FIELD TRIAL OF INNOVATIVE HYDROGEN SULFIDE REMOVAL PROCESS TREATING GAS FROM PRODUCTION SEPARATOR

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Abstract

Production contamination with hydrogen sulfide continues to present a threat to safe asset management and product quality. The oilfield is in need of lower cost applications to reduce both the price and complexity of removing this hydrogen sulfide from gas production economically. Hydrogen sulfide is generated in geothermal and biological processes within the formation and is not found at consistent concentrations across fields, wells, or lifecycles. This has presented unique challenges to removing the contaminant in a reasonable, reliable, and simple manner.

A completely new approach to hydrogen sulfide removal was presented in 2021 at LRGCC ("Innovative Hydrogen Sulfide Removal Process Reduces Costs with New Chemistry") and this paper will follow the development path forward for the ECOTREAT™ technology which has now completed field trials in the Permian Basin, specifically the Delaware Basin. The field trials will be presented with over a month's worth of activity, various wells, a wide range of hydrogen sulfide concentrations up to 2% by mol, and utilizing a new regenerable catalyst. The non-hazardous catalyst is recovered for the process. The economics will be presented, including a simple regeneration of the catalyst using only air and either pH adjustment or produced water from the same wells. Data is included about operating in the absence of produced water, with only pH adjustment for successful removal of H_2S. The final disposition of the sulfur is an aqueous waste stream which can be safely mixed back with produced water and sent for typical disposal.

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Introduction

United States oil production has shifted from Tier 1 acreage in recent years and is confronting new challenges in second tier assets, three of which are increasingly sour sources, higher gas ratios, and higher water ratios. This combination has introduced additional costs associated with production from these assets. Despite these shifts, environmental efforts have pushed to reduce flaring and reduce rates of water injection into saltwater disposal wells. While these are reasonable and important environmental requirements that should be viewed positively, they introduce complexity to the already arising challenges of secondary acreage. It was in this context that a new technology, ECOTREAT™ and it's chemistries has been developed for gas desulfurization utilizing produced water as a solvent for gas conditioning.

Chemistry

ECOTREAT™ uses a proprietary water-soluble scavenger which reacts with hydrogen sulfide by forming covalent bonds. The reaction is thus not reversible until additional chemical reaction is introduced. Changes in pH and temperature do not cause the release of hydrogen sulfide gas. Each molecule can react with hydrogen sulfide multiple times, allowing for similar mass of scavenger as existing liquid scavengers which absorb about 10% of their weight as sulfur. An irreversible reaction, Equation 1, the chemical reacts until completely spent or until hydrogen sulfide is completely removed from the gas as hydrosulfide. Unlike triazine derivatives, complete spending is not harmful to the product and does not produce amorphous dithiazine. The sulfur and scavenger form a bond which cannot be reversed with low grade heat or changes in pH.

$$Scavenger + 2H_2S \rightarrow (Scavenger - SH - SH) + 2H^+ \qquad \text{(Equation 1)}$$
$$2\,(Scavenger - SH - SH) + 3O_2 \rightarrow 2\,Scavenger + 2\,S_2O_3{}^{-2} \qquad \text{(Equation 2)}$$

The scavenger can be regenerated at ambient conditions in air via Equation 2. Once in contact with oxygen, the scavenger rapidly oxidizes hydrogen sulfide to thiosulfate anions and breaks the bond with the scavenger. The thiosulfate anion is highly soluble in water but also acidic. It is important that the water in the aqueous solution be of a suitable concentration of cations, but especially useful are carbonate salts. Produced water is available in locations, such as the Permian, where water is produced at an average of 5 times that of oil.[1] Produced water is a

[1] Steve Coffee, 2018

brine solution often composed of high concentrations of salts including cations such as sodium, calcium, and potassium. The high salinity, typically greater than 3.5%, means the water is heavily buffered with dissolved salts suitable for use in this reaction. The general cationic strength offers an excellent buffer for the thiosulfate ions produced from the oxidation reaction. Small amounts of water can be utilized, absorbing at least 5% of their weight in sulfur, and then diluted back into the bulk produced water stream where the total change in Sulfur-oxoanions ions is relatively small, often less than 1% of the existing total sulfur species in the water.

Process Description and Skid mounted unit

Implementation of the chemistry can be done in a variety of ways, but the simplest of those is a pair of vessels: one an absorber and one an oxidizer. Additional equipment, such as a condensate knock-out pot or flash tank may be required and are described. A flow diagram for this type of treatment system is shown in Figure 1.

