SHELL-PAQUES® BIO-DESULFURIZATION PROCESS DIRECTLY AND SELECTIVELY REMOVES H₂S FROM HIGH PRESSURE NATURAL GAS – START-UP REPORT

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ABSTRACT

NATCO licensed and built two Shell-Paques Bio-Desulfurization units, with identical design parameters, for XTO Energy’s East Texas natural gas operations. The Teague facility, designated Teague Paques Plant (TPP), was put in operation in December 2004 about four months ahead of the Eubank Paques Plant (EPP). Both plants are designed for the same capacity, 60 MMSCFD at 1100 psig, each with the capability to remove up to 4 Long Tons Per Day (LTPD) of sulfur from the gas. The initial months of operations saw carryover and foaming problems, insufficient throughput and corrosion issues. A root cause analysis was performed and corrective action taken. Today these plants are meeting the outlet specification of <4 ppm H₂S while processing all available gas. Plant availability has been 100% since the last turnaround and operating costs are as predicted.
INTRODUCTION

XTO Energy is a Fort Worth based energy producer engaged in the acquisition, development and discovery of quality, long-lived oil and natural gas properties in the United States with activities concentrated in Texas, New Mexico, Arkansas, Oklahoma, Kansas, Wyoming, Colorado, Alaska, Utah, and Louisiana. Focusing on properties located in the major producing areas of the United States, XTO increases production through low-risk means including the reduction of operating costs, re-completions and development drilling. This strategy has lead to very rapid growth over the last several years. As a result of growth activity, XTO required an economical solution for sulfur recovery from gas streams in small to medium quantities.

The recovery of small to medium quantities (0.2 to 20 LTPD) of sulfur from gas streams has typically been problematic for industry, especially at high pressure. Available processes are unreliable, costly to operate, require the use of expensive proprietary chemicals and/or generate undesirable waste products. In 1993 Paques commercialized Thiopaq®, an environmentally friendly process for treating biogas using naturally occurring bacteria to oxidize hydrogen sulfide to elemental sulfur in a simple, reliable and cost effective process. The process is explained in detail in Appendix I. Shell Global Solutions (SGSI) invested in the technology to extend its use to natural gas, amine acid gas, Claus tail gas and Syngas. In these applications the technology is branded as Shell-Paques®. Through license agreements with both SGSI and Paques, NATCO Group, Inc. designs, builds and services Thiopaq technology in the United States, Central and South America.

Initial start-up and operational issues can be categorized as either foaming related or material related. The symptoms of foaming exhibited as poor treat, insufficient throughput, high differential pressure in the contactor, or carryover. Materials related issues showed up as corrosion caused by coating failure, the result of improper application or mechanical damage. A root cause analysis was performed and corrective action taken. NATCO, Shell, Paques and XTO worked together to implement several innovative solutions. Today, both plants are processing all the available gas and meeting the 4 ppm outlet specification. Since the last modification was made in September 2006, plant availability has been 100%.

XTO ENERGY

XTO Energy’s strategy has been to identify and acquire high-quality properties and strive to enhance their value by increasing production and reserves. In the process, XTO has become a premier consolidator of resource basin plays in America. This will lead to future growth defined by a ‘manufacturing program’ of drilling inventory within tight-gas, shale, coal bed methane and long-lived oil properties. With a low-risk development inventory of about 5,000 wells, today XTO is targeting upsides of more than 4.2 Tcfe or 55% of its YE '05 reserve base.
XTO Energy is a dominant producer of natural gas in the U.S. with over 85% of its natural gas production originating in non-conventional plays. In East Texas, the Company is the top producer from the tight-gas formation within its Freestone Trend play. In the Barnett Shale, XTO ranks as the second largest producer and currently operates 22 drilling rigs. The Piceance Basin, technically an East Texas comparable, is the Company’s newest basin and represents future production and reserve growth of more than 2 Tcfe.

XTO Energy is also a prominent producer in East Texas and northern Louisiana, with the Freestone Trend leading the way. Current Freestone Trend daily production of about 570 MMcfe is anticipated to grow to more than 700 MMcfe over the next several years. XTO has identified up to 2,100 drilling locations in the Eastern Region, which represent 4 to 5 years of development spanning from East Texas into northern Louisiana. The primary producing horizons in the region include the Pettit, Rodessa, Travis Peak (Hosston in La.), Cotton Valley Sand, Bossier (Gray Sand in La.), Cotton Valley Lime and the Haynesville, ranging in depth from 5,000 to 13,000 feet.

Certain producing zones within the Freestone Trend hold sour natural gas containing 400 to 1800 ppm H₂S and up to 4% CO₂. This is the area were XTO elected to install two-4 LTPD Shell-Paques plants.

TECHNOLOGY GAP

In the 1990s, The Gas Technology Institute (GTI) sponsored several studies surrounding both small-scale and medium-scale H₂S removal processes. These studies were conducted primarily by Kellogg Brown and Root (KBR) and Radian International (now part of URS). One such study targeted direct treatment of high pressure natural gas using the available technologies such as LO-Cat® and SulFerox®. Both companies provided quarter ton per day pilot units and a site in West Texas was selected for testing. Plugging and foaming problems plagued these units. The conclusion reached by the GTI research team was that no existing technology was suitable for treating high pressure natural gas in the medium-scale
range. This conclusion is borne out by the fact that few high pressure applications have been attempted by either technology supplier and even fewer have been successful.

