AADE-11-NTCE-22

A New Oxygen Scavenger Suitable for High-Temperature Applications

Jay P. Deville and Jay Turner, Halliburton

Abstract

Oxygen scavengers are commonly added to drilling fluids and completion brines to mitigate the adverse effects of dissolved oxygen in downhole environments. The undesirable effects of dissolved oxygen include radical decomposition of polymeric additives and the corrosion of metal casing and drill pipe.

Some currently used oxygen scavengers will effectively remove dissolved oxygen from drill-in and completion fluids, but when used in high temperature environments they can degrade into potentially formation damaging compounds. Other oxygen scavengers have additional high temperature limitations, particularly when used in packer fluids. The industry has identified a need for a high temperature (over 300°F) oxygen scavenger without these shortcomings.

In response to the thermal limitations mentioned above, a new oxygen scavenger has been developed. This new scavenger offers excellent dissolved oxygen control in a variety of brines including NaCl, NaBr, $CaCl_2$, and $CaBr_2/ZnBr_2$. In addition to offering dissolved oxygen control comparable to current offerings, the new scavenger also shows greatly improved thermal tolerance. Brines prepared with the new scavenger retained thermal stability even after aging at temperatures as high as 500°F. This makes the newly-developed scavenger an excellent alternative to current oxygen scavenging chemistries for completion and drill-in applications in thermally demanding wellbores. Extensive performance and thermal testing of the new scavenger are discussed in this paper.

Introduction

The deleterious effects of dissolved oxygen in aqueous solutions plague a number of industries[1] including drilling and completion operations. Oxygen dissolved in drilling, drill-in, and completion/packer fluids can cause significant corrosion to downhole tubulars via general attack, pitting, crevice corrosion, and under-deposit corrosion.[2] Additionally, oxygen can promote radical degradation of polymeric additives that may be present in drilling and completion fluids through autoxidative mechanisms.[3]

Bulk removal of oxygen can often be achieved through mechanical deaeration, but near-complete removal of oxygen necessitates chemical additives. These chemical additives, known as oxygen scavengers, are oxidized by dissolved oxygen (the scavengers are therefore reducing agents). Upon reacting with the oxygen scavenger, the oxygen is no longer available for inducing corrosion or other unwanted effects. The ultimate fate of the dissolved molecular oxygen after reaction is dependent on the chemical nature of the oxygen scavenger.

For reasons detailed in the subsequent section, an industry need has arisen for a high temperature-stable oxygen scavenger that effectively and efficiently removes dissolved oxygen from brine-based reservoir drilling fluids and completion brines. The development of a new oxygen scavenger that fulfills this industry need is outlined in this paper. In describing the development endeavors, the following topics are discussed:

- Origin of industry need for new scavengers
- Data illustrating the effectiveness of the new scavenger at removing dissolved oxygen from a variety of brines
- Data illustrating the elevated thermal stability of brines containing the new scavenger

Industry Need for New Oxygen Scavengers

A variety of chemistries are available for removal of dissolved oxygen. Common scavengers include sulfites/bisulfites, hydrazine, hydroxylamines, and ascorbate chemistries.[4] While many chemistries are available for removal of dissolved oxygen, the number of candidates appropriate for use in completion fluids is severely restricted.

Completion brines limit the pool of acceptable oxygen scavenger candidates for a number of reasons. Many chemistries are effective only in freshwater or in low salinity solutions. Completion fluids generally utilize highly elevated concentrations of salts to achieve the desired densities and limit the amount of free water available.

The thermal demands of completion fluids further reduce the number of allowable scavenger candidates. Many scavenger chemistries will break down at elevated temperatures forming undesirable decomposition products which can discolor and/or render a completion brine opaque. Furthermore, decomposition products can precipitate and potentially cause formation damage to the producing reservoir.

Other scavengers may adequately remove dissolved oxygen without thermal decomposition, but are not acceptable because the reacted form of the scavenger can precipitate in high-density brines and lead to under-deposit corrosion. This is essentially why sulfite-based scavengers, which are inexpensive workhorses for drilling fluids, are generally not used in completion fluids. Sulfite is readily oxidized to sulfate by dissolved oxygen, but the sulfate formed is prone to precipitation in certain brine systems.

The above factors define the limits of current oxygen scavengers. New oxygen scavengers that offer rapid removal of dissolved oxygen at relatively low concentrations of scavenger are needed. The optimum scavenger should function at ambient temperature rather than requiring thermal activation or the improved kinetics at elevated temperatures. This feature would allow for surface deployment of the scavenger and confirmation of dissolved oxygen removal prior to sending the fluid downhole. Further performance expectations include the ability of the scavenger to function in a wide variety of brines and remain stable at high temperatures. To prevent unwanted discoloration and precipitation under harsh conditions, ideal additives would either resist decomposition at elevated temperature, or decompose to form harmless inert, uncolored by-products. Subsequent data sections support the authors' belief that an oxygen scavenger fulfilling both the above performance requirements and the pressing industry need has been developed.

