EXTREME H_2S REMEDIATION FOR PRODUCED WATER REUSE, IN FRACTURE-STIMULATION

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ABSTRACT

Hydrofracturing with 100% recycled water is very desirable in highly sensitive clay formations. In the Permian Basin, recycling of produced water can save operators many thousands of dollars per well in fresh water, trucking, and disposal costs. One obstacle to reuse for many produced waters is high hydrogen sulfide (H_2S) concentrations.

With typical H_2S treatments, such as scavengers, vapor recovery, thermal, chemical, and biological oxidation, the cost/bbl is prohibitive on produced water with high H_2S levels. A new, more economical H_2S remediation technique recycles H_2S containing formation water into low suspended solids water. The water is then clarified, creating a low total suspended solids (TSS) solution ready for hydrofracturing.

This paper discusses the treatment of 22,000 bbl of 900 ppm H_2S produced water used in the successful completion of an 8-stage continuous slickwater frac in the Ramsey formation, of the Black River South field, in Eddy County, New Mexico.

INTRODUCTION

In the Permian Basin, recycling of produced water can save operators many thousands of dollars per well in fresh water, trucking, and disposal costs. Hydrofracturing with 100% recycled water is also very desirable in highly sensitive clay formations.

One obstacle to reuse for many produced waters is high hydrogen sulfide (H_2S) concentrations. The corrosive and toxic nature of H_2S necessitates its removal. With many fields containing more sour water, more operators are looking for ways to recycle produced water containing significant levels of H_2S.

A New Mexico operator needed to complete wells in a formation that was extremely sensitive to clay swelling. The operator wanted to maintain the formation permeability by reusing produced water to minimize swelling.

Unfortunately, the produced water from wells in this area also have high levels of H_2S. If the operator couldn't reuse the water, an alternative and more expensive gas fracturing completion would have to be used. The operator called for recommendations after they had collected and stored nearly 25,000 bbl of produced water containing more than 900 ppm H_2S for fracturing.

The cost of mitigating such high levels of H_2S safely was a primary challenge. Traditional oilfield H_2S treatments cost more than USD 10 per barrel to treat this level of H_2S. After researching alternatives, the recommended solution was treatment with hydrogen peroxide (H_2O_2) oxidation to remove H_2S and maintain the water quality required to make up fracturing fluid.

Lab, pilot, and full scale treatments were performed on waters with H_2S concentrations ranging from 600 to 900 ppm. Results of treating 49 frac tanks filled with high H_2S water demonstrate the safe economical use of H_2O_2 for eliminating H_2S, while maintaining the formation water quality required for fracturing fluid makeup.

PROBLEM SOLUTION

Technologies to remove H_2S from water include treatments such as scavengers, vapor recovery, thermal, chemical, and biological oxidation. To assist in selecting an appropriate remediation technique, the following H_2S removal processes were candidates screened using Quality Function Deployment (QFD) methodology:

- Zinc Oxidation
- Thermal Oxidation
- Bacterial Oxidation
- Vapor Recovery

- Chlorine Dioxide
- Hydrogen Peroxide Oxidation
- H_2S Scavenger Chemicals

The QFD filtered out the following four processes as the best fit for customer needs (Table 1): Chlorine Dioxide, Vapor Recovery, Acrolein Scavenger, and Hydrogen Peroxide Oxidation. These final four processes are primarily chemical applications.

The pricing for these methods was determined from previous field experience and lab testing estimates on the H_2O_2 process (Table 1). The first three, more common oil industry methods have various degrees of efficiency and removal efficacy, but are cost prohibitive for reuse of produced water with high H_2S levels. With the QFD results and pricing considerations, the H_2O_2 oxidation method was advanced for further testing.

Lab Tests

Lab testing with H_2O_2 was performed to determine dosages and reaction time required to oxidize the H_2S to levels required to prevent excessive off-gas from reaction tanks. Tests at different dosages demonstrated which preferred ppm of active H_2O_2 for every ppm of H_2S would eliminate lead acetate detectable dissolved H_2S in less than 30 minutes at room temperature.

Full Scale Field Treatment Process

A 500 bbl pilot treatment was set up to inject H_2O_2 into the H_2S water. Following the successful replication of lab findings in the one tank pilot test, the customer's 49 tanks of high H_2S produced water were treated using the same treatment technique.

H_2S and Hydrogen Peroxide - Health and Safety Considerations

Treating produced water containing high H_2S levels with H_2O_2 poses other operational safety factors which need to be considered. High H_2S levels in the raw water pose off-gas safety concerns, and additional monitoring is needed. To address these additional hazards, the following strategies were utilized:

- Monitoring general work area and reaction tank H_2S levels with strategic placement of multiple H_2S and 4-gas monitors reporting to a central monitoring station
- Utilizing audible and visible alerts with NIOSH H_2S limit set points
- Use of standby rescue technicians, air trailer, and SCBA equipment

Concentrated H_2O_2 in contact with hydrocarbons under the right conditions could generate enough heat to promote combustion. Produced water generally has too low hydrocarbon content to give any appreciable reaction temperature increase.