**Tighter Regulations**

Prior to the tightening of air emissions regulations, the market for H$_2$S removal was served by small-scale and large-scale plants. The combination of an amine unit to extract the acid gases from the product gas stream and a flare to burn the H$_2$S to sulfur dioxide (SO$_2$), a contributor to acid rain, was sufficient in the absence of emission regulations. Each ton of H$_2$S produces two tons of SO$_2$ when burned in a flare or thermal oxidizer. Today, some grandfathered flares still exist but it is now very difficult to obtain a permit to emit significant amounts of SO$_2$.

Small-scale applications are served well by the numerous scavengers available on the market. At an operating cost of $8,000 to $40,000 per ton of sulfur removed, these solutions are limited to just a few hundred pounds per day.

Large scale applications are served by Claus units. The Claus process does not act directly on the gas stream. First the H$_2$S is separated from the host gas stream using amine extraction, and then it is fed to the Claus unit, where it is converted in two steps. Through partial oxidation, a portion of the H$_2$S is converted to SO$_2$ and reacts to form vapor-phase elemental sulfur. The remaining H$_2$S is reacted with the SO$_2$ at lower temperatures (about 200-350°C) over a catalyst to make more sulfur. The process is equilibrium limited so multiple catalyst beds are employed to achieve higher efficiencies. Still, a tail gas treating step may be needed to meet environmental requirements.

These tighter regulations have opened up a market for medium-scale sulfur plants where a scavenger is too expensive to operate and a large-scale plant is too capital intensive. Due to their high efficiency and flexibility, wet scrubbing processes have dominated the medium-scale process niche. These processes work either directly, by contacting the gas, or indirectly, by cleaning up amine acid gas. Until now, wet scrubbing processes have been applied directly to high pressure gas with minimal success.

**Direct Treat Sulfur Conversion Technologies**

Over the years several technologies have been developed to address the technology gap in the low to medium sulfur range. Examples of these wet scrubbing direct treat processes are Stretford, LO-CAT®, SulFerox® and CrystaSulf®. These technologies directly convert hydrogen sulfide (H$_2$S) to elemental sulfur by using solutions containing vanadium, chelated iron or sulfur dioxide. All of these technologies presented operational challenges including sulfur quality and handling issues, and minimal success in high pressure application. *These processes are explained in detail in Appendix II.*

The Shell-Paques Process (*see Appendix I*) is also a direct treat sulfur conversion technology. This is the technology chosen by XTO as the solution to medium range sulfur recovery on a high pressure natural gas stream.
FIRST HIGH PRESSURE SHELL-PAQUES PLANT

Challenges

Given the history of high pressure direct treat applications, XTO, NATCO, SGSI and Paques took on significant risk in implementing a technology which had not been commercially operated at these conditions.

- *Would the bacteria survive the pressure cycles?* Unlike some biological processes where the bacteria reside on a substrate which can be confined to one area of the plant, these bacteria are free swimming and exist throughout the process. Approximately every two hours the entire liquid inventory of the plant is pumped through the contactors. This means the bacteria are cycled from atmospheric pressure to 1100 psig 12 times a day. How would this affect their performance?

- *Would the process achieve the required outlet H₂S specification of < 4ppm?* The presence of carbon dioxide makes removing the last few ppm of H₂S more difficult. Both H₂S and CO₂ are acid gases and even though the concentration of CO₂ is low (less than 4 %), its partial pressure at 1100 psig is significant.

- Past experience has shown that plugging and foaming can be significant issues in Redox processes. Plugging and foaming are not seen in low pressure Paques plants. *Would the same hold true under high pressure conditions?*

- *Finally, would the selected materials of construction hold up?* Delivery requirements precluded the use of stainless steel for the contactors. The material simply was not available in the required timeframe so the decision was made to use an internal coating system on carbon steel. At the time, two medium pressure Shell-Paques plants (150 psig) were in service using the same coating system with no reports of corrosion.

Conclusions

Concerns over the health of the Thiobacillus bacteria proved to be unfounded. The bacteria have performed well under the operating conditions showing no ill effects due to pressure cycling. Since initial startup, the plants have never been reseeded.

The H₂S concentration in the outlet gas has averaged 1 ppm over the past 6 months exceeding the design requirement. The circulating solution is highly buffered so preferential absorption of CO₂ over H₂S has not been a problem.

Since start-up, significant effort has been expended to eliminate high pressure drop through the contactors, a symptom of foaming. Antifoam effectively controlled the foaming incidents while long term solutions were investigated and implemented. Stable operation has been achieved. Plugging of the piping has not been a problem although steps have been taken to reduce the possibility of sulfur settling in the flash tank and pump tank.
Where properly applied, the internal coating system performed well both in high pressure and low pressure areas of the plant. Corrosion was found in areas where mechanical action from repeated vessel entry and installation of vessel internals damaged the coating. Improper surface preparation and coating application is also suspected as a contributing factor in nozzle throats and flange faces. Finally, the use of metallic, spiral-wound gaskets caused the coating to crack at the flange face providing a pathway to the bare metal. The use of stainless steel or stainless steel overlay in these difficult to coat areas is a cost effective and reliable solution which will be used in future applications.

