SULFUR REMOVAL ON AN FPSO – A LIQUID REDOX PROCESS CASE STUDY

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ABSTRACT

Eni started producing oil reserves from the Aquila reservoir in the Adriatic Sea after the discovery in 1981. As primary production decreased, a decision was made to start enhanced recovery with artificial gas lift. Located in deep waters (815 meters) and 46 km off the southern coast of Italy, a floating production, storage and offloading vessel (FPSO) was needed.

As part of the production process scheme, the vessel needed to generate steam and electricity from the produced associated gas. Equipment was installed to remove hydrogen sulfide (H_2S) from a combination of the oil stabilizer overhead vapors, the sour water stripper overhead vapors and, if required, a slip stream of the produced gas. The treated gas must meet an H_2S specification of 100 parts per million vapor (ppmv) to provide stripping gas for the sour water stripper and meet post combustion emissions specifications from the steam boiler and turbine generator.

The anticipated sulfur removal requirement was 2.3 metric tons per day (MTPD). Eni requested a process that would be economical while minimizing environmental impact, operator attention and logistical support. Following a detailed evaluation, the liquid redox process from Merichem Company (Merichem) was selected for the Aquila Phase II Project and installed as part of the topsides on the FPSO Firenze.

After a five-year run (2013-2018), the FPSO Firenze has stopped production due to low oil production. This case study looks at the decision to use LO-CAT® H_2S removal technology (a liquid reduction-oxidation process), the cost of operation, and the unit availability over its' lifetime.

INTRODUCTION

As the energy industry searches for reserves in ever-deeper formations, there appears to be more sulfur with which to contend. Deep oil reservoirs in the Caspian Sea, Gulf of Mexico and offshore Brazil show significant amounts of H_2S in the produced well fluids. H_2S at low levels (just 100 ppmv) is a life-threatening, corrosive and flammable gas. Exploration and production of fields with significant H_2S levels must be done under very strict safety precautions. Ultimately, disposal of the H_2S must be designed into the production facilities.

Several H_2S removal technologies are available, including non-regenerative liquid scavengers (triazine-based), non-regenerative solid-bed absorbents and the regenerative liquid reduction-oxidation (redox) process. These technologies remove sulfur from associated gas streams and do not release them to the environment. The non-regenerative technologies are often referred to as scavengers.

PROCESS EVALUATION

During the initial design phase, several H_2S removal technologies were evaluated based on the following criteria:

- Turndown capability
- H_2S removal efficiency
- Operator attention requirement
- Maintenance requirement and waste material produced
- Proven reliability in marine conditions

The evaluation led to the selection of the liquid redox process after it received the highest marks in four of the five criteria above. Both liquid and solid H_2S scavengers were considered as alternatives to the liquid redox process for this installation. Following is a discussion of each criteria.

Turndown Capability

Oil and gas wells can undergo significant changes in flow and composition over the production life of a reservoir. The liquid redox process is very flexible and can be designed for changes in both flow and composition. Additionally, H_2S compositions can vary either up or down with flowrate changes. The FPSO Firenze unit maintained stable operations throughout these operational events while meeting the guaranteed product H_2S specifications.

The same may not be true for scavengers. At low gas flow rates, both liquid and solid scavengers can experience mal-distribution of the gas phase resulting in incomplete contact within the absorption media.

H_2S Removal Efficiency

The cost of consumable chemicals for a liquid redox process is significantly lower relative to scavengers. The following table shows some representative values based on recent pricing:

Table 1 – Approximate (Relative) Operating Cost per Weight of Sulfur Removed

Chemicals/ Sorbents	Redox Process	Solid Scavenger	Liquid Scavenger (Triazine-based)
US$ / Pound of Sulfur removed	0.30 *(1x)*	4.50 – 6.50 *(15 - 22) x*	7.50 – 10.00 *(25 - 33) x*
US$ / Metric Ton of Sulfur removed	672	10,080 – 14,560	16,800 - 22,400

For the liquid redox process, the operating cost includes both chemicals and electricity for pumps and blowers. For the scavengers, only chemical cost is represented. Because the redox process uses a circulating, regenerable solution, the consumption of chemicals is much smaller relative to non-regenerative scavengers. However, a liquid redox system requires a higher capital investment relative to either a solid or liquid scavenger system. In the current example, the lower operating cost helped to balance out the higher capital cost within the first 2 years of operation.