Testing Protocol

The ability of the new scavenger to remove dissolved oxygen was tested at room temperature by addition of a known concentration of the scavenger to a test brine. The brine/scavenger mix was contained in a nearly full glass jar to minimize air above the solution. Upon addition of the scavenger a lid was placed on the solution and the brine was agitated via magnetic stirring for 30 seconds. The dissolved oxygen concentration was measured at prescribed intervals using a YSI Model 55 Handheld Dissolved Oxygen Meter with temperature and salinity corrections. Readings were periodically verified with an Extech Instruments Model 407510 Dissolved Oxygen Meter. In all tests a control brine without added oxygen scavenger was measured alongside the scavenger-containing brines.

High temperature testing of brines was conducted in stainless steel aging cells with glass inserts to preserve the clarity of the brine. Cells were pressurized to 500 psi with nitrogen gas prior to static aging for 16 hours at the temperature of interest.

Oxygen Scavenger Efficiency Testing

The performance of the newly-developed oxygen scavenger was gauged by comparison to an existing brine oxygen scavenger which is used as a baseline throughout the testing. The baseline scavenger offers excellent dissolved oxygen control in a wide-range of brines, but suffers from discoloration and precipitation at elevated temperatures. Ideally, the new scavenger would offer dissolved oxygen control comparable to the baseline scavenger, but with improved thermal stability.

Comparative measurements were made in 9.5 lb/gal NaCl, 11.0 lb/gal $CaCl_2$, 12.5 lb/gal NaBr, and 15.5 lb/gal $ZnBr_2/CaBr_2$ in order to establish adequate comparison over a variety of commonly used brines. The optimum concentration for comparison of the new scavenger to the baseline brine oxygen scavenger was determined to be 0.5 lb/bbl. This concentration provided the best balance of rapid dissolved oxygen removal with minimal product addition. The new scavenger is an aqueous-based liquid product that was readily miscible with each brine tested.

Dissolved Oxygen Removal - 9.5 lb/gal NaCl

Figure 1 compares the two scavengers (both at 0.5 lb/bbl concentrations) in 9.5 lb/gal NaCl brine at room temperature (approximately 72°F). In this brine the new scavenger showed rapid removal of dissolved oxygen as both the new scavenger and the baseline scavenger showed reductions in dissolved oxygen concentration from over 6 mg/L dissolved oxygen to less than 0.5 mg/L (less than 0.4 ppm) in just one hour at room temperature.

Dissolved Oxygen Removal - 11.0 lb/gal $CaCl_2$

Figure 2 gives comparative performance of the two scavengers in 11.0 lb/gal $CaCl_2$ brine at approximately 72°F. Divalent brines are often problematic for fluid additives due to precipitation tendencies; however no precipitation of the new scavenger was observed. As was the case with the NaCl brine, the two scavengers showed comparable efficient activity in controlling dissolved oxygen. Dissolved oxygen levels were reduced from more than 2.5 mg/L to 0.6 mg/L (0.45 ppm) after one hour. Note the reduced initial concentration of dissolved oxygen in the calcium chloride brine (approximately 2.5 mg/L) compared to the initial value for the sodium chloride brine (approximately 6 mg/L) resulting from the reduced solubility of oxygen in the brine of greater dissolved salt concentration.

Dissolved Oxygen Removal - 12.5 lb/gal NaBr

Sodium bromide brine proved to be a more difficult challenge for the new scavenger (**Figure 3**). While the new scavenger was able to affect a roughly 50% dissolved oxygen reduction in the first hour, it was not until the measurement taken at 3 hours elapsed time that the new scavenger showed near-minimal dissolved oxygen concentration. This sluggishness could be mitigated by increasing the concentration of the scavenger to 1.0 lb/bbl (**Figure 4**). Whether it is preferable to utilize a lower concentration with a greater residence time or simply use a higher concentration for faster results will be determined by the well specifics.

Other than a slight lag time, the performance of the new scavenger was again comparable to the baseline oxygen scavenger. Dissolved oxygen levels were reduced from an initial concentration of 3.9 mg/L to 0.7 mg/L (0.5 ppm) after 3 hours at room temperature at the standard scavenger loading of 0.5 lb/bbl.

