pressure feed pump.

Rich solvent exiting the bottom of the absorber enters a plug flow reactor. A pump-around system allows a portion of the rich solvent to be pumped back to the absorber, if desired. The plug flow reactors allow testing to be conducted to determine the effects of residence time on the CrystaSulf chemistry. The rich solvent flows downstream to the high-pressure flash tank. In the flash tank, light hydrocarbon vapors, CO₂, and traces of the H₂S flash out of solution. The overhead gas is sent to the host site compressor. The liquid then flows to a low-pressure flash separator. This separator is identical in design to the high-pressure flash tank, but is operated at near atmospheric pressure. Additional amounts of these same gases flash out of solution. The overhead gas is sent to a pilot unit flare and the liquids flow to an oxidizer. In the oxidizer, air (instead of SO₂) can be used to oxidize reduced sulfur species to elemental sulfur. Spent air is

sent to the pilot unit flare. (The air stream is not currently used at the pilot unit because of the use of SO₂ as described in subsequent sections of this paper.)

Liquid leaving the oxidizer is sent directly to the crystallizer via gravity overflow. The crystallizer contains a quiescent upper clarifying zone and an agitated lower crystallizing zone. An overflow pipe in the upper portion conveys liquid to the solvent surge tank.

The lower portion of the crystallizer is both agitated and cooled by continuously pumping slurry from the bottom of the crystallizer, through a heat exchanger, and back to the crystallizer. A heat exchanger is used to control the crystallizer temperature by adjusting the slurry return temperature. The cooling water flow rate is adjusted to achieve the desired temperature using a temperature control valve.

A slipstream of the slurry from the cooling loop at the bottom of the crystallizer is sent to the filtration system (centrifuge). While filtering sulfur slurry in the centrifuge, filtrate is allowed to flow by gravity back to the crystallizer tank. After filtering, the sulfur cake is washed first with a wash solvent to recover CrystaSulf solution and then with water as a final rinse.

The solvent surge tank collects lean solvent from the crystallizer. Solvent in the surge tank is heated to operating temperature by a hot water coil. The warm solvent is then pumped from this tank to the absorber using the high-pressure, diaphragm pump described earlier. Accumulated salts (if they develop) can be removed from the bulk CrystaSulf solvent using a proprietary on-line removal process developed by Radian.

Known Differences Between the Pilot Unit and a Commercial System

There are several known differences in the process flow of the pilot unit compared to that of a commercial unit. Two flash tanks were used at the pilot unit to allow good data collection. However, CrystaSulf has a very low circulation rate; as a result, it is likely that most commercial units operating at high pressure will only have one flash vessel. Because the flash gas can have a high BTU value, it would often not be flared in a commercial application. Instead, the flash gas would either be recompressed or used as fuel gas in some other process in the plant.

Similarly, the pilot unit soak reactors and pump-around system allow good data collection on the effects of residence time and L/G. The absorber vessel would have all the necessary residence time in most commercial units, and neither the soak reactors nor the pump-around system would be required.

Because of the relatively small size of the pilot unit, it was most economical to purchase liquid SO₂ and inject it into the pilot unit. Depending on the commercial CrystaSulf application, different methods will be available for SO₂ supply (see results section).

PILOT UNIT OPERATIONS

The pilot unit was designed and fabricated in 1998 and installed at the host site at a west Texas gas plant in October 1998. The pilot unit is shown in Figure 2. Startup and shakedown were conducted in November and December, with testing and process optimization activities conducted from January through July 1999. All engineering, fabrication oversight, installation oversight, and startup/operation were performed using Radian engineering and operations staff members.

After several months of successful operation, all performance and economic targets were met, and operation demonstrated the ability to treat at pressure without foaming or plugging and at economical solution loadings. The CrystaSulf pilot unit was then shut down to make some improvements to allow the pilot unit to operate at low-pressure conditions (for Claus tail gas treating) and lower liquid circulation rates, and to allow time to review the data collected in the previous months.

Unit modifications were made during August and September to improve the absorber bubble-cap trays, modify the pump to allow lower liquid flow rates, and add equipment to allow long-term testing at low pressure. The pilot unit was restarted the week of 11 October 1999. Table 1 provides a brief chronological summary of the testing.

Table 1. Chronology of Testing at Pilot Unit

Timeframe	Focus of Pilot Unit Testing	Results/Outcome
1/99 to 2/99	Conducted comparison of oxidation approaches: use of air sparging alone, air sparging with simultaneous SO ₂ addition, and SO ₂ addition alone.	Lab results suggested operation with SO ₂ alone could provide several advantages. Based on pilot unit tests, decided to operate unit with the addition of SO ₂ alone.
3/99	Tested operating temperatures and liquid/gas (L/G) ratios. Added pump-around loop to the absorber to examine the effects of L/G. Generated data for process model. Tracked all solvent addition.	Used data from lab and pilot unit to further refine model.
4/99 to 7/99	Suspended sorbent component make-up. Monitored chemical concentrations to determine the chemical use rate. Used various operating temperatures. Conducted further L/G testing to support planned modifications to absorber.	Operation to shutdown (in late July) occurred without any chemical addition (1550 hrs of operation with no chemical addition and 2500+ total hrs of run time).
Late 7/99 to 10/99	Shut down unit to make improvements.	Modifications allow pilot unit to operate at low-pressure conditions (for simulating Claus tail gas treating) and lower liquid circulation rates.
10/99 to 12/99	Startup modified equipment. Test effect of new trays, lower liquid rates.	Tray design verified. Process model verified.



Figure 2. CrystaSulf Pilot Unit

PERFORMANCE CRITERIA RESULTS

The pilot unit was evaluated on several criteria, including foaming, plugging, chemical cost, H₂S removal, byproduct make rates/removal, impact of contaminants, sulfur quality, materials of construction, water balance, and effect of inlet hydrocarbons. A summary of the evaluation results is presented in Table 2. Overall, the pilot unit demonstrated good performance in all areas, validating that CrystaSulf represents a significant breakthrough for these applications. The evaluation results are discussed below.