Operator Attention Requirement

Operators monitor the operation of the liquid redox process daily to maintain efficient sulfur removal. Monitoring includes running simple tests on the circulating solution and checking operating liquid levels. Most operators report spending from one to two hours per day of interaction with the process. Solid H_2S scavengers do not require regular operator attention, but liquid H_2S scavengers and liquid redox units need daily monitoring.

Maintenance Requirements and Waste Material Produced

A big difference between scavengers and the liquid redox process is in maintenance and logistical support. Scavengers react with H_2S to form sulfur compounds which are not regenerable. They require complete change-out of material once it is spent. When sulfur loads are small, a scavenger system can be sized for long operating times between sorbent change-out. For sulfur loads over 1100 pounds per day (500 kg/day) the frequency of change-out tends to be more often to maintain reasonable equipment sizes. A LO-CAT® unit typically runs 1-3 years between shutdowns for maintenance.

Liquid scavengers are relatively easy to handle; however, disposal of the spent material may be an issue. The spent material cannot be dumped into the sea. The best disposal method is to route spent material into the produced water for treatment. Depending upon the chemicals used, additional processing of the sulfur compounds in the produced water may be required.

Spent solid scavengers can cause some serious handling problems when they need to be replaced with fresh scavenger. Although fresh solid scavenger generally flows easily, spent material can agglomerate into a solid mass within the reactor. Mechanical clean-out can become rather messy if this happens. Spent solid scavenger material may also contain iron sulfide that is pyrophoric when contacted with air. The material must be wetted or be allowed to oxidize in a controlled fashion before hauling it to shore for disposal. In addition to the extra handling required, wetting spent solid scavenger materials increases the total weight of the disposed material.

Another problem with solid scavengers is the large amount of spent material. For every pound of sulfur (0.5 kg) that is removed, about 10 pounds (~4.5 kg) of spent solid scavenger material is produced. The transportation of large quantities of solids to and from an offshore facility can be costly. The liquid redox process produces just 1.5 pounds (0.7 kg) of solid sulfur product for every pound of sulfur removed.

Proven Reliability in Marine Conditions

Scavengers have been used in the marine environment for small quantities of sulfur removal. When sulfur loads are small (less than one ton/day) scavengers offer the most economical choice. The liquid redox process has been used offshore to remove total sulfur above two tons/day. Two platforms in the Gulf of Mexico have used Merichem's liquid redox units for sulfur removal but they are no longer in operation. The companies operating those units reported good operating results and very high on-stream factors for the liquid redox process.

FPSO FIRENZE

Comart S.p.A., a subsidiary of Tozzi Industries Sud S.p.A., worked with Merichem Company to design the H_2S removal single-lift module for the Aquila Phase II Project. The FPSO Firenze vessel is 810 feet long by 140 feet wide (247 meters x 42.5 meters). The topsides can process 10,500 BPD of crude oil and 7.5 MMSCFD (205,000 SCMD) of associated gas. The hull has a crude oil storage capacity of 750,000 barrels. **Figure 1** below shows a picture of the Firenze FPSO. The arrow points to the liquid redox unit.

Figure 1 – Firenze FPSO

Figure 2 shows the basic topsides process scheme for the FPSO. In addition to the six main modules shown, the topsides included modules for black-start compression, stripping gas compression, fuel gas metering, fuel gas compression (to the power turbine), steam boilers and main power generation. Each module varied in weight from 10 to 530 tons and was designed as a single lift for topsides installation.