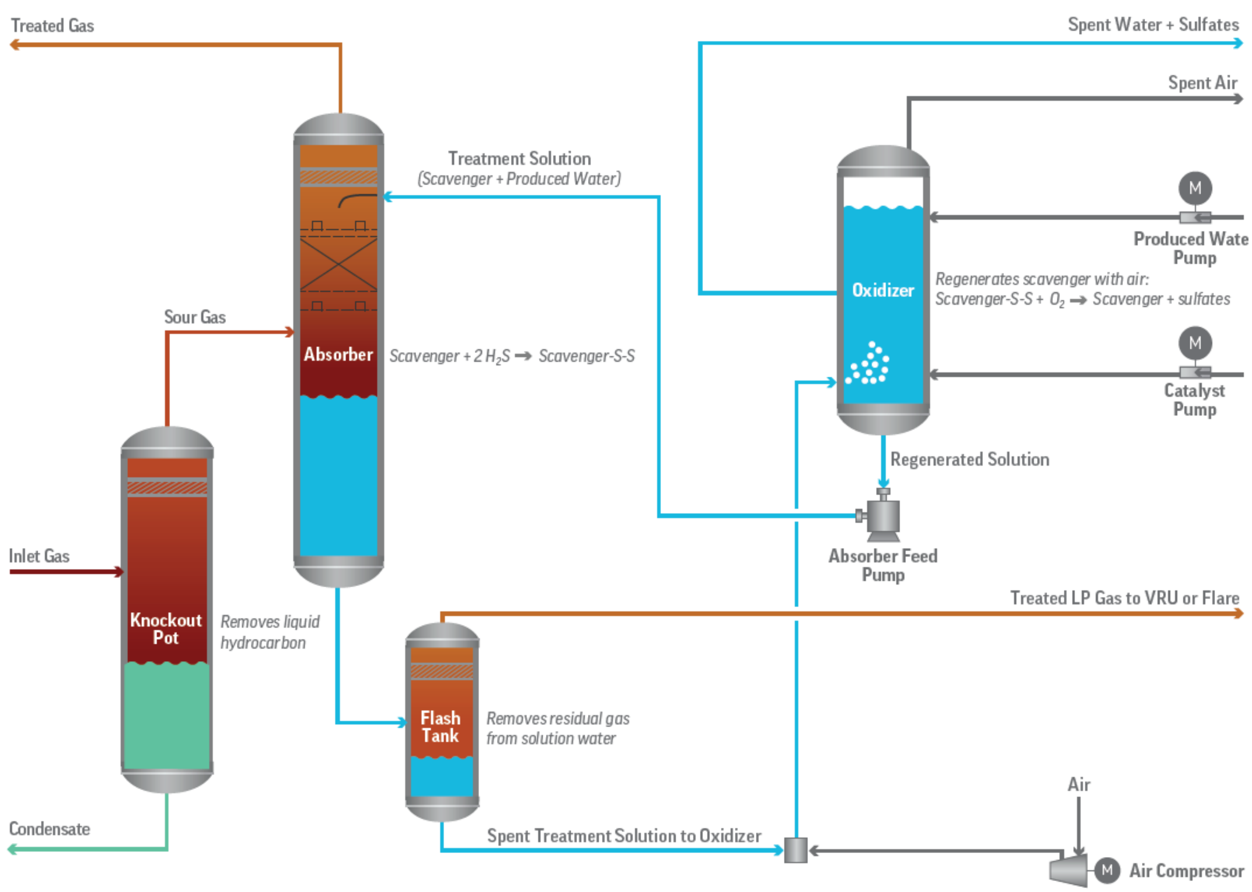

Figure 1- Flow Diagram for ECOTREAT™

Figure 2- ECOTREAT™ demonstration unit installed in the field

In Figure 2, the field installation of the unit is shown including two columns for testing, both a packed bed column and a bubble column (also called a liquid full absorber, LFA). The skid mounted test system is equipped with process control and a compressor to provide utilities. Due to the small size of tubing and relatively small flows, the unit is insulated and traced to prevent influence of temperature fluctuations from interfering with data collection accuracy. The columns shown on the unit (from furthest to closest) include an oxidizer, a flash drum, a bubble column, an inlet knock-out, and a packed column. A plan view from the back side is shown in Figure 3. From this angle, the air compression, control panel, and pumps can be seen more clearly.

