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Thermal Stability Enhancement of Organic Oxygen Scavengers

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Abstract

Corrosion has been considered a serious problem encountered within various stages of hydrocarbon production, such as drilling, production, transportation, and processing. Corrosion issues in the industry have been addressed by using corrosion resistant metals and corrosion inhibitors. Corrosion encountered during drilling and completion operations can be reduced by decreasing the dissolved oxygen concentration of the fluids. This can be achieved by adding suitable oxygen scavengers to the drilling and completion fluids.

It is generally preferred to use organic oxygen scavengers with drill-in and completion brines to reduce formation damage caused by sulfate precipitation from inorganic oxygen scavengers. At lower temperatures, most of the commercially available scavengers perform well by readily reacting with dissolved oxygen. However, the commonly used scavengers begin to lose their performance and degrade into a solid residue at temperatures above 275°F. The resulting residue could increase formation damage by plugging the pores of reservoir rocks.

A new stabilizer has been developed which can increase the thermal stability of existing scavengers up to 400°F. This stabilizer can extend the stability of available organic oxygen scavengers in variety of brines, including NaBr, $CaCl_2$, and $CaBr_2/ZnBr_2$. The new combination effectively reduces the dissolved oxygen concentration in brine within a short time period. The novel scavenger-stabilizer combination can be considered an excellent product to be used in drill-in and completion applications in high-temperature reservoirs.

Introduction

There are varieties of scavengers available to remove dissolved oxygen from the fluids in oil field applications. Common oxygen scavengers include sulfites/bisulfites, hydrazine, hydroxylamines, and ascorbate compounds (Jaffer 2006). However the scavengers which can be used in completion fluids are limited due to the different restrictions in the operations. Most of the scavengers are effective only at lower salinity levels. High salinity brines used in the drilling and completion fluids make such compounds unsuitable as oxygen scavengers.

Sodium sulfite is considered a very effective and inexpensive oxygen scavenger. It can be used with completion fluids over a variety of salinities and in different temperature reservoirs. Sulfites can reduce the free oxygen in the brines by reacting as given in **Fig. 1**. However produced sulfates (SO_4^{-2}) can be precipitated with divalent ions in the reservoir fluids and cause formation damage. Therefore it is preferred to use organic oxygen scavengers over sulfite scavengers in completion brines to reduce the formation damage caused by the sulfate precipitation.

$$2SO_3^{\ominus} \xrightarrow{O_2} 2SO_4^{\ominus}$$

Fig. 1 Sulfite oxidation to sulfate

Higher thermal limits of the completion fluids hamper the use of organic scavengers due to potential thermal degradation. Scavenger A (Sc-A) is a very effective organic oxygen scavenger currently utilized in oilfield applications. At lower temperatures Scavenger A performs effectively by readily reacting with the free oxygen. However, it starts to degrade at temperatures above 275°F and forms black solid residue as depicted in **Fig. 2**. This residue could increase formation damage by plugging the pore throats of reservoir rocks. Moreover degradation of the scavenger at higher temperature substantially affects the performance of Scavenger A.

Fig. 2 Scavenger A aged with 12.5 NaBr brine for 16 hours at 300˚F

This paper describes a method of broadening the utility of Scavenger A by adding a novel additive (Stabilizer 1) that interacts synergistically with Scavenger A to enhance its thermal stability. Furthermore, this paper also discusses the performance of the new scavenger blend in variety of brines.

Experimental Section

Experimental Methodology

Thermal stability was noted by observation of brine solutions containing the scavengers and stabilizers after heating at an indicated temperature and time. Brines were placed in glass cells that were then placed in aging cells and pressurized to 200 psi and aged at predetermined temperatures for 16 hours. This was to thwart any discoloration of the brine resulting from the interior of the aging cell.

Predetermined concentrations of oxygen scavengers and stabilizers were dissolved in different brines. Dissolved oxygen levels were measured at different time intervals using an YSI Professional Plus Handheld Dissolved Oxygen Meter at room temperature. The following brines were used in this study: 12.5 lb/gal NaBr, 11.6 lb/gal $CaCl_2$, and 15.5 lb/gal $CaBr_2/ZnBr_2$.

Thermal Stability Enhancement by Adding Separate Scavengers

Scavenger A and Stabilizer 1 (St-1) were added separately and aged with different brines (12.5 ppg NaBr, 11.6 ppg $CaCl_2$ and 15.5 ppg $ZnBr_2/CaBr_2$) at 300°F and 200 psi for 16 hours. Samples were examined after aging for any signs of degradation or discoloration.