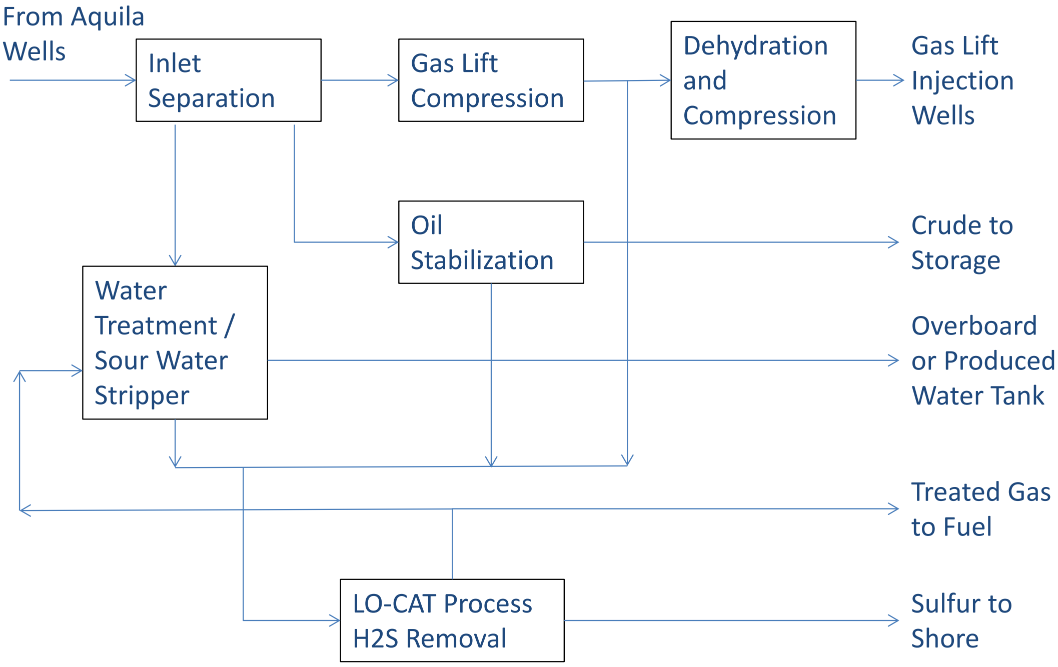

Figure 2 – Firenze Topsides Block Flow Diagram

THE LO-CAT® PROCESS

In this FPSO application, the liquid redox unit processes sour gas streams from the oil stabilizer, the sour water stripper and (if required) the gas lift compressor. The original design conditions were:

5.1 MMSCFD (144,400 SCMD)
H_2S in = 11,000 ppm
H_2S out = <100 ppm
2.3 Metric Tons Per Day (MTPD) Sulfur
Pressure = 73 psia (5.0 kg/cm^2_a)

A process flow diagram of the liquid redox system incorporated in the FPSO is shown in **Figure 3**.