**XTO SHELL PAQUES PLANT SPECIFICS**

*Schedule*

The Teague plant project was started in March 2004 with an aggressive total schedule to start the plant by December of 2004. The schedule had 6 months for design, engineering, fabrication, and procurement. This allowed for site work to begin 2 months prior to and for 2-3 months after final equipment delivery for erection and installation of equipment. This aggressive schedule also drove the decision to fabricate the high pressure equipment out of carbon steel rather than stainless steel. Stainless steel in the required thickness was simply not available on short delivery. Coated carbon steel had been successfully employed in this service, albeit at a lower operating pressure, and was thought to be serviceable.

*Design Basis*

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<tr>
<th>Component</th>
<th>Mole% Dry Basis (Gas is water saturated)</th>
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<tbody>
<tr>
<td>Methane</td>
<td>94.692</td>
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<tr>
<td>Ethane</td>
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<td>Propane +</td>
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Gas Flow Rate: 60 MMSCFD  
Gas Pressure, maximum operating: 1200 psig  
Gas Temperature: 110 F  
H₂S Concentration: 1750 ppmv  
Sulfur Capacity: 4.0 LTPD / 8,960 pounds per day  
Gas Pressure Range: 750 to 1200 psig  
Gas Temperature Range: 70 to 120 F
Major components

The attached process flow diagram (see Appendix III) illustrates the major process equipment. For easy reference the process steps are numbered. The process flows as follows:

1. Gas enters the process through the gas cooler. This is a liquid to gas heat exchanger. The cooling medium is cooling tower water.
2. Inlet separation consists of a Whirlyscrub followed by a coalescing filter.
3. Next the gas flows upwards through two parallel contactors containing approximately 50 feet of random packing. Solution flows down in a countercurrent pattern.
4. The gas exits the contactors through a knock-out vessel followed by a Whirlyscrub.
5. The gas leaves the process through a 1 micron coalescing filter.
6. Solution flows from the contactor bottoms to the Flash vessel.
7. Flash tank circulation pumps deliver degassed solution back to the flash tank for foam suppression and to prevent sulfur settling.
8. Flash gas passes through a Whirlyscrub and particulate filter before going to compression.
9. From the flash tank the liquid flows through the solution cooler.
10. To the bioreactors.
11. Air is compressed and sparged into the bioreactors.
12. Solution leaving the bioreactor passes through the pump tank.
13. which ensures that the solution is free of air before entering.
14. The booster pumps which provide suction pressure for.
15. Three 50% pumps (one in stand-by mode) are used.
16. The high pressure Reda pumps which deliver solution to the top of the contactors.
17. A slipstream from the booster pumps is directed to the settler vessel.
18. Progressing cavity pumps deliver the settled sulfur slurry to the centrifuge.
19. The sulfur is dewatered and dropped into roll-off bins.
20. The filtrate is returned to the process or directed to blowdown.

The plant can be divided in high and low pressure sections. The solution is corrosive to bare carbon steel so all parts in contact with the solution are either stainless steel, coated carbon steel, plastic, or fiberglass. In the high pressure section for the gas, the design pressure is 1440 psig. The inlet gas cooler and inlet gas separator are sour service carbon steel. The contactors, each treating 50% of the capacity are 75 feet tall and weigh about 100,000 pounds; were built as two towers for reasons of weight, cost, and for better operational flexibility.
XTO Teague Paques Plant
Bioreactors

Pump Tank and Settler  Tower Packing
Treated Gas WhirlyScrub

Centrifuge for Sulfur Dewatering
START-UP and OPERATION

The initial plant start-up and operation of the Teague plant began the first week of December 2004 and proceeded relatively smoothly for the first several days. Biomass was supplied from a Paques biogas unit in Nebraska. The biomass grew well and gas rates were increased as the biological activity of the system improved. H₂S removal was good and the plant was mainly stable.

A few weeks after startup, XTO ran a cleaning pig in the downstream piping as part of their routine pipeline maintenance program. This operation revealed a great deal of material in the pipe which was traced back to TPP. It was quickly concluded that foam in the contactors was blowing out of top and overwhelming the outlet scrubber. The foam carried with it sulfur particles that then deposited in the downstream piping.

A group of NATCO, Shell, and Paques personnel began working closely with plant operations and project engineers at XTO to analyze the problems and find solutions. Antifoam was used to help stop the worst foaming incidents and allowed the plant to process gas. A testing program was initiated to determine the best method of knocking down the foam in the outlet separation equipment.

More importantly, an investigation was launched to determine the root cause of the foaming. Nearly 60 Thiopaq plants are in operation and foaming incidents are rare. What was different about this equipment or process stream? Several areas were investigated including:

- Sulfur concentration in the circulating solution
- Sulfur particle size distribution
- Barrier fluid (synthetic oil) in high pressure pump seals
- Gas analysis – hydrocarbon dew point analysis
- Down hole operations and chemicals used including soap sticks
- Upstream operations such as chemical cleaning and corrosion inhibitors
- Inlet separator and coalescing filter operation
- Make-up water quality
- Gas temperature control
- Contactor Internals

Chemical Factors Examined

The plant solution was checked for sulfur concentration, particle size distribution, and for contaminants. The spray nozzle type and configuration used at the top of each contactor for liquid distribution was evaluated. The liquids being dumped from the inlet separator and coalescing filter were examined. The proportion of low pressure gas from compression versus high pressure gas directly from wells was checked. Most of the gas into the plant was from compression of low pressure wells, but several days into the start-up, high pressure wells were brought into the plant. The operation parameters of the high pressure solution pump seal system were checked. The barrier fluid that had been used was synthetic oil and it was noticed that there was a loss of fluid.
**Sulfur**
Sulfur must be removed from the process on a regular basis either continuously or intermittently. Paques recommends maintaining a sulfur concentration between 0.5\%wt and 1.5\%wt. Some low pressure plants operate as high as 5\%wt with no ill effects. Experience at XTO has shown that operating at the low end of the recommended range provides smoother operation and lowers the chance of upset.