Dissolved Oxygen Removal- 15.5 lb/gal $ZnBr_2$/$CaBr_2$

The final brine evaluated was a 15.5 lb/gal zinc bromide/calcium bromide blend (**Figure 5**). This is a potentially troublesome brine given its limited amount of free water and its acidic nature. Despite these potential hindrances, the new scavenger was able to efficiently and effectively remove dissolved oxygen. The dissolved oxygen concentration was lowered from the initial value of 2.3 mg/L to 0.9 mg/L (0.5 ppm) in one hour. A further reduction to 0.6 mg/L (0.3 ppm) was seen after 3 hours. As was the case with sodium bromide, an improved rate of oxygen removal could be realized by increasing the concentration of scavenger to 1.0 lb/bbl.

The new scavenger has demonstrated the ability to efficiently and effectively remove dissolved oxygen from a wide range of brine densities and compositions. The new scavenger is effective at a concentration of 0.5 lb/bbl. Lower concentrations can be utilized in some brines, but will typically require more time for minimization of dissolved oxygen content. Conversely, higher concentrations of the scavenger can be utilized if faster dissolved oxygen removal is desired.

High Temperature Testing

With the new scavenger's ability to remove dissolved oxygen in a broad spectrum of brines under mild conditions established, attention was turned to evaluating the thermal stability of the material. As discussed previously, some currently used scavenger chemistries undergo decomposition at elevated temperature with concomitant brine discoloration and frequent precipitation. This decomposition is aesthetically unappealing and has potential for causing formation damage. Developing an oxygen scavenger that does not yield these decomposition effects at elevated temperature was the goal of this study.

Testing at elevated temperatures was conducted on the new scavenger at an additive concentration of 1.0 lb/bbl. A higher concentration was used for this portion of the testing to ensure that no decomposition evidence was seen that might be missed at lower concentrations. For each of the high temperature tests, the new scavenger was compared to the existing baseline scavenger tested in the previous section.

High Temperature Testing - 9.5 lb/gal NaCl

Photographs of the 9.5 lb/gal NaCl brines after aging at 300°F for 16 hours with each of the additives are shown in **Figure 6**. Note that the brine containing the baseline scavenger has darkened appreciably and produced insoluble precipitates, while the new scavenger tested *at twice the concentration* (0.5 lb/bbl for the baseline scavenger and 1.0 lb/bbl for the new scavenger) shows no sign of discoloration or precipitation. A marked improvement in brine stability is observed with the new scavenger.

Even under the substantially more thermally demanding conditions of 16 hours/400°F and 16 hours/500°F, sodium chloride brine containing 1.0 lb/bbl of the new scavenger showed no discoloration (**Figure 7**). Some degree of precipitation can be observed in the sample aged at 500°F, but this may be attributable to the effect of the harsh conditions on the brine itself.

High Temperature Testing – 11.0 lb/gal $CaCl_2$

Figure 8 provides a similar photographic comparison of the new and baseline scavengers after aging for 16 hours at 300°F in 11.0 lb/gal $CaCl_2$ brine. As before the new scavenger remained clear and colorless while the baseline scavenger decomposed, turning the brine dark and producing solid decomposition products. As with sodium chloride, brines containing 1.0 lb/bbl of the new scavenger were aged for 16 hours at 400°F and 500°F. No discoloration or signs of decomposition were observed, however the 500°F sample showed slight precipitation. This is again possibly due to the brine itself (**Figure 9**).

High Temperature Testing - 12.5 lb/gal NaBr

Testing under the same conditions used for the other brines (0.5 lb/bbl baseline scavenger vs. 1.0 lb/bbl new scavenger, 16 hours/300°F) produced similar results in 12.5 lb/gal NaBr brine (**Figure 10**). The new scavenger remained clear and colorless, while the baseline scavenger produced a dark, opaque solution with precipitated decomposition products. Brines containing the new scavenger retained their clarity after aging at 400°F and 500°F for 16 hours (**Figure 11**).

High Temperature Testing - 15.5 lb/gal $ZnBr_2$/$CaBr_2$

The acidic zinc brine provided no complication as 1.0 lb/bbl of the new scavenger remained clear and colorless while 0.5 lb/bbl of the baseline scavenger discolored but did not show precipitation after aging at 300°F for 16 hours (**Figure 12**). **Figure 13** shows the results of aging 1.0 lb/bbl of the new scavenger in the zinc bromide/calcium bromide brine for 16 hours at 400°F and 500°F. No discoloration was seen in either sample, with only slight precipitation observed in the 500°F sample.