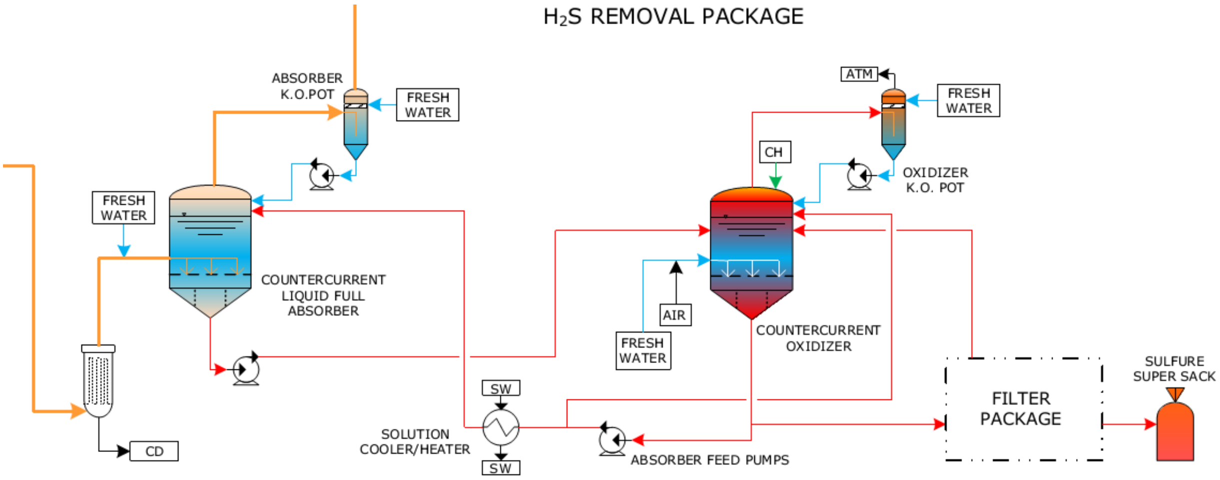

Figure 3 – Liquid Redox System Configuration

The combined sour gas streams pass through a coalescing filter first to remove any entrained liquids prior to entering the unit. The feed gas is then routed to a liquid full absorber (LFA) where it contacts with a proprietary aqueous solution of chelated iron. H_2S is absorbed into the water and then reacted with the iron to form solid elemental sulfur as follows:

$$H_2S + (H_2O) \longrightarrow S^{=} + 2H^{+} + Fe^{+++} \longrightarrow S^{o} + Fe^{++} + 2H^{+}$$

The sweet gas exits the LFA and passes through a knock-out pot with water wash to recover any entrained solution prior to entering the fuel gas system.

The solution leaving the bottom of the LFA is pumped to the Oxidizer for regeneration. In the Oxidizer, air is sparged through the solution and the ferrous iron (Fe^{++}) is oxidized to the active ferric state (Fe^{+++}) as follows:

$$\tfrac{1}{2} O_2 + H_2O + Fe^{++} \longrightarrow 2Fe^{+++} + 2OH^{-}$$

The air exiting the Oxidizer is routed to a knock-out pot to recover any entrained solution. This stream contains no H_2S so it is routed directly to the atmosphere. Most of the regenerated solution is circulated back to the LFA.

By adding the reactions shown for the LFA and Oxidizer, the overall reaction becomes the direct oxidation of H_2S to elemental sulfur as follows:

$$H_2S + \tfrac{1}{2} O_2 \longrightarrow S^{o} + H_2O$$

This reaction takes place at near ambient conditions in the aqueous phase. This makes the chemistry inherently safer than a fired process such as a modified Claus unit.

Removal of sulfur from the unit is accomplished by directing a slip stream of circulating solution to a pressure belt-filter. The filter uses high-pressure air and wash water to recover solution and produces a filter cake consisting of 65 wt% sulfur and 35 wt% dilute solution (mostly water). Consequently, for every pound of sulfur that is removed from the gas stream, ~1.5 pounds of sulfur cake is produced. This compares very favorably with the ~10 pounds of spent solid scavenger produced for every pound of sulfur removed. Although the sulfur cake contains 35 wt% water, the cake is dry to the touch, and there is no liquid leakage from the cake. As shown in **Figures 4** and **5**, the sulfur cake is collected in one-ton Super Sacks® and then stored on deck until the next supply boat arrives.

Figure 4 - Sulfur Loading

Figure 5 – Sulfur Storage

SPECIAL DESIGN CONSIDERATIONS

In addition to standard marine specifications, an FPSO requires special design considerations due to the constant movement or rocking of the vessel caused by wave motion. This movement is extremely important when trying to control liquid levels in vessels. Merichem used Computational Fluid Dynamic (CFD) modeling to design baffling systems within the LFA and the Oxidizer vessel that minimize liquid sloshing. These CFD modeling protocols enable Merichem to perform calculations for any set of motion parameters when designing new units.

The movement of the vessel also affected standard analytical procedures employed for on-shore operations. Weigh scales could not be used under these conditions, posing a significant analytical problem. Merichem developed volume-based techniques to determine the amount of sulfur contained in the circulating solution. Measuring sulfur content is an important operational variable.

Space and weight limitations on an FPSO affect equipment sizing and module layout. The H_2S removal module (**Figures 6** and **7**) was constructed for a single-lift onto the FPSO topside. To conserve space, the module was designed in a stacked fashion, building “up” rather than “out”. Because the system contained 141 MT of solution (mostly water), a fair amount of structural steel was required. The resulting module has the following dimensions:

Table 2 – Module Dimensions

Parameter	Length	Width	Height	Empty Weight	Operating Weight
Value	16 m	15 m	13 m	405 MT	546 MT

Figure 6 – H_2S Removal Module

Figure 7 – Single Lift

OPERATING RESULTS

After experiencing typical startup difficulties such as power outages, the liquid redox unit has performed very well. The unit quickly exhibited its turndown capabilities and process flexibility. The sour gas flow rate varied from 1.5 to 5.1 MMSCFD (42,500 to 144,400 SCMD), inlet H_2S concentrations varied from 8,000 ppm to 15,000 ppm and sulfur production rates have exceeded the design capacity (2.3 MTPD) of the unit. Despite these varying gas flows and sulfur concentration regimes, the unit consistently met the 100-ppmv outlet H_2S specification.

