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Novel Zinc-Free Heavy Clear Brine Fluid for HPLT Applications

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Abstract

In an effort to increase oil production over the past twenty years, the oil industry has moved into deep water for new field developments. Many of the reservoirs require the use of completion brines above 14.7 ppg. Historically, zinc bromide solutions have been used to provide the required density and true crystallization temperature (TCT) for these reservoirs. However, health, safety and environmental concerns around zinc bromide use have caused operators to seek other alternatives.

This paper describes Gravimax ™ a novel, zinc-free, high density, and low true crystallization temperature brine fluid that was developed. This new fluid is a patented eutectic mixture of inorganic salts that is thermodynamically stable and contains no Environmental Protection Agency (EPA) listed priority pollutants. This paper will discuss the thermal stability, physical properties, and compatibility with a common oilfield sealing elastomer, as well as the viscosifier compatibility of the new fluid. Data on the crystallization behavior as a function of density and pressure, as well as formation damage testing with Berea Sandstone, will be shared. In addition, corrosion data, with and without an inhibitor on carbon steel, and aquatic toxicity data will be reviewed.

A new, higher density, low TCT fluid has been developed that does not have the health and safety concerns of zinc and is not prohibitively expensive like cesium formate. As such, this new fluid fills an important niche in a density range where there are very few completion options.

Introduction

It has been recognized for decades that kill-weight density, clear brines (Suman, 1974) were useful in minimizing damage to oil and gas reservoirs from solids invasion. Zinc bromide was found to be of benefit in divalent halide fluids when densities above 15.1 ppg were needed. Cesium formate provided the same density benefit to the formate family of brines. Each of these brines has some serious limitations. Cost and supply limitations (Champeau, 2019) prevent cesium formate from being widely used. Zinc bromide is recognized globally as a priority pollutant, and environmental and HSE concerns are diminishing its use.

To meet energy needs the oil and gas industry has begun to conduct exploration and production in deeper waters. Early in this effort concerns arose regarding the stability of conventional brine fluids at the temperatures and pressures seen in this high pressure, low temperature environment. Of particular concern were the effects imposed by pressure and temperature on two-salt divalent brines often used for well control. (Freeman, 2000) noted that in deep water fluids formulated according to standard TCT blending tables, further exhibited a pressurized crystallization effect, known as Pressurized Crystallization Temperature, PCT. Freeman found that these PCT effects could increase the True Crystallization Temperature, or TCT significantly. The effect on the TCT is increased as the pressure is increased.

In practice this effect of pressure on crystallization of divalent brines required the use of a blended calcium bromide/zinc bromide solution for densities above 14.7 ppg, for protection to 10,000 psi. If 15,000 psi protection was required, the starting density was reduced to 14.2 ppg. Use and manufacture of zinc bromide is on the decline globally, due to its status as priority pollutant. In field operations its use adds complexity and HSE risk and can impose expensive measures to capture and dispose of waste brines. Downstream concerns have also been noted, (Argyle, 2013) regarding small amounts of zinc deactivating refinery catalysts.

Increasingly stringent environmental regulations in the North Sea, led to the development of cesium formate in the 1990's, as an alternate to blends of calcium bromide/zinc bromide. Formates were found to have some technical advantages such as increasing polymer stability for water-soluble polymers, (Cabot, 2015), and natural buffering and antioxidant properties. Balanced against these advantages were the substantially (order of magnitude) higher costs than equivalent density zinc bromide, that made it uneconomic for many projects. Reports suggest that known supplies of Pollucite ore from which the element cesium is extracted, are increasingly rare, and making its use in a high-volume deep water operation problematic.

As Champeau noted, these limitations and the need for an alternative to zinc bromide led the industry to call for a new brine that would exhibit the following criteria: zinc free, stability at densities above 14.2 ppg, with low TCT (and a PCT of <30 F) at 15,000 psi, non-damaging to the formation, compatible with completion hardware and elastomers, and be thermally stable at downhole temperatures.

Albemarle is one of the world's leading suppliers of bromine based clear completion fluids and we took on the challenge of developing a more environmentally friendly fluid that contains no priority pollutants for high density wells.