Conclusions

A new oxygen scavenger has been developed in response to an industry need for an efficient and effective oxygen scavenger with high thermal stability. The new scavenger was shown to give performance comparable to a successful existing brine oxygen scavenger in a broad range of brines. In addition to effective dissolved oxygen control, the new scavenger shows remarkable thermal stability. Aging at temperatures of up to 500°F produced no brine discoloration and only minimal precipitation at the highest temperatures tested.

The new scavenger is field-ready for any fluid operations including completion, drill-in, and packer fluids. While designed for use in brines, the new scavenger also effectively functions in freshwater or lower salinity brines allowing for use in drilling fluids as well.

Acknowledgments

The authors would like to thank Halliburton for the

permission to publish these findings and the AADE for the opportunity to present this paper.

References

1. Majnouni, M. and Jaffer, A.: “Improved Performance in Steam Plants with New Guidelines for Corrosion and Scale Control.” NACE 04081, CORROSION 2004, New Orleans, Louisiana, March 28-April 1, 2004.
2. Huang, K., Mao, F., Hoag, G., and Rothgery, E.: “Evaluation of Hydrazine Solutions vs. Several Alternate Oxygen Scavengers.” NACE 04082, CORROSION 2004, New Orleans, Louisiana, March 28-April 1, 2004.
3. Yachigo, S.: “Synergistic Stabilization of Polymers.” *Handbook of Polymer Degradation*; Hamid, S. H., Amin, M. B., Maadhah, A. G., Eds. Marcel Dekker, Inc. New York, New York, 1992; pp 305-331.
4. Jaffer, A., Fulmer, D., and Ensslen, J.: “Recent Developments in Organic Oxygen Scavenger Technology.” NACE 06687, CORROSION 2006, San Diego, California, March 12-16, 2006.

Figures

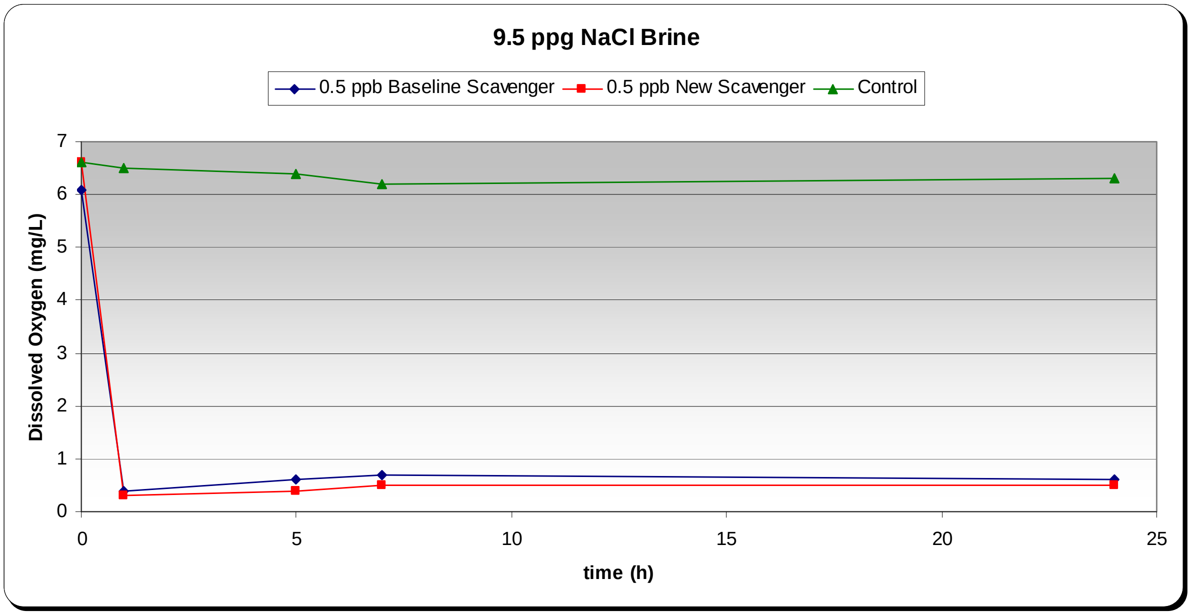


Figure 1. Comparison of Oxygen Scavenger Performance in 9.5 lb/gal NaCl Brine at Room Temperature (Approximately 72 °F)