The first set of experiments was carried out by adding Scavenger A and Stabilizer 1 to 12.5ppb NaBr brine as listed in **Table 1**. Samples were aged at 300°F and 200 psi for 16 hours in aging cells. Samples after aging are shown in **Fig. 3**.

Table 1. Thermal stability experiment with 0.5ppb Sc-A and varied Stabilizer 1 (St-1) concentrations in 12.5 NaBr Brine

Sample #	Scavenger A	Stabilizer 1
1	0.5 ppb	0
2	0.5 ppb	0.5 ppb
3	0.5 ppb	1.0 ppb
4	0.5 ppb	1.5 ppb
5	0.5 ppb	2.0 ppb

A substantial amount of brown colored degraded material was observed in the bottom of the sample which does not contain any Stabilizer (Sample 1). Discolorations of the samples decreased with the increase of Stabilizer 1 concentration. Very little degradation was observed in the sample which contained 0.5 ppb Scavenger A and 2.0 ppb Stabilizer 1. This test confirms that the addition of about 4 times or more Stabilizer 1 relative to Scavenger A will enhance the thermal stability of Scavenger A. This thermal stability enhancement results from a chemical synergism between these two compounds.

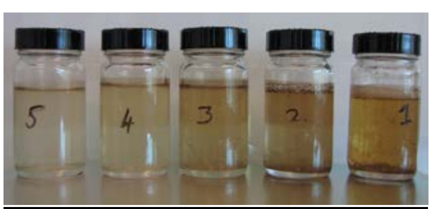

Fig. 3 Effect of St-1on thermal stability of Scavenger A in 12.5 ppg NaBr Brine

Next, another set of experiments was carried out to find the optimum Stabilizer concentration required to obtain higher thermal stability for Scavenger A. Concentrations of Scavenger A and Stabilizer 1 used in these experiments are given in **Table 2**. Seven samples were aged for 16 hours at 300°F and 200 psi. Aged samples are depicted in **Fig. 4**. An increase in thermal stability (decrease in discoloration) was observed with increasing Stabilizer 1 concentration (Fig. 4). Clear brine solution was observed in Sample 6 (test with the 1:5 Sc-A:St-1 concentrations). Additional thermal stability increase was not observed with increasing relative concentrations of Stabilizer 1 (Fig. 4).

Table 2. Thermal stability experiment with 0.1ppb Sc-A and different St-1 concentrations in 12.5 NaBr ppg Brine

Sample #	Scavenger A	Stabilizer 1
1	0.1 ppb	0
2	0.1 ppb	0.1 ppb
3	0.1 ppb	0.2 ppb
4	0.1 ppb	0.3 ppb
5	0.1 ppb	0.4 ppb
6	0.1 ppb	0.5 ppb
7	0.1 ppb	0.6 ppb

Finally another set of experiments was carried out to check the thermal stability enhancement of Scavenger A by addition of Stabilizer 1 in 12.5 ppg NaBr, 11.6 ppg $CaCl_2$ and 15.5ppg $ZnBr_2/CaBr_2$ brines. Compositions of the components used in each sample are listed in **Table 3**.

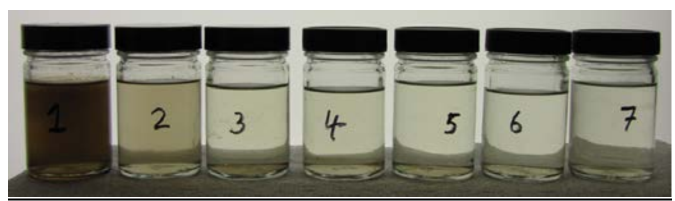

Fig. 4 Effect of St-1 on thermal stability of Sc-A in 12.5 ppg NaBr Brine

Samples were aged at 300°F and 200 psi for 16 hours and examined for any degradation and discoloration. Aged samples with different brines are depicted in **Fig. 5**, **6** and **7**. No degradation or discolorations were observed in the samples which contained Scavenger A and Stabilizer 1 with 1:5 concentration ratios. In contrast discoloration was observed in the samples which do not have Stabilizer 1. These results confirm that the novel thermal stability enhancing additive can be used with a variety of brines to enhance the thermal stability of Scavenger A.