**Upstream Operations**
Down-hole chemicals can have a negative affect on water based processes. Soap stick used to clear the well bore can leave water soluble chemicals in the gas stream that contribute to foaming. Fracturing fluids used to open up tight formations can also be carried out and impact downstream operations. It was difficult to obtain specific information about the quality and quantity of chemical used. No specific cause and effect was established, however, anecdotal information indicated that these operations may have contributed to foaming episodes in the plant.

**Make-up Water Quality**
Make-up water was supplied from an on-site well. Testing showed that the quality of the water had degraded. A new well was drilled and a softener added to insure good quality make-up water.

**Mechanical Factors Evaluated**
It was clear that something was getting into the plant that, when mixed with the solution, caused foaming. The inlet separation lineup was checked to see that it was operating correctly and determine whether additional equipment was needed.

During foaming episodes, solution was carried over with the treated gas and with the flash gas. The presence of foam in the outlet gas scrubber, outlet gas filter, and flash tank caused problems with the level measurement devices. There are foam suppression spray nozzles in various places such as the bottom of the contactor, flash tank, and bioreactors. The foam suppression spray for the flash tank used high pressure process solution and had a large pressure drop before entering the flash tank. This high pressure drop across the nozzle turned the foam suppression nozzle into a foam generator. The process was reconfigured to use low pressure degassed solution as a feed for the foam suppression sprays. Over time it also became apparent that sulfur was settling in the flash tank and building up in the bottom of the horizontal vessel. To keep this sulfur moving, spray bars were added to the bottom of the vessel.

Operation of the low pressure section of the plant (bioreactors, settler, pump tank, centrifuge) was relatively stable even when there were problems in the high pressure section. The biology of the process performed well and caustic use was in-line with predicted values. Plant operators learned the biological parameters quickly and were able to understand and control the biology and chemistry based on analytical testing and visual observations of solution samples.
Gas throughput was limited by higher than expected DP in the contactors. This was an indication that foam was building up in the packing and liquid was held up resulting in erratic sump levels. Finally, liquid would carryover to the downstream piping if the flowrate was not reduced. High contactor DP also caused channeling of both the gas and the liquid causing the outlet H2S count to go up.

**Materials of Construction**

FRP and thermoplastics have performed very well in the low pressure part of the plant. The bioreactors, pump tanks and settler are all FRP vessels. Interconnecting piping is Polypropylene up to the high pressure pumps where the specification changes to 316L SS. Stainless steel piping and components have also performed well showing no signs of corrosion.

The gas piping up to the contactors is sour service carbon steel. This material has performed well. Coated carbon steel has held up well in the flash vessel and the body of the contactors. Significant corrosion in the nozzle throats and flange faces of the high pressure contactors remains a problem. Coating was not properly applied over the flange face providing a place for corrosion to take hold. Also, the choice of metallic spiral-wound gasketing material for flanges and manways proved to be inappropriate. These hard gaskets cracked the coating on the flange face which propagated to wetted areas of the vessel. Traffic in and out of the vessels during installation of vessel internals resulted in damage to coating in the throat area. The use of stainless steel or stainless steel overlay in these difficult to coat areas is a cost effective and reliable solution.

**OPTIMIZATION**

**Root Cause Analysis**

In order to fix the problem rather than treat the effect, an effort was made to determine the root cause.

**Chemical Factors**

The circulating solution is pumped up to 1200 psig using three 50% Reda pumps manufactured by Schlumberger. These 24-stage centrifugal pumps use double mechanical seals with a barrier fluid. Upon installation, the factory recommended barrier fluid was used. The fluid, Royal Purple, is a synthetic oil. To prevent solution from flowing out the seal, the barrier fluid operates at a higher pressure than the solution. The result is ingress of synthetic oil, past the seal, into the process solution. The fluid reservoir needed to be topped up regularly providing further proof that the oil was getting into the process. A bottle test combined with lab testing at NATCO’s Tulsa facilities demonstrated that a tiny drop of this oil causes the solution to foam.

Testing by Schlumberger confirmed that the barrier fluid could be replaced with glycol. Glycol is soluble in water and does not cause foaming. Additional lab tests by Paques show that glycol is consumed by the bacteria so it does not build up in the system.
Gas Analysis
An extended gas analysis was obtained. A HYSYS run demonstrated that the gas was saturated at operating conditions. The dew point curve below shows that even a small reduction in temperature or pressure would result in condensate formation. Piping downstream of the coalescing filter was not insulated. A temperature drop, especially at night, would result in an increased tendency to foam. Restrictions in this section of piping such as flow control valves and reduced diameter block valves, created a pressure drop resulting in condensate formation in front of the contactor. Removal of these restrictions and the insulation of the pipe resulted in a marked reduction in foaming tendency.