This skid was transported to the site in the horizontal and set at a field near Jal, NM and powered by a diesel generator. Gas from the separator was collected and returned to the sales gas line prior to custody transfer, but free of hydrogen sulfide. Experimental planning included more than 30 days of testing but was broken down into 3 primary modes of testing. Treatment solution was evaluated for pure potassium carbonate vs produced water. Absorber design was evaluated for either packed bed or bubble column operation

Objectives	Demonstrate ability to remove hydrogen sulfide in sustained field operation
	Verify operating window and solution capacity
	Compare packed bed and bubble column performance
	Treat gas with produced water from same wells

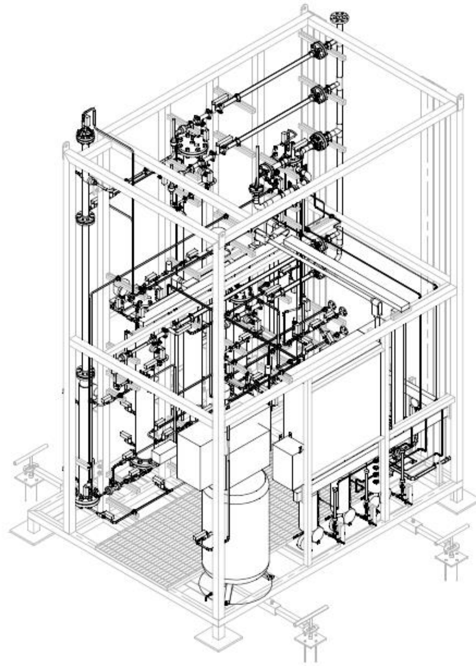

Figure *3*- ECOTREAT™ demonstration unit shown from rear

Results of Operational Field Trial

Trials started with a prolonged start-up period due to low sales gas pressure available. Merichem Technologies staff worked with the wellhead pumper staff to improve available pressure from an initial supply of less than 10 psig. This was insufficient to supply the skid and caused some of the data to be discontinuous. Once operation was smoothed out, several test runs were made. One of the runs is shown below where the operation clearly demonstrates greater than 99% removal of hydrogen sulfide until end of run. In this test, the unit was fed more than 14,000 ppm H2S and had only been designed to receive 10,000 ppm of maximum in the feed. In this condition the unit exceeded its name plate capacity of 2 lb hydrogen sulfide removal per day for several hours.

Operation Parameters	**Run with PBA**
Feed Gases	Sour Sales Gas @ 32 psig
H_2S in feed gas, ppmv	5200 - 15000
Gas rate, lb/min	0.03 ~ 0.07
PBA Liquid loading, gpm/ft^2	15 ~ 20
Catalyst to H_2S molar ratio	0.45 – 1.3
Treating Solution	20 %K2CO3 in water