RESULTS

Targeted Finished Water Parameters Treatment Results

The primary finished water parameters of concern during the treatment were H_2S, water clarity, H_2O_2 residual, friction loop performance, and frac fluid performance. As tested during treatment, in the attached analyses, and demonstrated by sand placement during the fracture:

- H_2S levels were reduced to zero after 30 minutes reaction time in all 49 tanks processed
- Final clarity was below 80 FTU with rapid clarification and below 30 FTU using overnight settling clarification
- H_2O_2 residuals drop from 100 ppm during treatment to zero after eight hours (Table 2)
- Friction loop results showed the 50% reduction achieved with typical FR addition rates (Figure 1)
- Designed quantity of proppant was placed with 5 gpt and 1 gpt slick water treatments

Peroxide Residual

Preliminary hydration tests using H_2O_2 treated water samples show that H_2O_2 residuals in the 25-100 ppm range do not interfere with hydration of polymers. Friction loop testing was done on post-H_2O_2 treated water with no H_2O_2

residual (Figure 1), but further testing is needed for friction reduction performance at various levels of residual. Until the levels of tolerable residual for various linear and cross-linked polymers are known, one of the goals of field treatment should be to keep H_2O_2 dosages at the minimum required for H_2S removal. H_2O_2 neutralizers could also be kept on hand for application if H_2O_2 is overdosed.

Increased Sulfate Concentration in Treated Water

Another parameter that was considered is the increase in sulfate concentration in the finished water due to sulfide oxidation. In neutral-to-alkaline conditions, the two following reactions take place:

1. Reaction which predominates closer to neutral pH: $H_2S + H_2O_2 \rightarrow S_0 + 2H_2O$
2. Reaction which predominates at pH 9: $S^{2-} + 4H_2O_2 \rightarrow SO_4^{=} + 4H_2O$

In the treatment of the H_2S water during this project, the sulfate concentration rose from 2111 ppm in the raw water to an average of 2550 ppm in the treated water. Sulfate increases were entered into scale modeling software to assist with prediction of sulfate scaling problems. The 400 ppm increase in sulfates at this treatment was not problematic, but is a factor which should be monitored and modeled for each different treatment. The remainder of the oxidized sulfur is precipitated and removed during clarification.

SUMMARY

Use of the peroxide oxidation process for remediation of high (900) ppm H_2S produced water has been demonstrated for 100% recycling into hydrofracturing fluid. The 24,000 bbl treatment demonstrated the H_2O_2 remediation technique can economically recycle H_2S containing produced water into low suspended solids water, while maintaining the formation water quality required for fracturing fluid makeup. In many formations containing sensitive clays, the cost of required levels of KCl alone, to make fresh water useable, is more costly than treatment and recycling of formation's own produced water. (Table 3)

Safe operating procedures with high H_2S water were successfully implemented to mitigate the risk of exposure to H_2S off-gas. With the demonstrated success of H_2O_2 oxidation in lowering costs for recycling H_2S containing produced water, operators can now save many thousands of dollars per well with this treatment.

Table 1

Estimated cost of various processes to remove 1000 ppm H_2S from produced water.

H_2S Removal Process	**Estimated Cost per BBL, to treat 1000ppm H_2S Water**
Chlorine Dioxide	>$10.00
Vapor Recovery	$6.50
Acrolein	$12.60
H_2O_2	$6.00

Table 2

H_2O_2 Residual vs. Time

Time After H_2S Eliminated	Residual [H_2O_2] ppm
30 Minutes	100+
6 Hours	8
24 Hours	0

Table 3

Cost of Various External Sources of Fracturing Water, Verses Re-Use of Formation's Own Water

Hauling and Disposal Costs per BBL for SWD Disposal of Fluid, (not recycled for fracturing)			**$/bbl**
	Disposal cost at Operator Owned SWD, for water not recycled to frac		**<.25**
	Disposal cost at commercial SWD, for water not recycled to frac		**.5-2.5**
	Hauling	$1/bbl/hr or .5-1.00/bbl Texas, $4.00-$8.00/bbl PA	**.50-8.00**
	Hauling and disposal costs, Rick McCurdy, Chesapeake Energy, "Underground Injection Wells for Produced Water Disposal"		
Fresh Water Costs			
	Purchase Fresh Water	(2012-2013 Price ranges in Permian)	**0.15-2.5**
	Hauling	$1/bbl/hr or ($.5-$1.00/bbl in Texas) ($4.00-$8.00/bbl in PA)	**.50-8.00**
PURCHASED FRESH WATER COSTS:			
Cost/BBL	**Example Using Purchased & Transported Fresh Water at only $.50/BBL Fresh Water Cost**		
	Produced water disposal (since not used) at Operator Owned SWD, (.25 Disp + 1.75 Transport to Disposal)		**2.00**
	Purchase Fresh Water at $.50 per bbl		**0.50**
	Hauling of Purchased Fresh Water		**0.75**
	KCl	$3.50 Min for 2% KCl	**3.50**
	*Model Assumes no cost for risk of formation damage, from synthetic KCl water		
			6.75
Example Cost/BBL		**Approx Customer Cost, for H2PROHD Treated Water (40,000 bbl treatment)**	
		Customer cost per BBL for a 40K bbl treatment of 700 ppm H2S, already in holding tanks	**4-5.00**
		Customer cost per BBL for a 40K bbl treatment of 200 ppm H2S, already in holding tanks	**3-4.00**
		Customer cost per BBL for a 40K bbl treatment of 1000 ppm H2S, as produced	**3-5.00**
		Customer cost per BBL for a 40K bbl treatment of 200 ppm H2S, as produced	**1.25-2.00**