![HYSYS Dew Point Curve](image)

**HYSYS Dew Point Curve**

Upstream Operations
Attentive operators noticed a correlation between upstream pigging operations and foaming incidents in the plant. Chemical cleaning fluids, corrosion inhibitors and condensate are all pushed into the plant as a result of pigging operations. The frequency of operation of the dump valves on the inlet Whirlysub and coalescing filter indicated that liquids were being pushed to the plant. The condensate was black in color and the consistency of syrup. A sample of this liquid was collected and again a bottle test showed that this material caused the solution to foam. Many of these processes use chemicals such as soap sticks and fracturing fluids that should be kept out of the plant, if possible.
In an attempt to improve pretreatment, a water wash consisting of a high pressure pump and some static mixer elements was added. Due to less than definitive results, use of the water wash has been discontinued to eliminate the expense of waste water disposal. The 0.3 micron coalescing filter elements were replaced with 0.1 micron elements. Post-compression cooling was maximized to reduce the gas temperature as much as possible in an effort to improve coalescing filter effectiveness. Downstream of the coalescer, the piping was heat traced and insulated to prevent further cooling of the gas. The inlet control valves are kept at 100% open to prevent throttling of the gas prior to entering the contactors and reduced-bore valves have been replaced with full-bore valves to eliminate pressure drop. In future designs where multiple contactors are used in parallel, gas flow control valves will be placed downstream of the contactors.

**Contactor Operation**

Because the foaming presented itself in the contactor, efforts were made to understand what was going on inside. A series of tower scans were performed by Quest TruTec at various operating conditions. The scans showed areas of liquid hold-up and foam build-up during highly loaded operating conditions. Main areas of concern proved to be the sump area and the redistributor trays below the top and middle beds. The trays are designed to hold-up some liquid and redistribute it across the packing below. The concern is that channeling will occur if the solution is not collected and redistributed at certain intervals. The scans showed that the trays were acting like bubble machines, serving as a point of origin for the foam which was then carried up through the packing.

![Redistributor Tray Detail](image-url)
Redistributor tray prior to installation in contactor
Notes:
[1] Contactor Delta P=0, no foam/liquid carry-over
[2] Contactor Delta P=5.5 psi, with high foam/liquid carry-over
Tower Modifications
In the spring of 2006 the redistributor trays were removed and the resulting open space was filled with packing. All three bed supports were left in place so the entire load of packing would not bear down on the bottom support. This proved to be the right choice. Gas throughput improved, pressure drop across the beds was lessened and the H₂S outlet concentration stayed below 4 ppm.

A foam suppression spray nozzle points down towards the sump. As the solution in the sump degasses, bubbles are created. The purpose of the spray is to mechanically knock down the bubbles at the surface. The correct liquid flow must go to the nozzle in order for the nozzle to generate appropriately sized droplets. Too much flow and the droplets become a mist, too little flow and the spray pattern is not maintained. After performing some tests on nozzles outside of the contactor and consulting the nozzle manufacturer’s charts, the correct flow rate was determined. A flow meter was added to the nozzle feed line to insure proper flow settings.

Outlet Filter Enhancements
It was discovered that excessive carryover of solution from the contactors had overwhelmed the outlet coalescer. The filter elements had failed allowing solution and sulfur to enter the pipeline. Simultaneous to finding a solution to the foaming, a plan was put in place to insure that carryover did not enter the pipeline. After extensive testing, a high velocity cyclonic separator known as a Whirlyscrub was installed upstream of the outlet coalescer. This reduced the load on the filter allowing operation of the plant to continue. Similarly, another Whirlyscrub and coalescing filter were added to the flash gas outlet. Previously, the high sulfur content in the flash gas precluded sending this stream back to compression. These modifications allowed the plant to operate at a reduced flow rate while long term solutions were evaluated.

Pump Tank Modifications
Solution passes from the bioreactors into a pump tank on its way to the circulation pumps. The pump tank serves to insure that the solution is completely degassed prior to entering the contactor. Because the velocity through the tank is slow, some settling of sulfur occurs. An observant operator noticed that at times of high differential pressure in the contactors, a sample of solution leaving the pump tank contained an unusually high concentration of sulfur. Inspection of the pump tank internals revealed that settled sulfur was building up on the wall opposite the outlet nozzle. It was surmised that when the sulfur built up to a certain point, it would slough off entering the pump suction. When the solution reached the contactors, pressure drop would momentarily increase until the sulfur was washed through.

A plan was devised to modify the flat bottom of the pump tank to eliminate sulfur buildup. This was accomplished by building an inverted cone into the bottom of the tank. Velocities in the bottom of the tank increased sufficiently to keep the area swept, eliminating the occurrences of high sulfur loading on the towers.
The last time the plant was taken off line was in September 2006 for the pump tank modification. Between September and the writing of this paper in January 2007, TPP has had 100% availability. In the four month period the plant has processed 6 bcf of natural gas with an average outlet H$_2$S content of 1 ppm. Antifoam is dosed on a continuous basis and the operators make every effort to minimize its use.

Plant operators have determined that reducing the concentration of sulfur in solution to very low levels (0.6 to 0.8 wt%), improves operations and reduces antifoam use. The operators feel that controlling this single parameter has had the greatest impact on the stability of the plant. They found that bypassing the settler and sending solution directly to the centrifuge, makes it easier to keep the sulfur at these low levels. As a result of these findings, the settler has been taken out of service. This is not unprecedented as several other Paques plants have bypassed their settlers. A review is currently under way to determine if capital cost savings can be had by eliminating this vessel at the design stage.