H₂S Removal

Summary:

- Process met and/or exceeded removal specifications at pilot site (achieves lower outlet H₂S than host's iron-based system)
- Process modeling, pilot measurements, and laboratory testing indicate ability to achieve removal requirements for all applications

Table 2. Summary of Pilot Unit Evaluation Areas

Evaluation Area	Results
H ₂ S removal	Met and/or exceeded host site removal specifications during pilot test. Should be able to achieve specifications for all applications.
Chemical costs	Approximately \$250/LT. Implementing R&D expected to further reduce pilot chemical costs to \$100-\$200/LTS. [Historically, pilot unit chemical usage is higher than commercial unit costs – upwards of \$900/LTS for aqueous-based systems.]
Byproduct make rates/removal	Less than 0.2% of inlet sulfur. Byproducts easily removed with Radian-proprietary, on-line process that has no solution blowdown and which processes a slipstream while continuing to operate.
Sulfur quality	> 98% sulfur purity (dry basis). Pilot sulfur is “worst case” due to hydrocarbon contaminants in gas.
Plugging	Some sulfur deposition encountered during initial shakedown testing due to inadequate insulation/tracing on some lines (sulfur redissolved easily on heating); minor modifications fixed trouble spots. Not expected to be a problem for commercial plants.
Foaming	Not experienced in pilot operations.
Impact of inlet gas contaminants	CO ₂ – Not reacted. COS/CS ₂ – Not reacted. RSH – Believed to not react; does not cause odor as with aqueous iron processes. Hydrocarbons – Excellent tolerance for these; much better than aqueous iron processes.
Materials of construction	Months of laboratory operation with CS filter housings show no appreciable corrosion. Additional corrosion tests underway. Carbon steel construction should be acceptable.
Water balance	Water vapor can exit with sweet gas, flash gas, or SO ₂ absorber gas. CrystaSulf's warm absorber (130-150°F) allows much water to exit with sweet gas. Solution carries significant dissolved water that can be stripped in the SO ₂ absorber.
Effects of inlet hydrocarbons	Vapors: Vapor components reach steady-state values in CrystaSulf solution. Steady-state concentration in pilot unit is about 11 wt% in the lean solution. [This EOR application has quite a few heavy hydrocarbons.] Liquids: Does not induce foaming. Occasional slugs do not harm operation or removal but could dilute system. Should use appropriate knockouts to prevent excess liquids from entering the CrystaSulf system.

The CrystaSulf pilot unit was able to consistently reduce the H₂S content of the inlet gas from 1800 ppm to approximately 25 to 50 ppm, far exceeding the removal specification for the host site (100 ppm H₂S in the sweet gas). Because the pilot unit absorber was originally designed with the focus of meeting the host site H₂S specifications, additional data were collected to evaluate whether the process would be able to meet more stringent 4-ppm H₂S specifications required for direct-treat natural gas specifications. Since the sweet gas partial pressure of H₂S cannot be lower than the partial pressure of H₂S in the lean solution to the absorber, the H₂S concentration in the surge tank was monitored. The measured H₂S content in the surge tank averaged about 40 ppm at 1 atm, which is equivalent to less than 4 ppm H₂S at high operating pressures. Tests with the lab-scale, atmospheric-pressure, CrystaSulf unit in Austin show very low sweet gas H₂S concentrations (less than 4 ppm H₂S at 1 atm). This indicates that with the proper process design there should not be practical limitations on H₂S removal in the CrystaSulf process.

During pilot unit testing, it was observed that H₂S removal could be adjusted by varying the concentration of a certain component in the process chemistry. An example of this is shown in Figure 3. As the manipulated variable increased, the H₂S concentration in the outlet gas decreased proportionally. Having access to a removal control variable is a significant benefit for commercial applications. Commercially available aqueous-iron redox processes do not have this level of control on removal efficiency.

Laboratory and field work also demonstrated that a temporary loss of SO₂ feed to the system will not cause an immediate reduction in removal. The sorbent has a buffering capacity; it contains a large amount of SO₂ that is chemically bound in solution. The solution can build up a large inventory of 'excess' SO₂ that does not come out of solution or strip into the sweet gas.