Treating solution's S.G.	1. 14 – 1.16

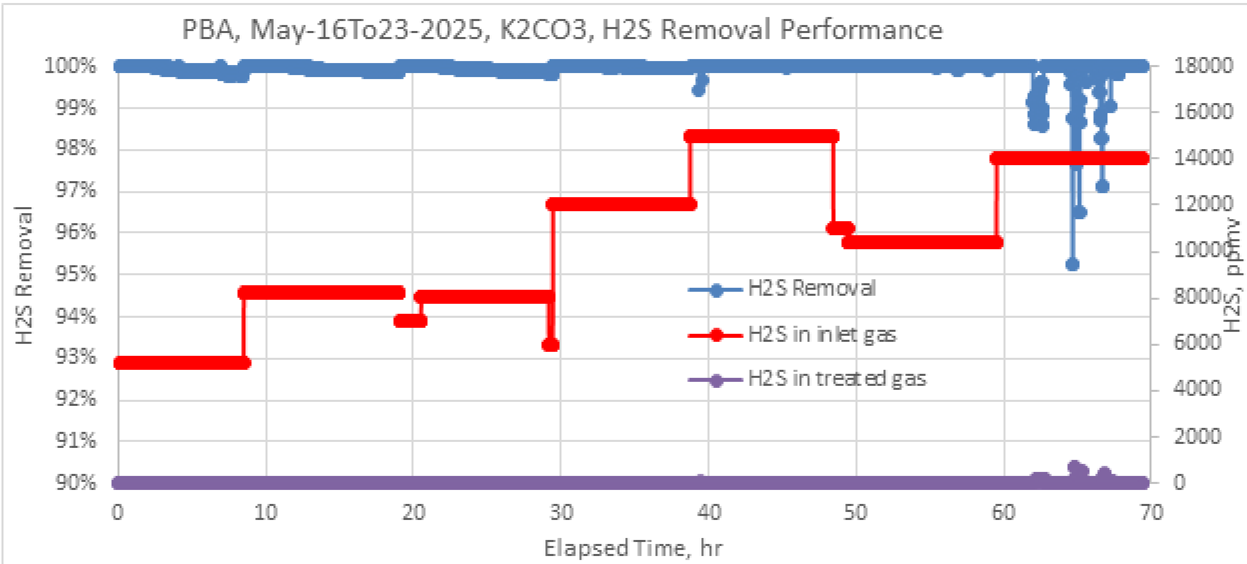

Figure *4*- ECOTREAT™ packed bed operation data set

For several days further, operation was changed to utilize the liquid full absorber system. Similar to the packed bed, solution was continuously circulated from the absorber to the oxidizer, and then back to the absorber in a loop. In this condition, similar supply gas was utilized but the overall concentration was much more steady for this period. Once again, sustained removal of > 99% hydrogen sulfide was achieved. This trial showed a smooth operation.

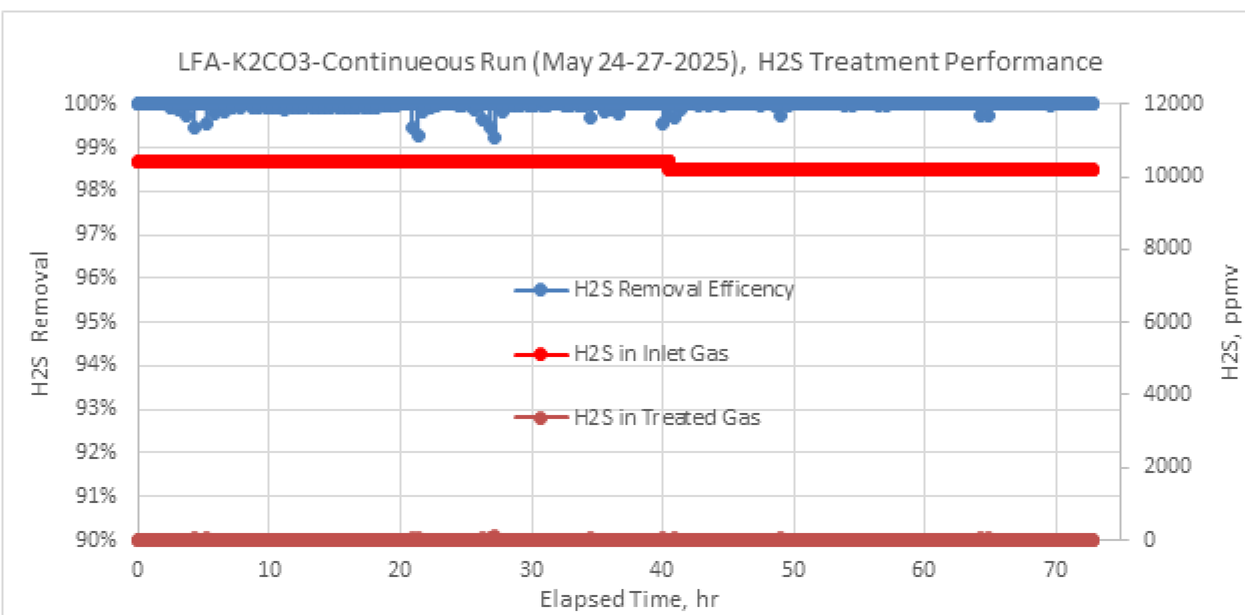

Figure 5- ECOTREAT™ liquid full absorber operation data set

The final test was conducted utilizing produced water. During this run, 16 gallons of produced water was charged into the system each day and allowed to spend to completion during operation. In each day's run, about 0.5 lbs of sulfur was removed. This created a ratio of about 30 gallons of produced water per pound of sulfur removed. As shown, in the table below, the alkalinity of the fresh produced water was very low. The produced water contained very small amounts of carbonate and mostly high levels of chloride. This made the produced water used at this site one of the worst samples of produced water for the purpose of the ECOTREAT™ process ever tested, yet the hydrogen sulfide concentration, gas ratio, and water ratio were sufficient to treat all of the sales gas with produced water from the same wells.