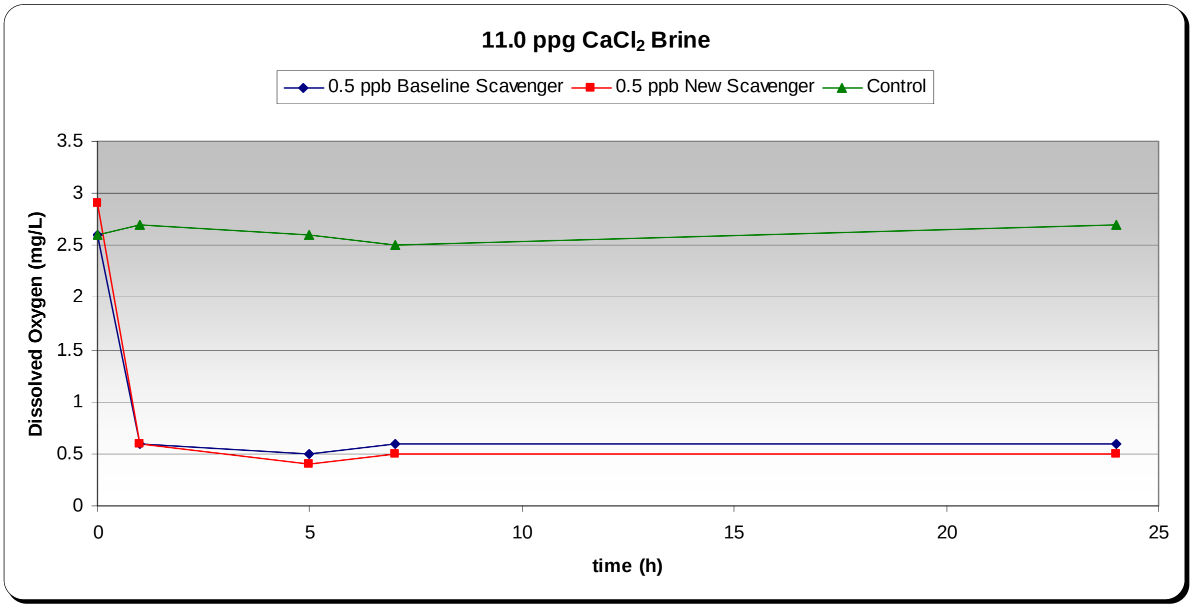


Figure 2. Comparison of Oxygen Scavenger Performance in 11.0 lb/gal $CaCl_2$ Brine at Room Temperature (Approximately 72 °F)

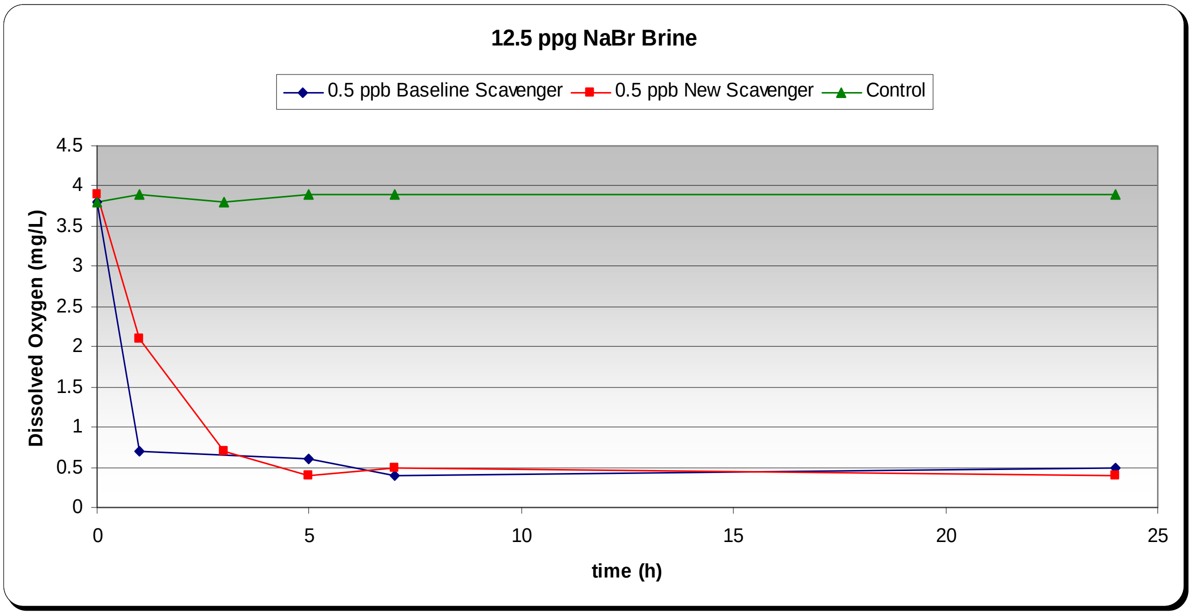


Figure 3. Comparison of Oxygen Scavenger Performance in 12.5 lb/gal NaBr Brine at Room Temperature (Approximately 72 °F)