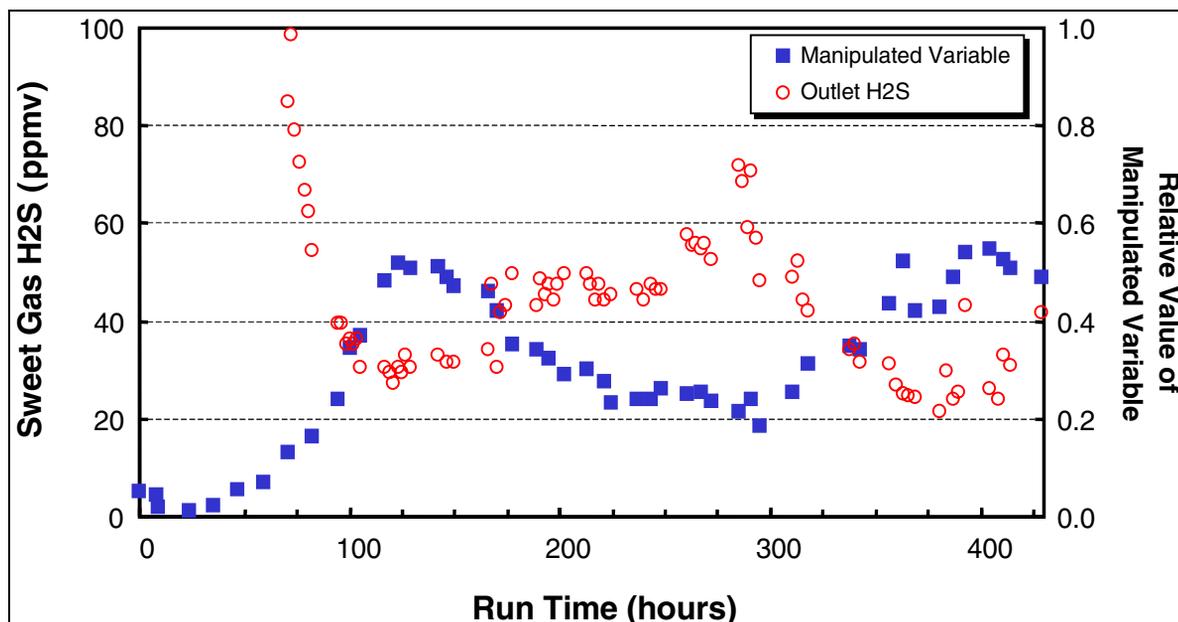


Figure 3. H₂S Removal as a Function of Manipulated Variable

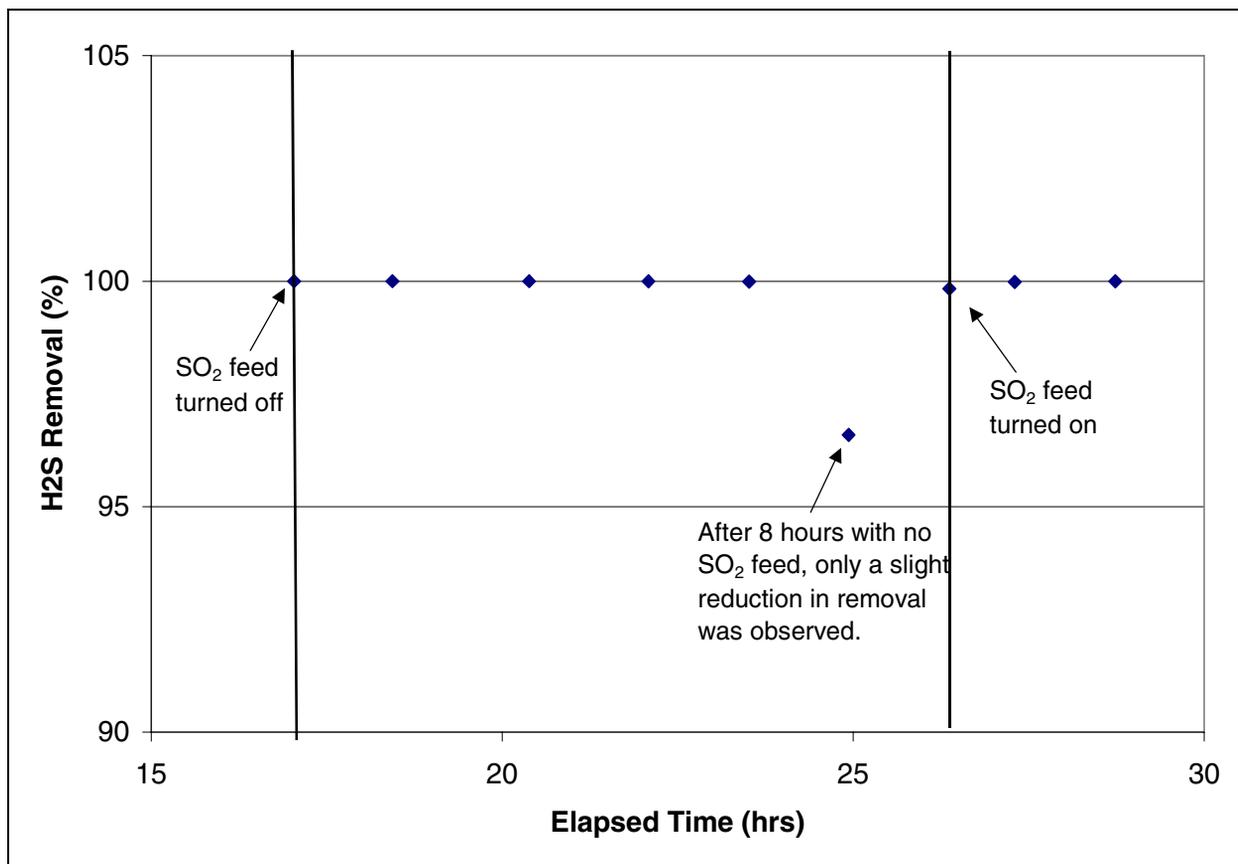


Figure 4. Buffer Effect on H₂S Removal

This allows the system to continue achieving good removal even without the addition of SO₂ for significant periods of time. In fact, as shown with the laboratory data in Figure 4, it typically took 6 to 12 hours to see even a slight reduction in removal when the SO₂ feed was shut off during some portions of the testing.

Tests were also conducted to determine the optimal operating temperature for the system. The data suggest that operating the pilot unit absorber at 130 to 150°F will enhance the kinetics of key reactions and improve removal.

H₂S losses from the flash tanks were typically less than 20 ppm (less than 0.15% of the inlet H₂S). This amount can be reduced even further, if necessary, by increasing the reaction time in the bottom of the absorber or in a separate vessel. Losses of the other gas constituents were also minimal (approximately 1.9% of the CO₂ and only 2.2% of the inlet hydrocarbons.) This was very encouraging considering that the high CO₂ and high heavy hydrocarbon environment in which the pilot unit was operating is typically troublesome to the commercially available aqueous-iron technologies. Further, pilot unit flash losses are believed to be biased high. The data given above were taken at the minimum solution flow rate possible with the original lean solution pump. Recent modifications to this pump allow operation at lower flow rates. It is expected that flash losses can be reduced by half to three quarters by simply reducing the solution flow rate.

Chemical Costs

Summary:

- Chemical costs of CrystaSulf pilot unit measured about \$250/LTS
- Historically, pilot unit chemical usage is higher than commercial unit costs – upwards of \$900/LTS for aqueous based systems
- Implementing R&D expected to further reduce pilot chemical costs to 100 – 200 \$/LTS

To be competitive with other sulfur removal processes, chemical costs must be low. There are three chemicals that make up the CrystaSulf solution: a nonaqueous solvent that has a high sulfur solubility, a tertiary amine, and another ingredient that solubilizes some of the reaction intermediates that might otherwise separate out of solution. All of the sorbent components in the CrystaSulf solution have been carefully chosen to have low volatility and high chemical stability. Long-term pilot unit testing was conducted to evaluate chemical costs.

The pilot unit was operated for 1550 hours with no chemical addition. The concentration of the tertiary amine and solubilizer decreased only slightly. The measured chemical costs during this period were on the order of \$250/long ton of sulfur (LTS) entering with the sour gas. This is considerably lower than other aqueous-based technologies on both the pilot and commercial level. The chemical losses reported in the literature for one common aqueous-iron liquid redox technology are 2000 lb/LTS for a pilot operation and \$600/LTS to \$700/LTS for on-going commercial operation (1995 dollars).^{2,4} Chemical costs (1995 dollars) for another aqueous-iron process were reported at \$895/LTS for a pilot operation and ranged from \$250/LTS to \$530/LTS for ongoing commercial operations.^{3,4} These references show that pilot unit chemical usage may be higher than commercial unit chemical usage due to the small size and intermittent operation. If this observation also holds for the CrystaSulf pilot results, then chemical losses from a full-scale CrystaSulf unit may be lower than that experienced at the pilot unit.