Gas flow rate and outlet H$_2$S concentration are measured continuously, recorded and trended. The inlet H$_2$S concentration is measured one per shift using stain tubes. The chart below reflects operational data collected for TPP over the past 4 months of operation. Average gas flow rate is 47 mmol and average H$_2$S inlet is 702 ppm. The outlet H$_2$S concentration has averaged 1 ppm over the same time period. Total sulfur load at these conditions is 1.25 LTPD or 31% of design load.

![TEAGUE PAQUES PLANT H$_2$S INLET / OUTLET & GAS FLOW](image)

TPP Operating Data
LESSONS LEARNED

Pretreatment is Critical
Oil and water do not mix. Add particulate to the solution and the potential for foaming increases greatly. The best solution is to design a pretreatment process that takes into consideration the full range of potential contaminants. This analysis should include intermittent operations such as pipeline cleaning and well services in addition to varying gas composition from different production zones and fields. When faced with a saturated gas, the pretreatment should include dew point control – cooling, coalescing and reheat – prior to entering the contactor. The line from the coalescer to the contactor should be as short as possible, without low spots, and heat traced and insulated. All restrictions in this line such as control valves, reduced-bore valves and orifice plates should be eliminated.

Sulfur Settling
Unwanted sulfur settling occurred in three areas of the plant, the flash tank, the pump tank and the outlet piping header from the bioreactors. To ensure settling does not occur, flow velocities in piping, under all operating conditions, must be carefully reviewed. In future plants, the flash tank will be a vertical rather than horizontal vessel and the pump tank will feature a cone bottom.
Contactor Internals
With the removal of the redistributor trays, the plant saw an increase in throughput, reduced pressure drop and more consistent treat. Because of the low gas velocities and high wetting rates, channeling is not a problem as long as foam is not allowed to develop in the contactor. In order for foam suppression sprays to be effective, they need a specific liquid flow rate. Flow measurement is needed to generate effective droplet sizes under operating conditions.

Materials of Construction
FRP and thermoplastics have performed very well where used in the low pressure part of the plant. Stainless steel piping and components have also performed well showing no signs of corrosion. Coated carbon steel has held up well in the flash vessel and the body of the contactors. Significant coating failure in the nozzle throats and flange faces of the high pressure contactors remains a problem. While stainless steel for high pressure vessels remains the first choice, in situations where economics or delivery dictate coated carbon steel, certain precautions will be taken. Extra care will be taken in surface preparation and application of the coating system. NACE depressurization procedures will be followed to allow permeated gasses to escape the coating safely. Nozzle faces and throats will be stainless steel or SS overlay. Steps will be taken to protect the coating during vessel entry and installation of internals to prevent mechanical damage. Soft gasket material will be used in place of metallic gasketing to protect the integrity of the coating.

CONCLUSIONS

XTO, NATCO, SGSI and Paques took on significant risk in implementation of the first, high pressure application of Shell-Paques. Until now, directly recovering sulfur from high pressure natural gas in the 0.2 to 20 LTPD range has been very difficult. The initial months of operations saw carryover and foaming problems, insufficient throughput and corrosion issues. A root cause analysis was performed and corrective action taken. Today these plants are meeting the outlet specification of <4 ppm H$_2$S while processing all available gas. Plant availability has been 100% since the last turnaround and operating costs are as predicted. With proper pretreatment, the Shell-Paques process has been demonstrated to be a reliable and cost effective treatment option. Lessons learned from the XTO project have already been applied to new projects and are being incorporated into the Shell-Paques best practices design manual for future work.
PAQUES’ Thiopaq® Bio-Desulfurization Process, which economically removes H₂S from sour gas streams, has been successfully implemented on over 60 applications in Europe and North America.

Thiopaq® is a two step process. The sour gas is scrubbed with a mildly alkaline solution. Hydrogen Sulfide is absorbed into solution and sweet gas exits the contactor. The solution then flows to a bioreactor where a controlled amount of air is introduced. The Thiobacillus bacteria, a naturally occurring organism, consume the sulfide ions and excrete elemental sulfur which is filtered out of the circulating solution. The process evolves a hydroxide ion effectively regenerating the caustic used in the absorption step which further reduces the need for added chemicals.

The nature of the sulfur produced in this process is also unique. Biologically produced sulfur is hydrophilic. Chemically produced sulfur (Claus or Redox) is hydrophobic. This may seem like a minor distinction, but from an equipment design and operations standpoint, the impact is substantial. Chemically produced sulfur tends to float, is sticky, and acts as a nucleus for growth of more sulfur. The result is increased foaming, plugging and a requirement for surfactants – another chemical that must be added to the process to “wet” the sulfur particle allowing it to settle. On the other hand, biologically produced sulfur settles naturally without addition of chemical agents. Because sulfur is formed in the bioreactor, plugging is not found in contactors and foaming events are greatly reduced. When land applied, biologically produced sulfur is far superior as a fertilizer becoming available to the plants ten times faster than chemical sulfur.