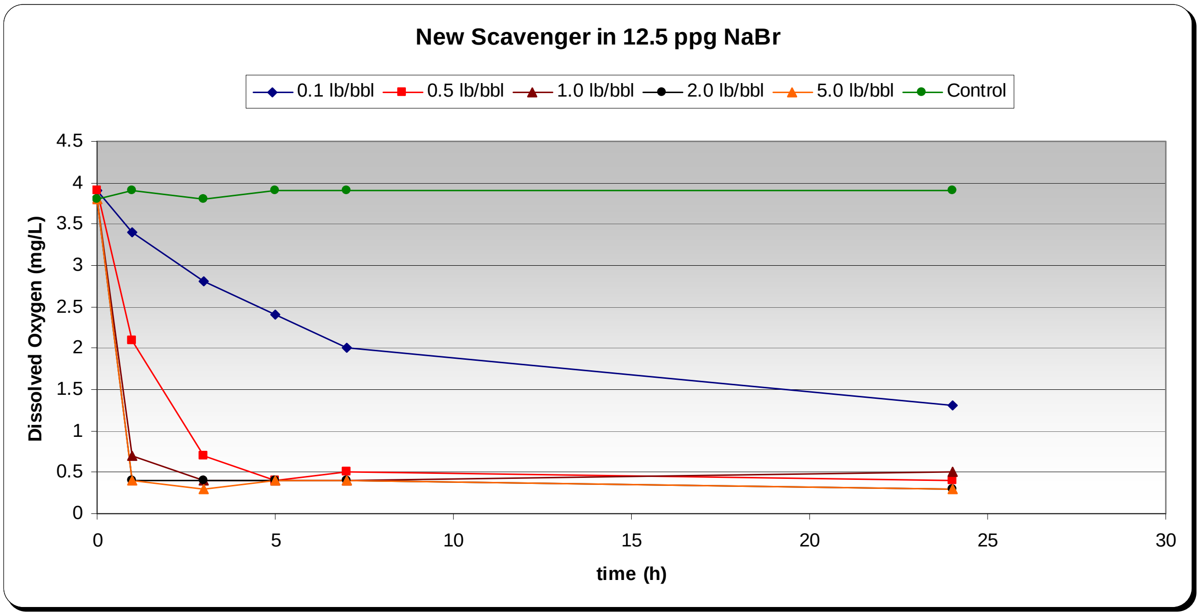


Figure 4. Effect of Concentration on Efficiency of Dissolved Oxygen Removal in 12.5 lb/gal NaBr at Room Temperature (Approximately 72 °F)

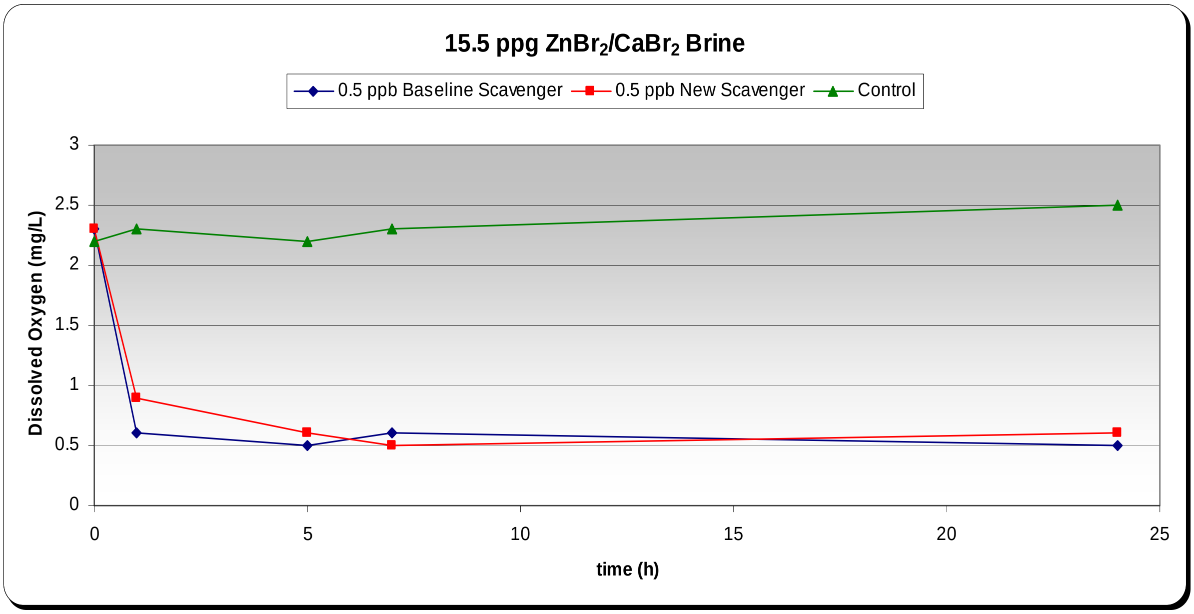


Figure 5. Comparison of Oxygen Scavenger Performance in 15.5 lb/gal $ZnBr_2/CaBr_2$ Brine at Room Temperature (Approximately 72 °F)