Table 3. Thermal stability experiment with Sc-A and St-1(1:5) with different brines

Sample	Brine	Sc-A	St-1
1	12.5 ppg NaBr	0.5 ppb	0 ppb
2	12.5 ppg NaBr	0.5 ppb	2.5 ppb
3	11.6 ppg $CaCl_2$	0.5 ppb	0 ppb
4	11.6 ppg $CaCl_2$	0.5 ppb	2.5 ppb
5	15.5ppg $ZnBr_2/CaBr_2$	0.5 ppb	0 ppb
6	15.5ppg $ZnBr_2/CaBr_2$	0.5 ppb	2.5 ppb

Fig. 5 Comparison of 0.5 ppb Sc-A (1) and 0.5 ppb Sc-A + 2.5 ppb St-1 (2) in 12.5 ppg NaBr Brine

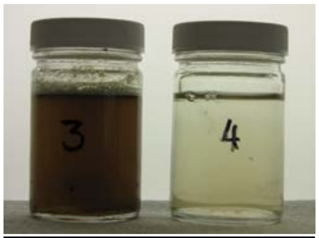

Fig. 6 Comparison of 0.5 ppb Sc-A (3) and 0.5 ppb Sc-A + 2.5 ppb St-1 (4) in 11.6 ppg CaCl2 Brine

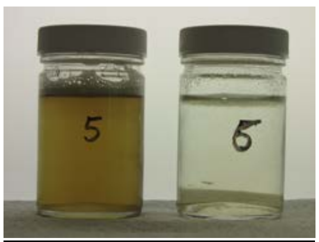

Fig. 7 Comparison of 0.5 ppb Sc-A (5) and 0.5 ppb Sc-A + 2.5 ppb St-1 (6) in 15.5ppg ZnBr2/CaBr2 Brine

Oxygen Scavenger Performance of Brines with Scavenger A and Stabilizer 1

The ability of the new formulations to remove dissolved oxygen was evaluated with different concentrations of Scavenger A and Stabilizer 1 and measured in 12.5 ppg NaBr, 11.6 ppg CaCl2 and 15.5ppg $ZnBr_2$/$CaBr_2$ brines for 24 hours. Brines were kept at ambient temperature in closed containers. Results are listed in **Figs. 8**, **9** and **10** respectively. The results show that the concentration of Scavenger A can be decreased by 50% when it is applied with the stabilizer and still achieve the same performance as pure Scavenger A. This demonstrates that a synergistic effect with respect to dissolved oxygen removal is also observed.

Conclusions

Thermal stability of Scavenger A can be increased by separate addition of Stabilizer 1 at 1:5 (Sc-A:St-1) concentration ratios. The addition of Stabilizer 1 in this manner educes the concentration of Scavenger A needed to provide equivalent performance by 50%.

The novel scavenger and stabilizer blend can be used in high temperature drilling, completion and fracture fluids applications.

Acknowledgments

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References

1. Majnouni, M. and Jaffer, A. 2004. Improved Performance in Steam Plants with New Guidelines for Corrosion and Scale Control. NACE 04081 presented at CORROSION 2004 Conference and Exposition held in New Orleans, Louisiana, March 28-April 1.
2. Jaffer, A., Fulmer, D., and Ensslen, J.: 2006. Recent Developments in Organic Oxygen Scavenger Technology. NACE 06687 presented at CORROSION 2006 Conference and Exposition held in San Diego, California, March 12-16.