Through our research efforts, a new binary eutectic fluid mixture which will be called HDALB throughout the rest of this paper was developed. This patented material is thermodynamically stable and contains no zinc. It requires no crystallization inhibitors and has a TCT below -5ºF at 15 ppg. The rest of this paper will discuss the properties of this new fluid.

Experimental

Typical Properties

HDALB is a binary eutectic mixture based on new salt chemistry. Some typical properties of a 15.0 ppg HDALB fluid are given in Table 1.

Table 1: Properties of HDALB

Viscosity at 70°F	15 cp
Flash Point	None
pH neat	Approx. 4
pH (1:10)	Approx. 7

Heat Stability

HDALB was heated at 350ºF for 28 days in a glass lined Fann aging cell under 200 psi nitrogen pressure. There was no thermal degradation of the fluid based on the lack of changes in appearance and properties. This is not unexpected given that it is an inorganic salt solution.

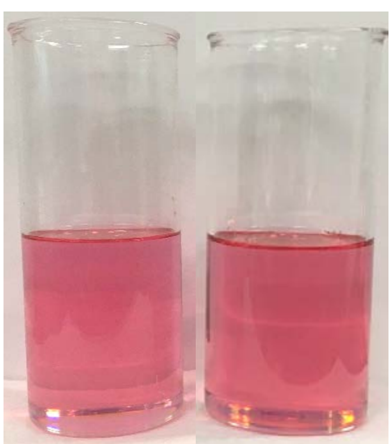

Figure 1. The sample on the left is before thermal stability testing and the sample on the right is after 28 days at 350º F.

Crystallization

An essential property for fluids in these applications is to have low crystallization temperatures. Figure 2 displays the LCTD (last crystal to disappear) as a function of fluid density. By comparison the LCTD of a 15.0 ppg $CaBr_2$ solution is very close to ambient temperature. Since HDALB contains no crystallization inhibitors this is a thermodynamically stable crystallization temperature.

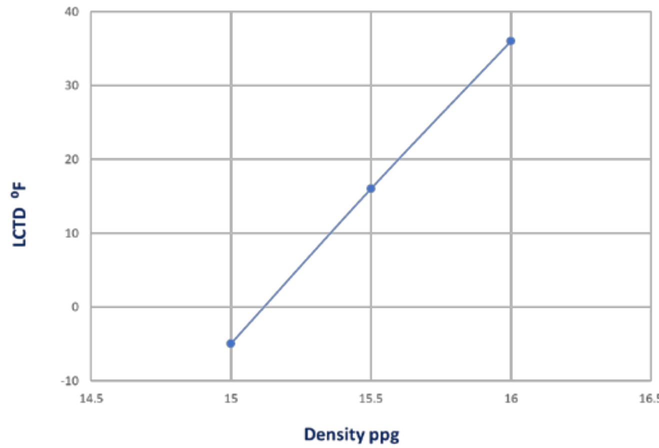

Figure 2. The LCTD plotted as function of fluid density for HDALB.

Pressurized Crystallization Temperature (PCT)

The work by Freeman demonstrated the significant effect pressure has on crystallization behavior in divalent brines. To measure the effects of pressure on crystallization temperature for HDALB a sample of a 15.0 ppg fluid was sent to a commercial testing laboratory. Figure 3 shows the PCT data for HDALB.