The THIOPAQ® process is characterized by the following features:
- High removal efficiency for hydrogen sulfide from gas
- High biological activity, so that peak load and other variables in the production processes can be handled effectively
- Short system start-up time
- Easily controlled process
- Operation at ambient temperature
- Operation at wide pressure range (0 to 1300 psi)
- Very low operational costs
- No sulfide containing waste stream
- No use of chemical chelating agents
- No hazardous bleed streams
- Beneficial use of produced elemental sulfur (agricultural)

The same desulfurization principle can be used for the removal of H₂S from gasses like natural gas, refinery fuel gas, pyrolysis gas, and ventilation (air) streams.
Process Chemistry
In the THIOPAQ® process a mildly alkaline solution (pH 8 to 9) is circulated from the bioreactor to the contactor where hydrogen sulfide is absorbed. Sweet gas exits the contactor and the rich solution is returned to the bioreactor. The absorption of H$_2$S and dissociation to hydrosulfide proceeds according to the following equation:

$$H_2S + NaOH \rightarrow NaHS + H_2O$$

From this equation, it follows that alkalinity is consumed.

High H$_2$S removal efficiencies are feasible, because the H$_2$S concentration in the washing liquid will be very low (virtually zero) due to biological activity in the bioreactor.

The alkalinity consumption due to the absorption of H$_2$S is completely reversed when hydroxide is produced as a result of the oxidation of the hydrosulfide ion to elemental sulfur according to the following equation. Air flow to the bioreactor is controlled to limit further oxidation.

$$NaHS + \frac{1}{2}O_2 \rightarrow S^0 + NaOH$$

The THIOPAQ® process uses bacteria to oxidize the hydrosulfide ion. Variations in the H$_2$S loading rate are easily handled due to significant biological over capacity in the reactor.

A small part (<5%) of the dissolved sulfide will be further oxidized to sulfate. The acidic byproduct of this side reaction must be neutralized through the addition of a small amount of sodium hydroxide. This leads to the production of a small bleed stream. The bleed stream (containing sodium salts and some sulfur) is harmless and can in most cases be discharged to sewer.

$$2NaHS + 4O_2 \rightarrow 2NaHSO_4 \leftrightarrow Na_2SO_4 + H_2SO_4$$

Compared to caustic scrubbers, the bleed stream is negligible and expensive treatment of spent caustic is not necessary.

The main product of this process is elemental sulfur. A slipstream of the circulating solution is directed to a filtering step which may involve a settler, centrifuge, belt filter and / or filter press. The exact configuration will depend upon how much sulfur is produced and the site specific disposal options available. The final sulfur product is suitable for landfill or may be put to some beneficial use such as agricultural or in the production of industrial chemicals like sulfuric acid. Biologically produced sulfur has been certified as “organic”.
Process Configuration

The process of removing H₂S from biogas consists of three main sections, an absorber, an aerobic (biological) reactor and a sulfur separation step. A schematic overview of the system is shown in figure 1.

![Figure 1: THIOPAQ® process for gas desulfurization.](image)

**Absorption section**

Hydrogen sulfide is absorbed in a countercurrent absorption tower. The gas enters at the bottom of the column and flows upwards. The washing liquid is sprayed downwards from the top by means of a nozzle. The “rich” washing liquid flows to the aerobic reactor in which the sulfide is oxidized.

**Reaction section, aerobic reactor**

Thiobacillus micro-organisms oxidize the absorbed sulfide into elemental sulfur and hydroxide. Reactor internals are used to ensure complete mixing and optimal mass transfer of oxygen into the liquid phase. The volume of the aerobic reactor is designed in accordance with the total sulfur load and optimal activity of the bio-organisms.

The exhaust air from the reactor can normally be emitted without further treatment. The solution leaves the bioreactor and is recycled back to the absorber column to serve as scrubbing liquid.

An important process parameter is the amount of air being pumped into the reactor. This is controlled accurately in order to limit the formation of sulfate. The air dosage is automatically controlled through a feedback loop that keeps the oxygen content in the bioreactor within a prescribed range.
**Sulfur recovery section**

The produced sulfur is separated from the liquid by means of a centrifuge. The circulating solution normally contains between 0.5 wt% and 2.0 wt% elemental sulfur. A slipstream is circulated to the centrifuge to maintain the desired solid content in the system. The filtration step produces a sulfur cake that is 45-60% solids by weight.

On dry basis, the sulfur cake has a purity of 95-98%. The balance is biomass and salts. The final sulfur product is suitable for landfill or may be put to some beneficial use as a fertilizer, fungicide or in the production of industrial chemicals like sulfuric acid. Biologically produced sulfur has been certified as “organic” and can be used as part of organic farming program.

**Performance and Product**

The biological conversion rate is high, resulting in a negligible sulfide concentration in the bioreactor and washing liquid. Due to this effect, very high removal efficiencies (over 99.9%) are obtained and the H$_2$S concentration in the gas can be reduced to values below 4 ppm.

The aspect that makes this technology most distinctive from other technologies is its ability to recover caustic soda through the conversion by the microorganisms. Generally, caustic recoveries of 94% and more have been observed in existing installations.

The start-up of the THIOPAQ® Scrubber process is simple and quick. The required H$_2$S removal efficiency of the system is achieved almost immediately after startup. Operation of the system is fairly easy. Depending on the complexity of the plant, operator attention can be as low as 30 minutes per day or as high as one operator for 24 hours.

A large biological over capacity ensures a stable process. Fluctuations in gas flow and gas quality within design parameters can be handled without any problems.