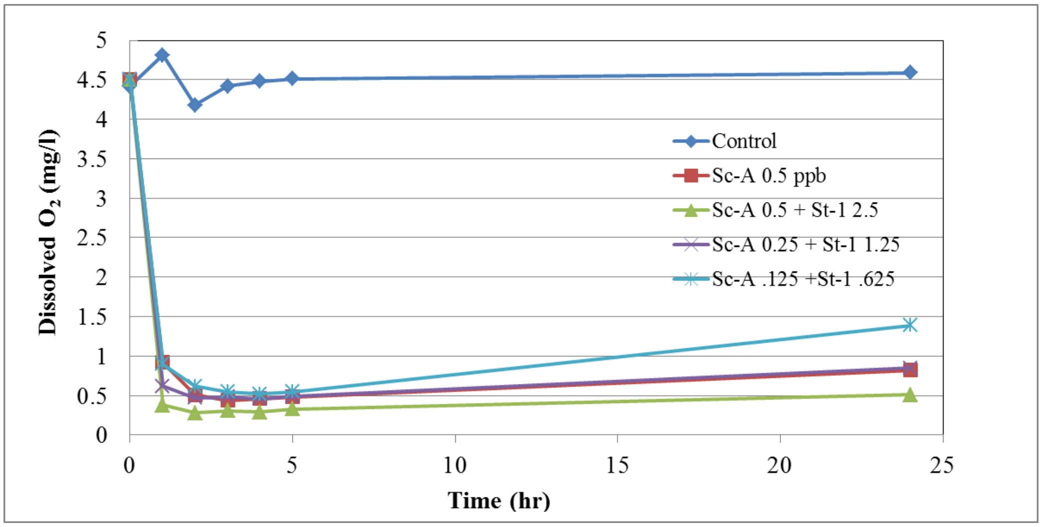

Fig. 8. Performance of Different Scavenger Concentrations in 12.5 ppg NaBr Brine

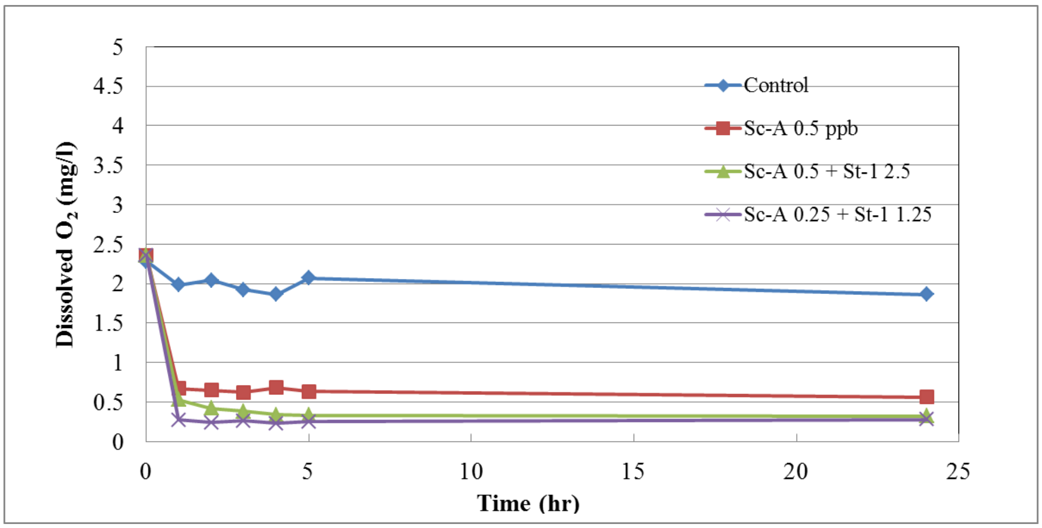

Fig. 9. Performance of Different Scavenger Concentrations in 11.6 ppg $CaCl_2$ Brine

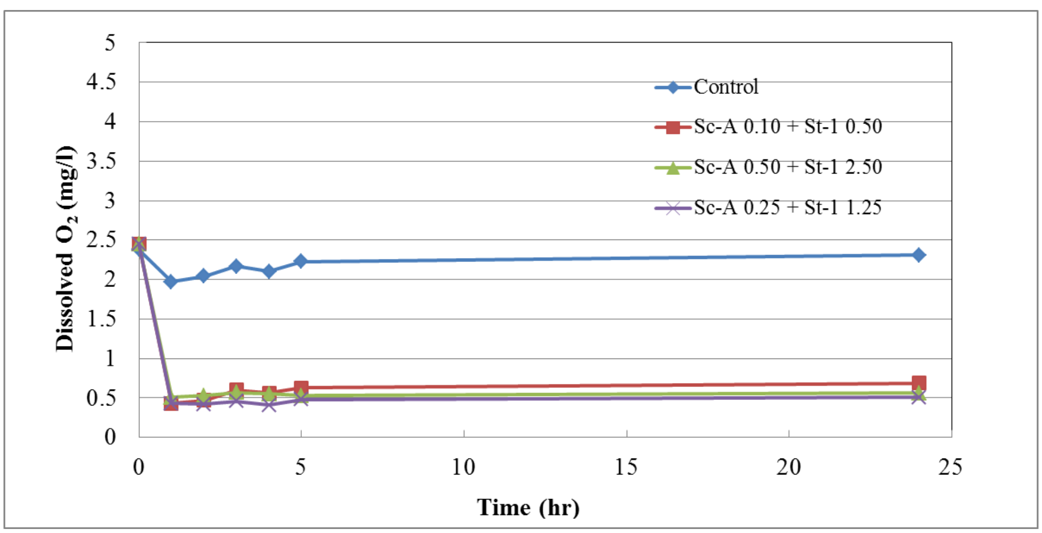

Fig. 10. Performance of Different Scavenger Concentrations in 15.5ppg $ZnBr_2/CaBr_2$ Brine