Although there is a small amount of degradation of the CrystaSulf sorbent in the SO₂-enhanced process, a large portion of the losses at the pilot unit was due to vaporization into the sweet gas and flash gas streams. A new mixture in which one component has been replaced with a lower vapor pressure chemical and another component has been reduced in concentration has been proven in the laboratory to provide good H₂S removal. This mixture will be tested at the pilot unit to further reduce chemical costs. Based on calculations that account for vaporization losses, the expected pilot unit chemical costs for the new mixture are on the order of \$100 to \$200/LTS entering with the sour gas.

The chemical addition system at the pilot unit was turned off in April 1999 and no chemical make-up to adjust component concentrations was necessary through the end of 1999. This provides further anecdotal evidence of CrystaSulf's low chemical use rate.

Byproduct Salts Formation and Removal

Summary:

- Byproduct sulfur salt formation is less than 0.2% of inlet sulfur converted to sulfur byproducts
- Byproducts are easily removed with a Radian-proprietary, on-line process that has no solution blowdown and processes a slipstream while continuing to operate

Only a very limited amount of the absorbed H₂S is converted to byproducts during the operation of the SO₂-driven CrystaSulf process. Removal of the byproducts is quite easy compared to other aqueous processes. Radian has developed and tested a proprietary approach for on-line regeneration of the sorbent. This simple process involves sending a slipstream of the CrystaSulf solvent to a separate tank and reacting the byproducts with an inexpensive reagent to precipitate solid salts. The slipstream is pumped through a filter to remove the precipitated salts and then returned to the main solution stream. Using this method, byproduct levels can be controlled while operating the unit and without the solution purging that is required with other sulfur removal technologies.

Figure 5 shows the sulfur byproduct concentration in the CrystaSulf pilot unit. A concentration rise rate is related to the “make” rate of the byproducts. As shown in the figure, the byproduct build up in the pilot unit was less than 0.2% (mole byproduct/mole H₂S reacted). It is believed that there is no additional byproduct formation associated with SO₂ removal. Figure 6 shows the byproduct response when the salts removal system was turned on. As shown in the figure, the byproduct concentration was reduced from 90 to 30 mM in 25 hours of intermittent use. In fact, when testing with SO₂ through July 1999, it was only necessary to operate the salts removal system three times (4% of the total elapsed run time). Salts removal is not expected to be a significant capital or operating expense for commercial units.

Sulfur Quality and Wash System

Summary:

- 98+% purity at pilot unit
- Pilot sulfur is “worst case” due to hydrocarbon contaminants in gas

The process solvent must be removed from the sulfur product to minimize chemical costs and enhance sulfur purity. A two-stage wash process is used to remove solution components from the sulfur product. First, a low-boiling wash solvent is used to wash the filter cake and remove the residual CrystaSulf solution from the sulfur. The sulfur is then rinsed with water to displace the wash solvent. The CrystaSulf solvent/wash solvent stream from the filter is sent to a small, skid-mounted solvent recovery still for separation. The wash water is sent to a storage tank where the wash solvent can be skimmed off the top and pumped to the still for additional recovery. The solvent recovery skid has provided good separation of the wash solvent from the CrystaSulf solvent. The recovered CrystaSulf solution and the wash solvent are recycled back to the crystallizer and filter, respectively. The water cycle appears to provide adequate displacement of the wash solvent because laboratory tests performed on sulfur washed in this manner show that it is not ignitable (according to RCRA SW846 method 1020A).