Operation Parameters	**Run with LFA**
Feed Gases	Sour Sales Gas @ 32 psig
H_2S in feed gas, ppmv	11000- 15000
Gas rate, lb/min	0.03 ~ 0.05
Fresh Alkalinity of produced water	0.06%
Catalyst to H_2S molar ratio	0.45 – 1.3
Treating Solution	Produced Water

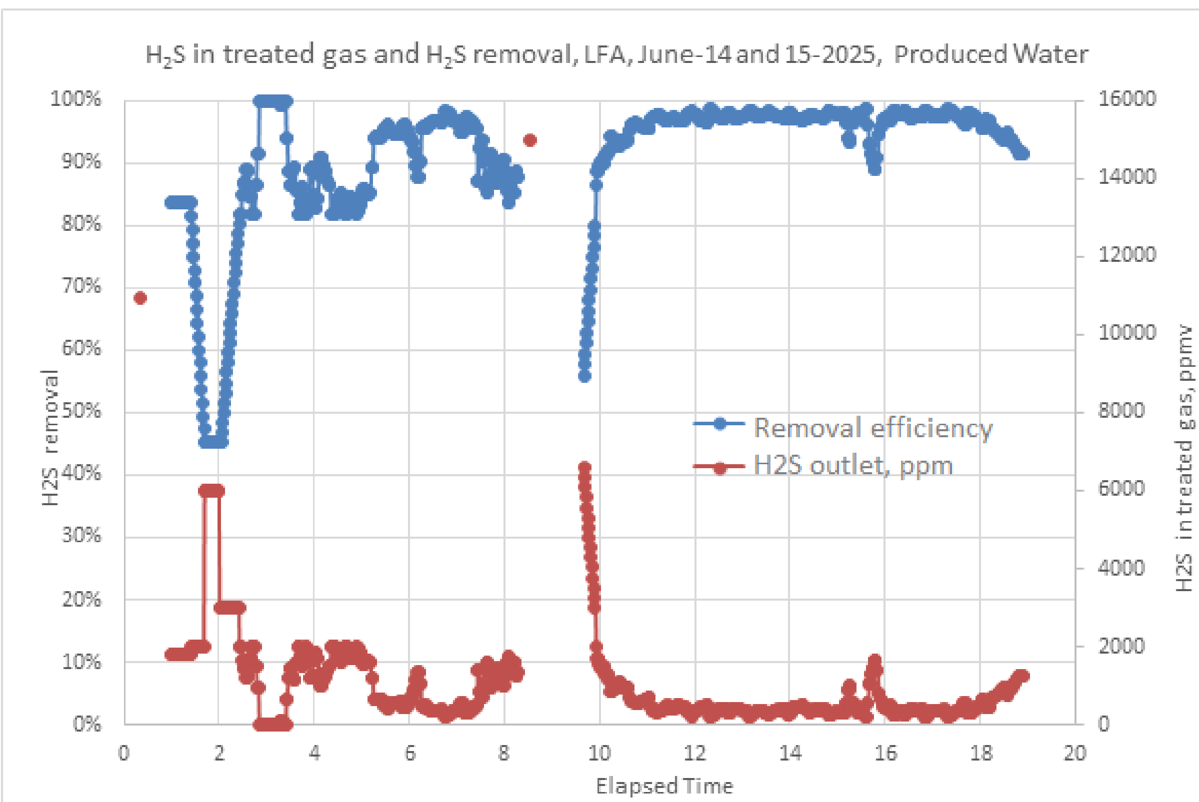

Figure *6*- ECOTREAT™ liquid full absorber operation data set

Conclusion

Utilizing ECOTREAT™, produced water offered an excellent low cost treating opportunity at this well site, able to effectively treat the entirety of gas production with water from the associated wells during production. Even the utilization of pure potassium carbonate would have been a new and exciting opportunity for improved treatment options. The majority of components required to conduct treating are already available at the wellhead, requiring only catalyst and electricity to remove hydrogen sulfide in an environmentally advantageous way. Any hydrogen sulfide dissolved in the produced water was also treated, reducing the hazard associated with handling this product downstream.

Typical Barrel Produced, API	40
Water to Oil Ratio	4
Gas, scfm/BBL	1000
Gas H_2S level, ppm	15000
Maximum H_2S capacity of produced water, %	0.3
% of produced water needed for scrubbing, %	10.4

With a reduced requirement for shipping and maintaining chemical inventories, this alternative scavenger is environmentally friendly with substantial cost savings. There are a variety of advantages to this technology over existing applications and they have now been demonstrated in a field application.

Reduced regenerable scavenger CAPEX for switchover utilizing existing separator/contacting infrastructure
Liquid treating avoids solid handling complexity
Selective reaction with hydrogen sulfide
Primary reagent is produced from the oil well
Primary reagent already contains byproducts, new species are not introduced
Primary reagent has existing disposal paths – Salt Water Disposal
Aqueous application with reduced potential for plugging
Oxygen is scavenged from natural gas and improves scavenger efficacy
Sustainable sourcing of materials