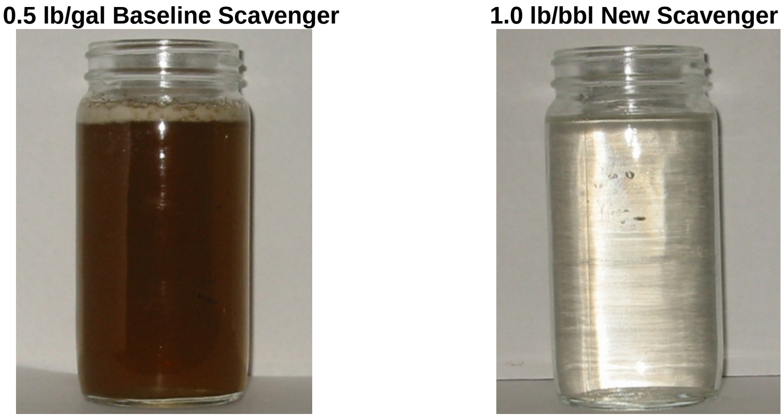
0.5 lb/gal Baseline Scavenger **1.0 lb/bbl New Scavenger**

Figure 6. 9.5 lb/gal NaCl after Aging at 300 °F for 16 hours with Oxygen Scavengers

1.0 lb/gal New Scavenger
400 °F

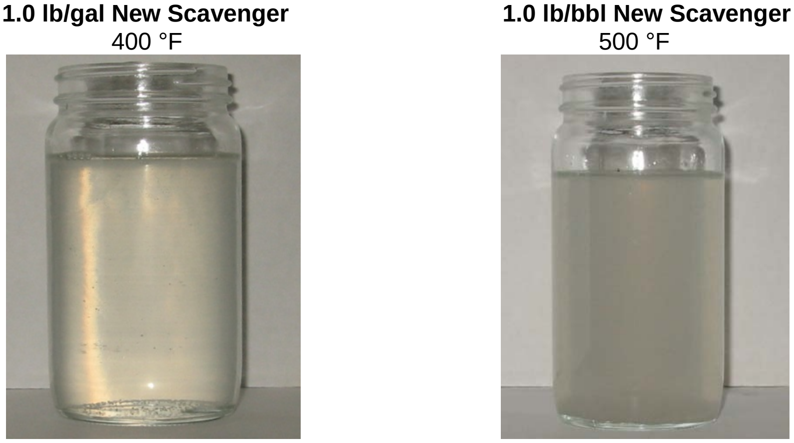
1.0 lb/bbl New Scavenger
500 °F

Figure 7. 9.5 lb/gal NaCl after Aging at 400 °F and 500 °F with the New Scavenger


0.5 lb/gal Baseline Scavenger

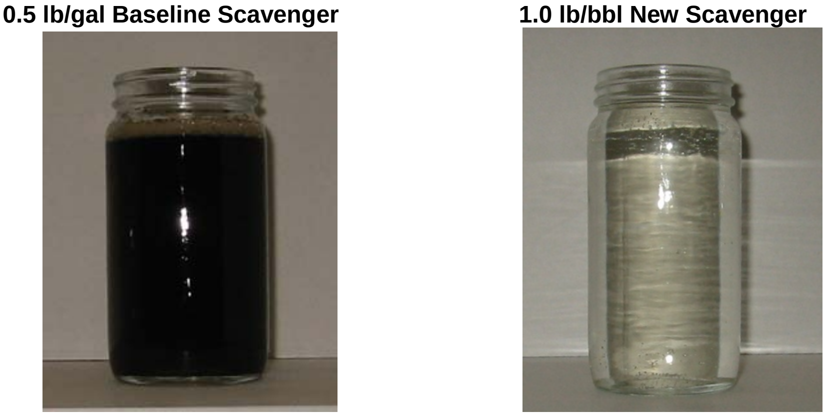
1.0 lb/bbl New Scavenger

Figure 8. 11.0 lb/gal $CaCl_2$ after Aging at 300 °F for 16 hours with Oxygen Scavengers