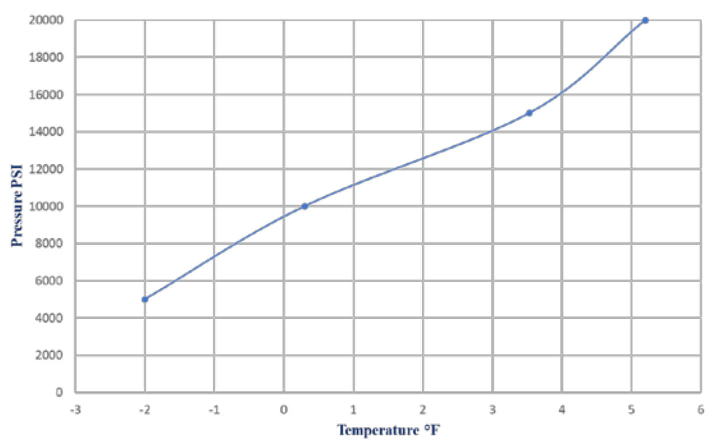

Figure 3. PCT data to a pressure of 20,000 psi for HDAPB at 15.0 ppg

General Corrosion

The specialty steels used in completion operations on oil and gas wells are susceptible to wall thickness attack from contact with completion brines. Referred to in terms of weight loss in thousandths of an inch per year (MPY), if signs of attack at a rate greater than 5-MPY are seen, concerns about completion integrity have been noted. In some situations, the low pH of brines has been noted as a contributor to weight loss corrosion. However some authors have observed that these effects can be minimized with inhibitor chemistry and brought to a level below 5-MPY, or may not present a challenge at all (Champeau, Pimenta, 2018 and Intiso, 2018). Conclusions should only be drawn from well specific testing.

Corrosion testing was performed on C1010 coupons with 15 ppg HDALB. The coupons were heated for 28 days at 300ºF with 300 psi Nitrogen overpressure. Tests were run with and without corrosion inhibitors and compared to a 15 ppg Ca/Zn bromide. The data in Table 2 shows that acceptable corrosion rates can be achieved when a corrosion inhibitor is used. It also shows that HDALB has lower general corrosion rates than a similar density Ca/Zn bromide under these test conditions on C1010.

Table 2. General Corrosion Data for 15 ppg fluids on C1010

Fluid	Corrosion Rate, mpy
Ca/Zn bromide	9.0
HDALB	7.1
HDALB + 3200 ppm Corr. Inhib. A	2.6
HDALB + 1600 ppm Corr. Inhib. B	5.3

The coupons were also inspected visually under 10X magnification and showed no evidence of pitting. Figure 4 is a picture after testing.

Figure 4. A test coupon after exposure to HDALB. The fluid contained a corrosion inhibitor.

Stress Cracking Corrosion

Down hole equipment, (screens, valves, gauges) used in sand management operations are often constructed from high strength steel alloys such as 13 Cr, S-13 Cr, and Duplex-22 Cr. Pimenta found that concerns about stress cracking, hydrogen embrittlement, and pitting in the higher strength grades of these steels would drive fluids selection more toward monovalent brines (NaCl, NaBr) and away from the divalent brines ($CaCl_2$, $CaBr_2$), Influencing factors included: purity of source brine materials, test temperature, and the presence of oxygen.

Intiso extended this work where calcium bromide fluids were evaluated against cesium formate brines at 140°C. Intiso found that both systems exhibited a decline in pH (9.73-4.39 for $CaBr_2$), (10.07-7.49 for cesium formate) when aged in the presence of CO_2, likely from buffer exhaustion. This was not found to be an excluding factor in either brine systems, although the steels used in conjunction with the formate brine exhibited some sign of microcracking and hydrogen embrittlement that was not deemed to be potentially catastrophic to the completion equipment. Champeau also received similar results when a specially designed divalent calcium bromide brine was observed to have a pH range of (2.0-6.0) in a test conducted at 275° F and 30 days duration, and concentrations of CO_2 varying between (2-4%) with no adverse effects on the completion equipment.

Stress cracking corrosion testing was performed on 13Cr. A 15 ppg HDALB fluid was tested at 300ºF for 30 days under a nitrogen overpressure. The specimens were stressed to their elastic limit before being exposed to HDALB. No cracks, pitting or corrosion was visibly present. Figure 5 shows pictures of the coupons after testing. A dye penetrant test was performed to check for the presence of microcracking. No microcracks were observed in this test.

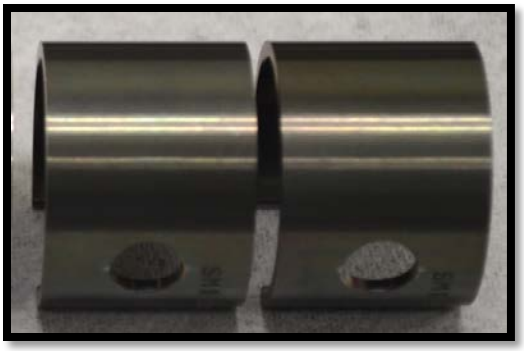

Figure 5. C-Ring coupons after testing at 300ºF. No cracks or pitting were observed.