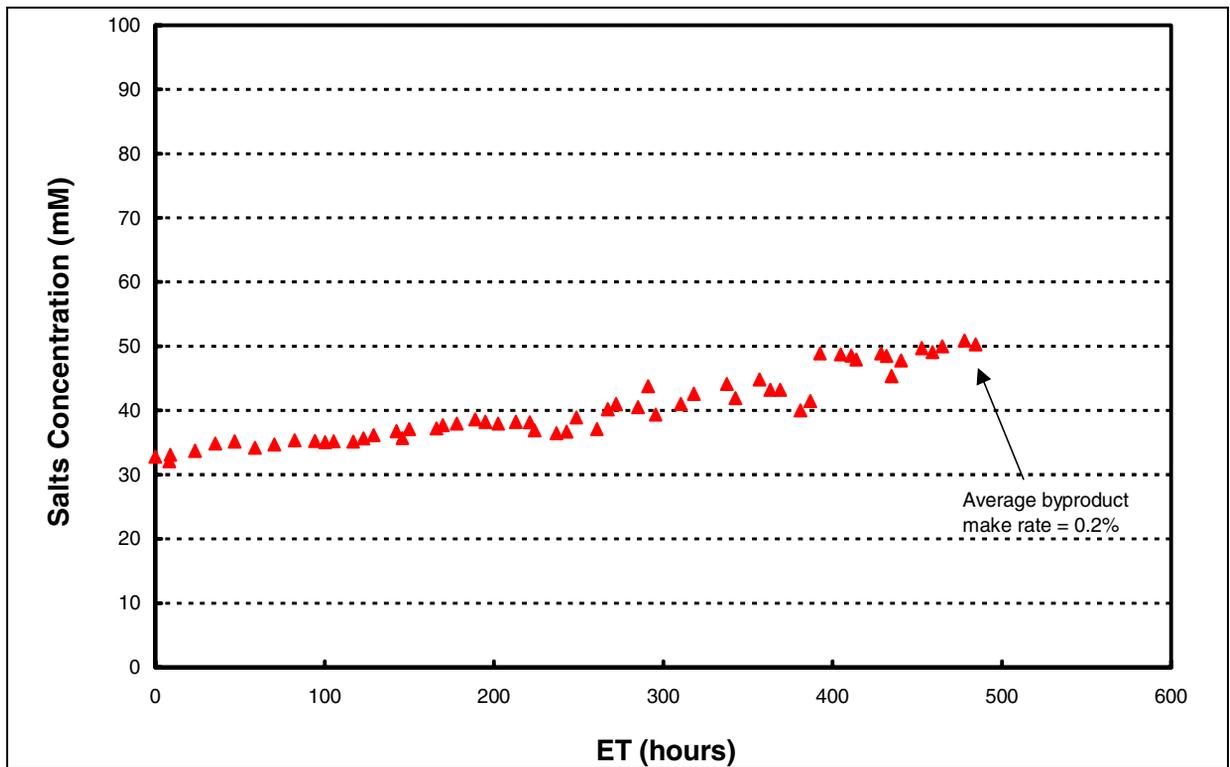


Figure 5. Example of Pilot Unit Byproduct Formation

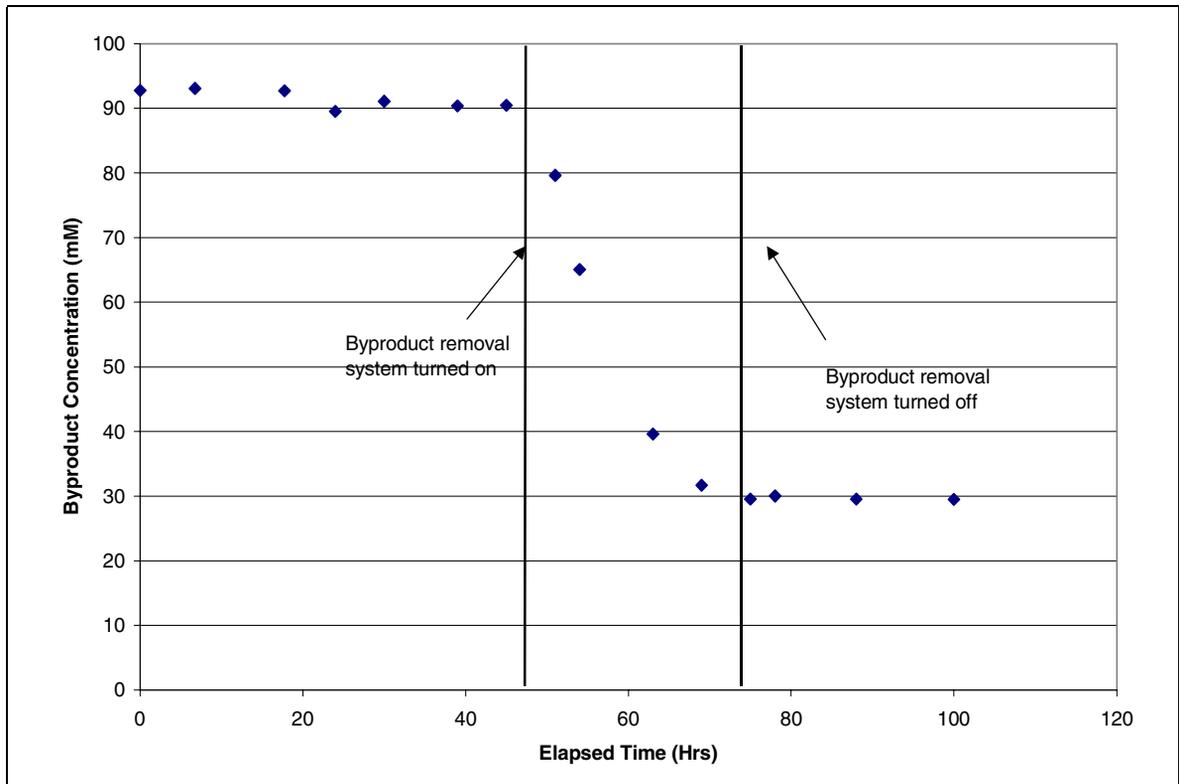


Figure 6. Byproduct Removal from CrystaSulf Pilot Unit

Table 3 compares the CrystaSulf pilot unit sulfur composition (from the centrifuge) to that from an aqueous liquid redox pilot unit operated by Radian in 1994 with a vertical pressure filter of a type known to produce better sulfur cake than can be obtained with less complicated (rotary drum or vacuum belt) filter designs. As shown in the table, the CrystaSulf pilot unit produced sulfur of 96% purity on a wet basis and 98% purity on a dry basis. The purity for the aqueous-produced sulfur, on the other hand, ranges from 81% on a wet basis to 93% on a dry basis². Sulfur purity for most liquid redox processes is known to generally range from 70 to 90% purity (all on dry basis).⁴ (Rotary drum and vacuum belt filters are typically used in these types of commercial liquid redox plants.)

Table 3. Comparison of Pilot Unit Sulfur Purity

Parameter	Sulfur from Recent CrystaSulf Pilot Run (Centrifuge) Wet Basis	Sulfur from Aqueous Pilot² (1994, Vertical Press Filter) Wet Basis	Sulfur from Recent CrystaSulf Pilot Run (Centrifuge) Dry Basis	Sulfur from Aqueous Pilot² (1994, Vertical Press Filter) Dry Basis
Sulfur, wt%	95.92	81.13	98.32	92.68
Carbon, wt%	0.39	1.00	0.40	1.14
Water, wt%	2.44	12.46	–	–
Other, wt%	1.25	5.41	1.25	6.18

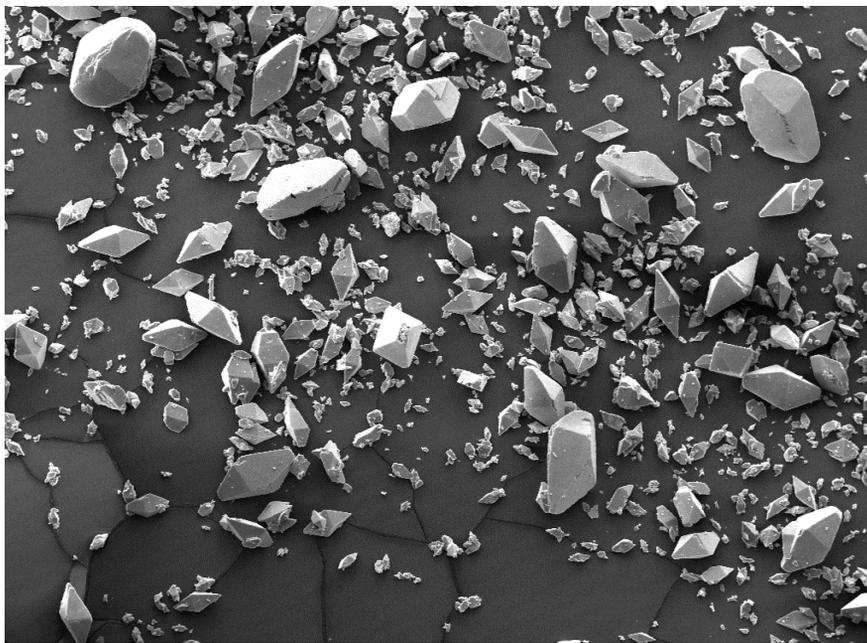
The pilot unit sulfur was blended with an industrial source of sulfur from a Claus plant. The sulfur from the CrystaSulf plant was blended at 2, 4, and 6 wt% with the Claus sulfur. The analytical results, shown in Table 4, indicate that the blended samples have the same purity as the original Claus sulfur within the constraints of analytical accuracy. Also included in Table 4 are the data from the analysis of the pilot unit sulfur sample before blending with Claus sulfur. The analytical results from this sample compare well with the results from a previous pilot plant sample shown in Table 3. In addition to blending with Claus sulfur, the high-purity sulfur formed in the CrystaSulf pilot unit suggests that commercial sulfur can likely be disposed of as solid waste, used as an additive to asphalt, or used as a soil amendment in agriculture. Testing is currently underway to verify that pilot plant sulfur may be used as a soil amendment in agriculture and as an asphalt blend.