Modifying liquid redox technology for functionality in an FPSO environment has not negatively impacted unit performance. Since going online in January 2013, the LO-CAT® unit has required about 25 hours per week of operator attention or about 3 hours per day on the continuously manned facility. This is somewhat higher than land-based units due to the change-out of Super Sacks®. The unit consistently exceeds the H_2S removal requirement (typically <20 ppm in the treated gas) and has achieved all performance guarantees and operational requirements.

Due to the value of the sulfur cake as a fertilizer and fungicide in the Italian vineyards, Eni disposed of its sulfur byproduct on-shore at no cost.

Availability

In the past, reliability of liquid redox processes has suffered due to solid sulfur falling out of solution and plugging piping and equipment. Merichem has adopted design and operating practices that keep sulfur from settling in the wrong places within the unit. In addition to strict adherence to velocities in design of the unit, the main operational method is to use “air blasts” or water injection that are placed strategically throughout the unit in regions of low flow. Nozzles send bursts of air or water into stagnant areas, preventing sulfur buildup.

In 2015, the amount of sulfur to be removed started to exceed the design of 2.3 MTPD. This occurred over production periods from days to weeks. The sulfur belt-filter was not able to keep up with the added load and this caused the solution to carry more solids than design. The result was more frequent outages to clear plugging in some piping. Eni operators were able to clear these sections of pipe in just a few hours. Their diligence and quick recognition of these issues resulted in only a minor increase in downtime.

Availability of the unit on the FPSO Firenze has been very high, ranging from 97 to 98% on-stream. There was no shut down for maintenance in the first 18 months of operation. Eni then moved to a yearly turnaround schedule. The annual turnaround takes just 4-5 days from gas-off to gas-in. The remaining time off-line consisted of infrequent, short outages when sulfur removal was high.

Cost of Operation

The two largest operating cost components for a liquid redox system are chemicals consumption and electrical usage. Tables 3 and 4 show the average operating costs of the unit on FPSO Firenze.

Table 3: Electrical Demand

Major Electricity User	FPSO Firenze
Air Blowers (kW)	230
Circulation Pumps (kW)	75
Sulfur Filter + Smaller Users (kW)	30
Total Electricity (kW)	**335**

The electrical demand is constant, even with changing sulfur load. Electricity is generated on site. Since the gas to fire the turbine would otherwise be injected as artificial gas lift for the reservoir, fuel cost is near zero.

Table 4: Operating Cost per Amount of Sulfur Removed

Operating Cost	$US / Long Ton	$US / Pound
Merichem Catalyst / Chemicals	530	0.24
Potassium Hydroxide (KOH)	117	0.05
Electrical (@ $0.0/kW-hr)	0	0
Major Operating Cost	**647**	**0.29**

The basis for the values above is an average of 2.1 MTPD of sulfur removal over the 5-year operating period. Minor costs include 3 hours per day of operator time to conduct solution testing and other operator tasks. Operator responsibilities included activities for other process units on the FPSO in addition to the liquid redox unit.

SUMMARY

Experience on the FPSO Firenze has shown the versatility of the LO-CAT® process to operate across a wide range of operating conditions and Merichem's capability to modify liquid redox units for specific floating offshore applications. The unit has proven its reliability in floating marine conditions.

When H_2S levels exceed the economic limits of scavengers, liquid redox technology is a viable option that demonstrates efficient H_2S removal, excellent turndown capabilities and minimal operator attention. In particular, the low maintenance and transportation support required to handle the sulfur cake offers a significant improvement over the volume and weight of waste material produced by scavengers.