Elastomers

A 15 ppg HDALB fluid and a 15 ppg Ca/Zn bromide were tested with Viton Type A. The elastomer was tested for 7 days at 150ºC. No visual damage and no change in Shore A hardness was observed. HDALB performed similarly or better than the Ca/Zn bromide solution for break stress, elongation, modulus and tensile stress.

Viscosity

Hydroxyethyl cellulose, (HEC) has been used for decades to provide viscosity to clear brines in several completion operations scenarios. Chief among them are:

• Sweeps used to circulate the hole free of as much particulate debris as possible in well bore cleanup operations
• Fluid loss control pills meant to slow the rate of working fluid loss to the formation

To provide maximum benefit to the operation and avoid formation damage from microgels created by HEC granules that are not fully hydrated in the brine (Hodge, 1997), or precipitate out of solution after mixing, it is important that the HEC polymer yield in the brine to the maximum extent possible (Darlington, 1982). Various techniques to achieve dispersion and hydration have been discussed in the literature. Darlington discussed how brine composition could affect the final dispersion and yield of HEC in a dense brine fluid. Hodge discussed how these microgels could adversely affect the permeability of the formation. Among the techniques employed by the industry to ensure maximum HEC polymer and yield are:

• Slow addition of the polymer to the brine
• High rates of axial shear to disperse the polymer granules in the subject brine
• Brine formulation to enhance water availability
• Pre-slurrying the HEC in an aqueous, or aqueous compatible medium to promote its complete hydration.

As part of our effort to qualify the new HDALB brine with this polymer, a series of laboratory experiments were run using HEC polymer from industry leading sources. Our goal was simple and straight-forward. We wanted to know if the new HDALB brine would viscosify under ambient conditions with commonly used forms of HEC.

The standard mixing procedure was to put HDALB with deionized water, if being diluted, into a Hamilton Beach mixer. As the fluid was mixed, the HEC was slowly added over the course of 1 to 2 minutes to minimize the chance that the HEC would clump together. The fluid was then mixed for 2 hours. After mixing, the fluid was left to sit, typically overnight, in the sample cup to allow the foam and liquid to separate so that the liquid could be tested. The liquid was then tested using a Fann 35A rotating bob viscometer.

Multiple rounds of testing were conducted varying the density of the HDLAB between 14.7 ppg and 15.1 ppg, as well as the concentrations of HEC polymer (0.25-2.25 ppb) added in a given test. The $CaBr_2$ data shown in Figure 6, was taken from prior work by one of the author's (Messler, 2012) and used as a reference for this testing.

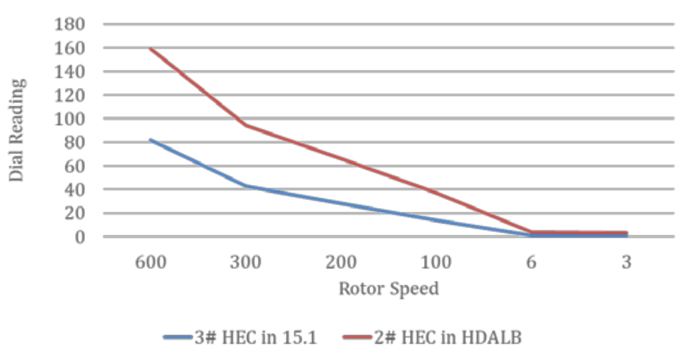

Figure 5. HEC yield comparison of a 15.0 ppg HDALB fluid with a 15.1 ppg $CaBr_2$ fluid at 70ºF.

Observations in the broader HDALB testing were noted as follows:

• Higher temperatures caused a decline in properties measured
• Lower densities enhanced properties
• Higher polymer concentrations elevated properties at high shear rates

This was largely in line with expectations noted in prior work on other high density brines by Darlington. We feel this testing has shown HDALB can be viscosified with HEC but acknowledge that more work would need to be done to qualify a formulation for field deployment.