Because of the relatively large amount of heavy hydrocarbons in the pilot unit gas stream, the pilot sulfur purity is believed to represent somewhat of a worst case. Sulfur produced from cleaner non-EOR streams (e.g., Claus tail gas, natural gas) should be significantly more pure than observed at the pilot.

As a result of the crystallization process by which it is formed, the product sulfur from the CrystaSulf pilot unit is also larger in size than that produced in an aqueous liquid redox plant. In contrast to the large particles shown in Figure 7 (which are typically 10's to 100's of microns in size), aqueous processes produce sulfur in the 1 to 10 micron range, and must use surfactants and additives to allow the sulfur agglomerate to be removed. Managing the additive levels can be difficult and ultimately leads to many of the plugging and foaming experiences that can occur in these processes.

Table 4. Comparison of Pilot Unit Sulfur Purity When Blended With a Claus Sulfur (Dry Basis)

Composition	Sulfur (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Ash (%)
Pure elemental Claus sulfur	99.94	<0.5	<0.5	<0.5	<0.1
98% Claus sulfur with 2% CrystaSulf sulfur	100.1	<0.5	<0.5	<0.5	<0.1
96% Claus sulfur with 4% CrystaSulf sulfur	99.1	<0.5	<0.5	<0.5	<0.1
94% Claus sulfur with 6% CrystaSulf sulfur	100.2	<0.5	<0.5	<0.5	<0.1
CrystaSulf sulfur	98.96	0.66	<0.5	<0.5	<0.1



←-----1000 μm-----→

Figure 7. Sulfur Particles from Pilot Plant (50x magnification)

Plugging

Summary:

- No plugging of majority of equipment since startup
- Formed plugs at cold spots in piping at startup
- Occasional plugging of crystallizer exchanger (crystallizer/filter is only area where slurries are present)
- Plugs dissolved in warm solution

Major improvements were observed compared to pilot testing of aqueous systems, which at times plugged entire sections of the plant so that extended run times were not possible.^{2,3} The

CrystaSulf solution has a high solubility for sulfur. Only in the crystallizer is the solution allowed to become supersaturated. For this reason, sulfur slurries or deposits tend to dissolve in the main circulation stream. Some sulfur deposition was encountered in cold spots in the line from exposed steel during winter conditions. However, one of the major benefits of the CrystaSulf process is that crystals will redissolve into the solvent on warming the sorbent. By simply fixing the heat trace and insulation at the exposed area, the plugging problems were reversed/eliminated. In addition, this type of plugging is not expected to be an issue on a full-scale unit because of the added thermal inertia of larger size piping (0.5-inch diameter tubing is used for solution lines in the pilot unit).

The potential for plugging in the crystallizer slurry loop exists since the solution temperature is being reduced at that point. Rough spots or high turbulence fittings in the piping can provide a surface for crystal nucleation. For this reason, commercial processes will be designed with redundant slurry loop equipment so that one exchanger can be operated and the other can be cleaned out with hot process solution if necessary. No other significant plugging problems have been observed during the pilot unit testing.

Foaming

Summary:

- No foaming problems encountered

Foaming was not a problem at the CrystaSulf pilot unit. The inherent nature of the system (i.e., hydrocarbon solvent, no sulfur particles in absorber) is resistant to foaming. Although water can potentially get into the process (from the inlet gas and overall chemical reaction), the formation of a second water phase has not been observed at the pilot unit. Some of the hydrocarbons in the gas are soluble in the CrystaSulf solution, but do not increase the foaming tendency of the process. The absence of solids in the main circulating solution also reduces the likelihood of foaming.

Only one brief (3 hour) carryover episode has occurred during testing. The carryover was likely related to the addition of used chemicals to the system. The chemicals were stored outside of the bulk circulating solution for several months and could have contained water or other contaminants. The carryover episode could not be repeated when the unit was restarted even though the pilot was still operating with the same solution. Foaming incidents were not observed during laboratory testing and are not anticipated to be a problem on a commercial scale unit.

Impact/Fate of Inlet Gas Contaminants

Summary:

- CO₂ – Not reacted
- COS/CS₂ – Not reacted
- RSH – Believed to not react; does not cause odor as with aqueous iron processes
- Hydrocarbons – Excellent tolerance for these; much better than aqueous iron processes

The extremely high CO₂ partial pressure (17 atm) at the host site may be considered an extreme case of the common CO₂ contaminant present in natural gas and tail gas treating applications. CO₂ reduces the pH of the aqueous solution, thus inhibiting H₂S removal in aqueous liquid redox processes. Because the CrystaSulf sorbent is nonaqueous, CO₂ is physically absorbed by the process to a limited extent but is essentially non-reactive with the sorbent and the chemical ingredients. Tests will be run to determine if any significant removal improvements are observed at low CO₂ partial pressures, such as might be found in many natural gas applications.

Unlike glycol-based sorbents that have been proposed in other sulfur removal processes, water has only a very limited solubility in the CrystaSulf sorbent. Water does not tend to dilute the CrystaSulf solution, and no separate operations to strip water to maintain sorbent strength are required.

So far, no adverse effects of other components in the host site gas have been observed. Samples of used sorbent from the pilot plant have been tested in the Austin bench-scale apparatus and show at least as good H₂S removal and operating properties as sorbent freshly prepared in the lab. In addition, bench-scale testing indicates that the COS and CS₂ compounds in Claus tail gas applications do not adversely impact the CrystaSulf process although they are not removed from the gas.