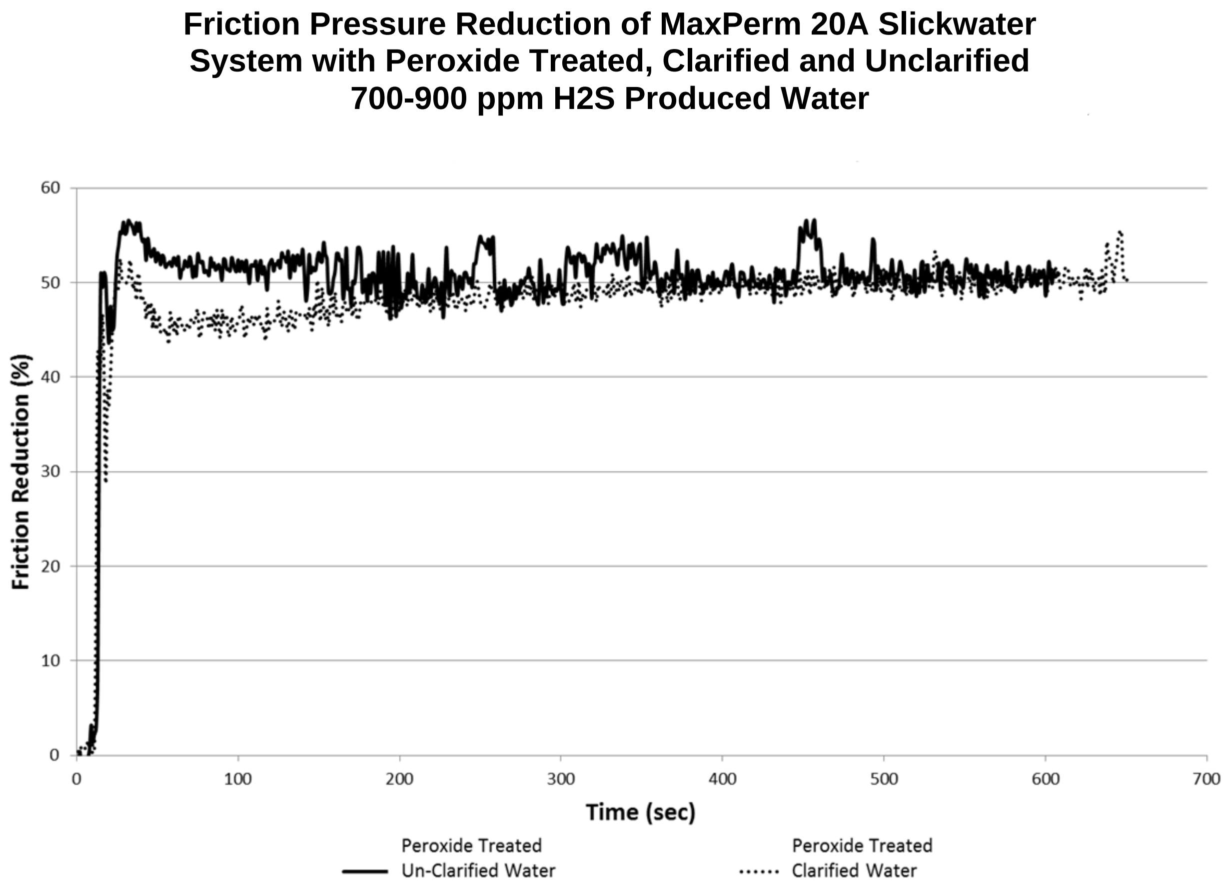
Friction Pressure Reduction of MaxPerm 20A Slickwater
System with Peroxide Treated, Clarified and Unclarified
700-900 ppm H2S Produced Water
60
50
40
30
20
10
0
Friction Reduction (%)
0
100
200
300
400
500
600
700
Time (sec)
Peroxide Treated Un-Clarified Water
Peroxide Treated Clarified Water

Figure 1