The product from the desulfurization process is elemental sulfur. The produced sulfur can be recovered as a sulfur cake (60% dry solids with a purity of 95-98%). The sulfur cake can further be used for the production of sulfuric acid at sulfuric acid plants with facilities for burning waste acid and slurries. In some areas the biological produced sulfur can also be applied as a fertilizer.
APPENDIX II

Direct Treat Technologies Stretford, LO-Cat®, SulFerox®, and CrystaSulf®

**Stretford**

The first liquid phase, oxidation process, which gained widespread commercial acceptance, was the Stretford process. The process was developed by the North Western Gas Board and the Clayton Aniline Company in England to remove \( \text{H}_2\text{S} \) from town gas. The original process utilized an aqueous solution of carbonate/bicarbonate and anthraquinone disulfonic acid (ADA). The process kinetics were improved by the addition of alkali vanadates to the solution, which, in essence, replaced dissolved oxygen as the oxidant in the conversion of hydrosulfide ions (HS\(^-\)) to elemental sulfur. In the reaction the vanadium ions undergo a valance change from \(+5\) to \(+4\). To reoxidize the Va\(^+4\) ions back to the \(+5\) State, ADA is added as an oxygen carrier, and the ADA is subsequently regenerated with air.

Although the addition of vanadium to the Stretford Process increases the reaction rate of hydrosulfide ions to sulfur sufficiently to make the process commercial, it still produces a significant amount of byproduct thiosulfate. The reaction is still slow enough that air streams cannot be treated due to the high rate of thiosulfate formation.

Hundreds of Stretford units have been installed throughout the world; however, their popularity vanished in the mid 1980’s as it became difficult to dispose of sulfur containing vanadium salts, a heavy metal that makes the sulfur hazardous waste.

**Chelated Iron Processes**

SulFerox® and LO-Cat® are very similar. Both are aqueous, use iron as a catalyst and chelating agents to increase the solubility of iron in water. In the reaction the iron ions undergo a valance change from \(+3\) to \(+2\). To reoxidize the Fe\(^+2\) ions back to the \(+3\) state, oxygen is added. In practice the iron is regenerated with air. The solution is maintained in the slightly alkaline range and circulated to a contactor where \( \text{H}_2\text{S} \) is absorbed from the host gas. Iron in the oxidized ferrous (Fe\(^+3\)) state transfers electrons from the sulfide ion to produce elemental sulfur. The solution is circulated to an oxidizer where air is introduced. The dissolved oxygen reacts with iron in the reduced ferric (Fe\(^+2\)) state effectively regenerating the iron to the ferrous state. A slipstream is sent to a filter separator where elemental sulfur is taken out.

Up to six chemicals are added to the process all of which must be kept in balance. Chelated iron is added to make-up for losses in the blowdown and produced sulfur cake. Chelates are added to compensate for degradation of chelating agents under process conditions. Caustic is added to counteract acidic reaction byproducts such as thiosulfate and to maintain alkalinity due to blowdown losses. A surfactant is added to reduce the water surface tension allowing the sulfur to sink. Antifoam is added continuously and/or on an as needed basis. A biostat is
added to control biological activity in the solution that, if unchecked, can cause rapid degradation of the chelating agents.

CrystaSulf®

Seeing a technology gap, GTI funded research into a new process with the goal of direct treating natural gas while eliminating foaming and plugging problems. Foaming occurs when water, hydrocarbons and solids are agitated, so GTI settled on a non-aqueous scrubbing liquor. Chemically produced sulfur from chelated iron processes is sticky and forms throughout the process building up in undesirable locations resulting in plugging. To address this issue, the CrystaSulf scrubbing liquor includes a component that dissolves elemental sulfur at temperatures over 90 degrees F. When the solution is cooled, the dissolved sulfur forms a crystal (thus the name CrystaSulf) that can be filtered out of the solution. By controlling the temperature of the solution, plugging is eliminated and sulfur crystals are formed only in the part of the process designed to handle solids.

Following the existing Redox processes, CrystaSulf was designed to use oxygen from air as the electron acceptor from sulfide. In practice, the oxygen absorption is too slow. They discovered that Sulfur Dioxide (SO₂) went into solution readily and according to the Claus reaction, reacts with H₂S to form elemental sulfur. This is the current approach. For smaller units, the operator will truck in SO₂, a commodity chemical, and inject it into the process in stoichiometric 2:1 ratio to H₂S. Larger units will either convert one third of the incoming H₂S to SO₂, through combustion, or the produced elemental sulfur will be burned and the flue gas scrubbed into solution. This SO₂ requirement adds complexity to the process.

Additional complexity is found in the sulfur filtration step. The hydrocarbon based solution must be washed from the sulfur product using a light hydrocarbon such as heptane. The heptane is washed from the sulfur in a second step with water. The scrubbing solution, heptane and water are separated in a distillation step and recovered. In yet another sub-process, thiosulfate byproducts are removed by adding anhydrous ammonia to form ammonium thiosulfate. This insoluble salt precipitates and is filtered from the scrubbing solution.

Compared to water based solutions, CrystaSulf® solution is expensive. Think of it as a distillate like kerosene. The treated gas leaving the contactor is saturated with solution. In a system treating a large gas flow, the solvent loss can be substantial. An application with high flow rate and low H₂S concentration will have a very high cost per ton of sulfur removed. As a result, CrystaSulf is limited to a very narrow niche – high pressure, high concentration, low CO₂, and less than 20 LTPD.

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SulFerox is a service mark of Shell Global Solutions Inc.
CrystaSulf is a service mark of CrystaTech, Inc.
APPENDIX III

Process Flow Diagram for XTO Teague Paques Plant
Bibliography