Materials of Construction

Summary:

- Months of laboratory operation with CS filter housings show no appreciable corrosion
- Additional corrosion tests underway
- Carbon steel construction should be acceptable

Although laboratory tests suggest that the CrystaSulf solution is not corrosive to carbon steel, the pilot unit was built of stainless steel as an initial safety precaution. No corrosion was observed, although some of the seals and elastomers in liquid service deteriorated over time. A database is being developed to identify the material requirements for these gaskets and o-rings (viton and PTFE work well). Incidental contact of CrystaSulf solution with tools, carbon steel pump bases, and other mild steel components showed much less corrosion than experienced during aqueous-iron pilot testing efforts.^{2,3} Additionally, carbon steel filter housings used in the lab unit for months at a time showed no appreciable corrosion.

Extensive corrosion testing will take place as part of the current round of pilot unit operation. Testing will focus on the feasibility of using plain low carbon steel in plant construction and whether excessive general corrosion, cracking, or weld-related attack will occur.

Water Balance

Summary:

- Water vapor can exit with sweet gas, flash gas, or SO₂ absorber gas

- CrystaSulf's warm absorber (130-150°F) allows much water to exit with sweet gas; solution carries significant dissolved water that can be stripped in the SO₂ absorber

Essentially all processes that convert H₂S to elemental sulfur also form water as a byproduct. Each mole of H₂S converted results in one mole of H₂O. This water reaction product can exit the CrystaSulf process with the sweet gas, flash gas, and the SO₂ absorber vent stream (when present in non-Claus tail gas treatment applications). The sweet gas and the SO₂ absorber vent streams are the largest potential exits for water and are discussed below.

CrystaSulf operates at temperatures of 130 to 150°F. In comparison, the aqueous-processes typically operate at temperatures of 115 to 130°F in order to avoid excessive solution degradation. Since the sweet gas exiting CrystaSulf is warmer, more water can exit with the sweet gas. The amount of water that can exit with the sweet gas is determined by the operating temperatures and pressures. For a given temperature, the lower the pressure, the more water that may exit with the sweet gas. This means that more concentrated H₂S streams may be processed at low pressure because the sweet gas can carry away more of the resulting moisture.

Although nonaqueous, the CrystaSulf solution contains some dissolved water (typically on the order of 0.5 molar). At the circulation rates being considered (for non-Claus tail gas treatment cases), the rate of dissolved water circulating in the solution is higher than the rate at which water is formed by the overall H₂S to sulfur reaction. Therefore, some or all of the water formed in the reaction can potentially be stripped from the solution. Initial tests simulating an SO₂ absorber indicate that water strips easily from the solution; thus, the SO₂ absorber, when present, may remove much of the water dissolved in the solution.

Through proper design, commercial units will not have any problems maintaining a water balance. Finally, after 2500+ hours of operating the pilot unit on a water-saturated gas stream, a second water phase was never observed in solution.

Effect of Inlet Hydrocarbons

Summary:

Hydrocarbon vapors

- Vapor components reach steady-state values in CrystaSulf solution
- Steady-state concentration in pilot unit is about 11 wt% in the lean solution (This EOR application has quite a few heavy HCs)

Hydrocarbon liquids

- Does not induce foaming
- Occasional slugs do not harm operation or removal but could dilute system
- Appropriate knockouts should be used to prevent excess liquids from entering the CrystaSulf system

The inert vapor components in the inlet gas will reach steady-state concentrations in the CrystaSulf solution. The steady-state concentration in solution depends on the vapor

concentration of each component in the inlet gas. As an example, the inlet gas at the pilot unit host site (being an EOR application) has quite a few heavy hydrocarbons; as a result, the steady-state concentration in the pilot unit solution is believed to be about 11 wt% in the lean solution stream. These additional hydrocarbons act only as a diluent to the main CrystaSulf components and have not affected operating performance at the pilot unit. In fact, slugs of hydrocarbon contaminants from the host site have been purposely added to the atmospheric bench unit in Radian's Austin laboratories at up to approximately 25 volume percent with no effect on operations. In contrast, hydrocarbon contaminants often cause extreme operating problems in aqueous processes, even though there are much lower concentrations of hydrocarbons at steady state.

For the reasons cited above, occasional slugs of liquid hydrocarbon do not harm operation of the CrystaSulf process. However, slugs of liquid containing very heavy components will stay in the system for a long time. Continuous slugs of heavy hydrocarbons would result in undesirable dilution of the CrystaSulf solution. As with any process, appropriate knockouts should be used to prevent liquids from entering the CrystaSulf stream.

DATA FOR MODELING AND SCALE-UP

Process Modeling

Reliable and accurate process modeling is essential to the successful scale-up and commercialization of the CrystaSulf process. Radian has developed an in-house model of the CrystaSulf process using the commercial process simulator ASPEN PLUS. The model incorporates data generated in the laboratory and at the pilot unit to determine the kinetics of the key reactions, sulfur solubility and crystallization, vapor-liquid equilibrium of the gas constituents, gas/liquid mass transfer in the absorber, and other chemical properties. The model has accurately predicted removal performance when operating conditions at the pilot unit are changed. Thermodynamic data indicate that there is no practical limitation on H₂S removal performance in the CrystaSulf process. The model predicts that low H₂S concentrations (< 4 ppmv) in sweet gas can be achieved with reasonable contactor sizes. The model will be used to optimize the CrystaSulf process for each potential application, as well as to operate the process effectively at a commercial installation. In-house cost models have also been prepared to provide comparative cost estimates for different commercial CrystaSulf applications.

“Controlled” H₂S Removal

Pilot unit data have shown a direct correlation between a species in the CrystaSulf solution and H₂S removal. This will be an important control parameter for operators of commercial units. Simple analytical methods have been developed so that on-line measurements of the control variable can be made to help operators ensure that the unit is operating properly and H₂S gas specifications are met.

SO₂ Delivery Options

Pilot unit operation confirmed that there are several viable methods for introducing SO₂ to the system. Sulfur dioxide has been introduced into the absorber in three ways: directly into the

absorber as a pressurized liquid, carried by the lean solution to the contactor, and evaporated into the gas entering the contactor. During each of these instances, the pilot unit continued to operate well and achieve good H₂S removal. There do not appear to be any unique issues associated with the manner in which SO₂ is supplied to the system; both liquid- and gas-phase injection are acceptable. This is important because different commercial CrystaSulf applications may require different means of SO₂ delivery depending on the application and economics.