Formation Damage

Extensive testing has been done over the years with calcium bromide based completion and workover brines. They have generally been found to be non-damaging to sandstone reservoirs with several general exceptions noted in literature. Ppotential adverse precipitation reactions with high pH calcium brines (Morgenthaler, 1986) were observed in the presence of carbonate ions, CaO, and $CaCO_3$. Adding 8% $ZnBr_2$ was recommended as a solution which lowered the pH. Morgenthaler went on to note incompatibilities with these brines and formation waters containing sulfate. Later work by (Hamzaoui, 2018), confirmed this effect in monovalent brines and described the ion exchange implications associated with high pH brines in some detail. A destabilizing influence in formation clays in the presence of low salinity, high pH brines was described by (Valdya, 1992). Finally, Champeau found that a specially prepared lower pH calcium brine modestly outperformed a standard calcium bromide brine in a formation damage test using field core, with all delivering return permeability scores above 89% return to flow.

A formation damage test on the new HDALB was run at a commercial lab using a Berea sandstone core. This was designed as an initial screening test for the HDALB brine.

A known Gulf of Mexico field formation brine recipe was utilized in the test. After saturating the core with the field brine, the initial permeability was established in the injection direction. This was followed with 5-pore volumes of the HDALB brine. The test was then shut-in for 16 hours, and flow initiated with the field brine in the production direction to establish final permeability. The permeability results are shown in Figure 6. There was over 96% retained permeability in this test.

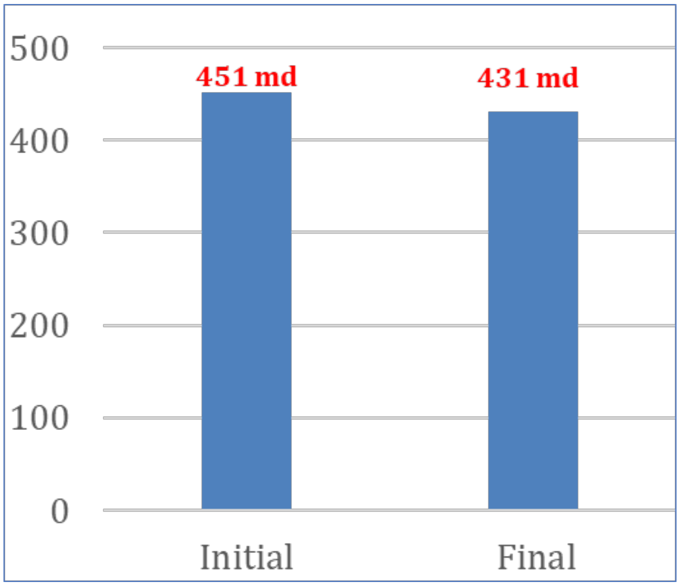

Figure 6. Formation damage test on 500 md Berea core at 275ºF. There was 96% retained permeability.

Environmental

The HDALB system was tested to ensure it complied with Gulf of Mexico environmental regulations. It passed the EPA Method 1617, Static Sheen and EPA Method 1664 Oil and Grease. It also contains no priority pollutants listed in 40CFR Part 423, Appendix A.

Aquatic Toxicity

The aquatic toxicity of a 15 ppg HDALB was measured and compared to an equivalent density Ca/Zn bromide fluid and cesium formate. The data for the cesium formate was obtained from a Sinomine SDS. The data is summarized in Table 3. This table shows that HDALB has similar aquatic toxicity as cesium formate and has significantly better aquatic toxicity than the zinc containing fluid.

Table 3. A comparison of aquatic toxicity of three fluids used for high density applications.

Fluid	LC50 48 Hr Mysid Shrimp	LC50 48 Hr Inland Silverside
$Ca/ZnBr_2$	31 ppm	216 ppm
HDALB	582 ppm	1390 ppm
Cesium Formate	521 ppm	787 ppm

Conclusions

Gravimax is a new patented class of clear brine fluids suitable for the HPLT environment where low PCT fluids of 15 ppg or higher are needed. This new fluid has demonstrated excellent basic compatibility and applicability tests with other completion elements, has good permeability with a Berea core and has a much lower price point than cesium formate.

The general corrosion and stress crack corrosion data show no adverse effects on completion material integrity**.** Also very importantly, this new fluid contains no priority pollutants and has a favorable aquatic toxicity profile.

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