1.0 lb/gal New Scavenger
400 °F

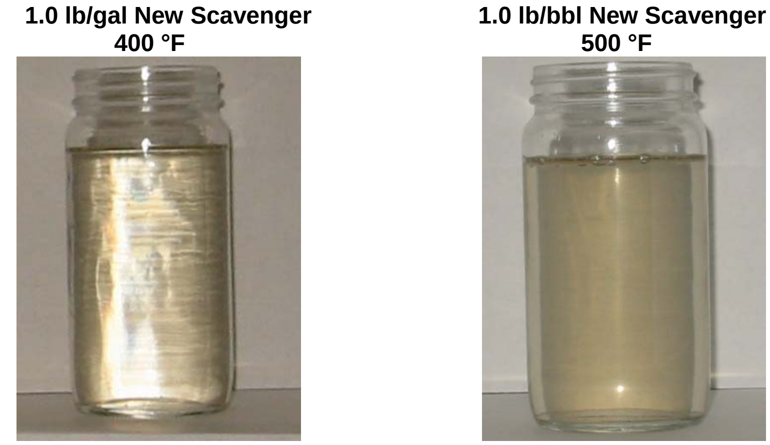
1.0 lb/bbl New Scavenger
500 °F

Figure 9. 11.0 lb/gal $CaCl_2$ after Aging at 400 °F and 500 °F with the New Scavenger


0.5 lb/gal Baseline Scavenger

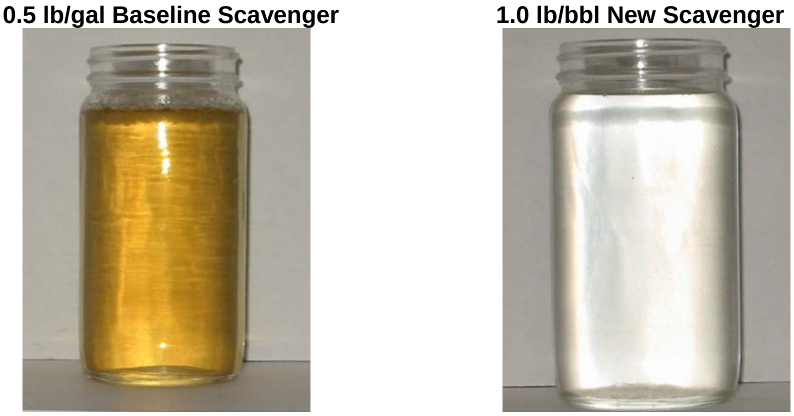
1.0 lb/bbl New Scavenger

Figure 10. 12.5 lb/gal NaBr after Aging at 300 °F for 16 hours with Oxygen Scavengers


1.0 lb/gal New Scavenger
400 °F

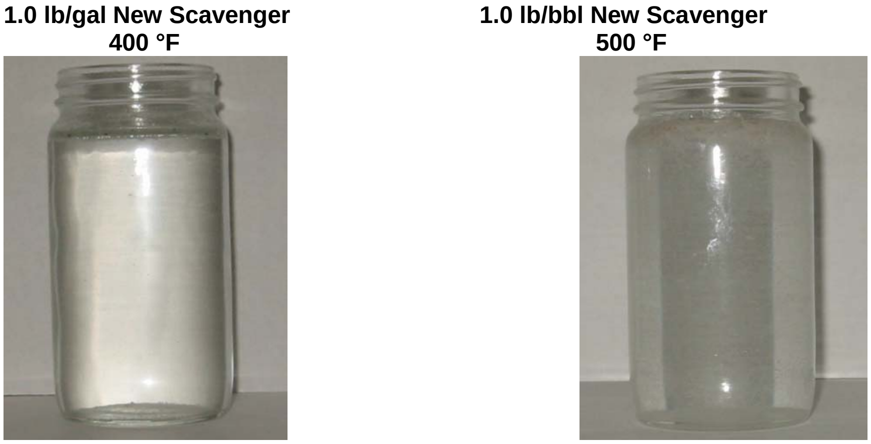
1.0 lb/bbl New Scavenger
500 °F

Figure 11. 12.5 lb/gal NaBr after Aging at 400 °F and 500 °F with the New Scavenger


0.5 lb/gal Baseline Scavenger

1.0 lb/bbl New Scavenger

Figure 12. 15.5 lb/gal $ZnBr_2$/$CaBr_2$ after Aging at 300 °F for 16 hours with Oxygen Scavengers


1.0 lb/gal New Scavenger
400 °F

1.0 lb/bbl New Scavenger
500 °F

Figure 13. 15.5 lb/gal $ZnBr_2$/$CaBr_2$ after Aging at 400 °F and 500 °F with the New Scavenger