For direct treat facilities with very low sulfur production, commercial liquid SO₂ may be more economical to use than trying to generate it on site. Liquid SO₂ costs about \$200/LT of sulfur removed. Liquid SO₂ is relatively easy to add to the system and can be vaporized into the gas or pumped into the scrubbing liquid. Although storing the liquid SO₂ on site requires proper safety precautions, storage and routine usage has been proven in other industries.

Several options are currently under consideration for on-site production of SO₂ for larger sulfur units. A commercially available sulfur burner could be used to melt and burn a portion of the product sulfur to produce SO₂. The main technical uncertainty associated with this method is oxygen control and the effect on the CrystaSulf solution; however, laboratory testing of this scenario has shown no negative effects. If liquid SO₂ or a sulfur burner were used in a commercial application, the SO₂ would be added into the process in the same location as the pilot unit. (The SO₂ is highly soluble in the sorbent and, in the case of the sulfur burner, would be added to the lean sorbent through a small scrubber column on the sulfur burner exhaust.) Another SO₂ production method involves converting one-third of the inlet H₂S to SO₂ in the gas phase. This could be done catalytically or by separating and burning a portion of the H₂S.

Being able to achieve good H₂S removal when introducing SO₂ in the gas phase also has implications for using the CrystaSulf process in Claus tail gas applications. This is especially true since the CrystaSulf chemistry operates with the same 2:1 H₂S:SO₂ ratio as a Claus unit.

Absorber Design

Pilot unit operation proved the ability to use a countercurrent, trayed-absorber design with CrystaSulf. Although tray towers typically can be used with amine sweetening systems, they are not normally used with iron-chelate processes because of severe plugging concerns. During the initial 2500 hours of operation at the pilot unit, only minor solids formation occurred on stagnant surfaces in the contactor. The solids formation is believed to be a result of the presence of SO₂ in the vapor phase. This did not adversely impact performance on the pilot unit and can be avoided in commercial applications by ensuring that the SO₂ is absorbed into solution prior to the trayed portion of the H₂S absorber or by using well-irrigated trays/packing. This is primarily a design issue for Claus tail gas applications. The ability to use traditional contactor designs in CrystaSulf plants provides an added degree of flexibility not found with iron-based processes.

The effects of liquid holdup and liquid-to-gas (L/G) ratio on H₂S performance were examined. The data suggest that very high H₂S removal (like that required by sweet natural gas specifications) could be achieved by increasing the liquid holdup in the column. Therefore, new trays were designed to double the liquid capacity in the existing column by increasing the weir height of each tray from 3 to 6 inches. Six-inch weir heights are not uncommon in industry and

should not represent a significant capital cost increase for commercial units. The new trays were installed in the pilot unit absorber and perform effectively. An alternative to using few trays but deep weirs would be to have more trays with shorter weir heights. The pilot unit data also showed that good removal could be achieved with L/G ratios comparable to or less than those used in other liquid-phase sulfur removal processes.

SUMMARY

The pilot unit operations have been successful in demonstrating the feasibility and benefits of CrystaSulf for the commercial market. The CrystaSulf sulfur recovery process has lower treating costs, better operability, and higher sulfur loading than the competitive processes operated at the pilot scale. CrystaSulf is now ready for commercial applications, and dialogue is being conducted with several companies regarding potential use of the process. Expected applications for the CrystaSulf process and future work are described below.

Expected Commercial Applications for CrystaSulf

Because of the characteristics described above, it appears as if CrystaSulf can be applied to two different cases: 1) the direct removal (or “direct treatment”) of H₂S from a gas stream, such as the desulfurization of natural gas or refinery fuel gas streams; and 2) Claus tail gas treatment. These potential commercial applications are described below.

Direct Treat. CrystaSulf can be applied directly to sour gas streams in the natural gas and processing industries. The SO₂ required in the process for oxidation can be purchased as a pure product, created by burning product sulfur, or produced from the inlet gas H₂S. Case-by-case economics will impact which method should be used. CrystaSulf offers several advantages over other direct treat applications including: solids-free circulating liquor, direct treat of high-pressure streams, large sulfur particles, and no solution purge. Economic comparisons show that CrystaSulf treating costs approximately 20 to 30% less in direct treat applications (compared to amine/aqueous-iron liquid redox processes) in the 0.2 to 25 LTD range. (The CrystaSulf cost estimates were compared to an amine/aqueous-iron process because past tests suggest that aqueous-iron processes alone cannot be used in high pressure, direct treat applications.)^{2,3}

Claus Tail Gas. The CrystaSulf chemistry already uses the same 2:1 H₂S:SO₂ ratio used in the upstream Claus units. CrystaSulf also offers the advantage of being able to meet H₂S gas specifications during Claus upsets due to the “buffering” effects of the solution chemistry. The CrystaSulf process operates at better conditions (i.e., lower temperatures) for the liquid phase H₂S/SO₂ reactions to occur.

CrystaSulf will require less equipment as compared to other tail gas treating applications. A quench system will not be required because the CrystaSulf process can operate at temperatures above the inlet gas water dewpoint. No reducing gas generator and hydrogenation reactor will be required. In addition, CrystaSulf has no recycle streams, eliminating this potential cause of reduced Claus capacity.

CrystaSulf is expected to produce sufficiently pure sulfur so that it can be mixed with the Claus plant sulfur and sold. COS and CS₂ are not removed in the CrystaSulf process; therefore, the first catalyst bed in the Claus process may have to be operated at high temperatures and the use of a special catalyst (TiO₂) to destroy these compounds may need to be considered for one or more beds if present in significant quantities. Economic comparisons show that CrystaSulf costs approximately 30 to 40% less in Claus tail gas applications than H₂S recycle processes.

Future Work

The pilot unit will continue to be used as a development tool to optimize process conditions and further lower chemical and operating costs. The pilot unit will also be used to test different unit configurations and inlet gas compositions that may be observed in the marketplace.

Pilot Plant Tours

If you are interested in learning more about the CrystaSulf process and would like to tour the pilot plant, please contact one of the authors at Radian International, 512/454-4797.

Acknowledgement

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