

Formate brines in extreme HPHT well construction operations – Do they have limitations?

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Abstract

Formate brines have been successfully used in hundreds of HPHT drilling and completion operations over the past 10 years and have exhibited remarkable thermal stability. This has been confirmed by analyses of brines recovered from extreme HPHT wells after lengthy exposure (months/years). Laboratory testing cited in the literature has, however suggested that significant formate brine decomposition to bicarbonate and hydrogen gas should occur at even relatively low temperatures if the brine is in contact with catalytic surfaces

The inconsistency between laboratory and field behavior raised strong suspicions that standard laboratory autoclaves are not suited for reproducing or simulating downhole conditions. Typical differences between these two environments are pressure, presence of gas cap, and amount and type of catalytic surfaces.

The objectives of the studies reported in this paper were to a) try to reproduce the downhole conditions in the laboratory and so develop a technique for simulating formate behavior under hydrothermal conditions and b) look critically at what changes, if any, occur in formate brines in deep HPHT wells. The experimental study involved an examination of formate brine compositional changes in specialized hydrothermal equipment and comparing these results against chemical analysis of formate brines retrieved from HPHT wells after lengthy exposure to downhole conditions.

A flexible gold test cell was used for the decomposition testing, immersed in a high pressure high temperature autoclave filled with water. The flexibility of the gold cell has allowed experiments to be conducted and sampled at high pressure without the presence of an artificial gas cap. Initial tests have shown that any decomposition reactions taking place in formate brine under hydrothermal conditions eventually reach equilibrium with bicarbonate.

The well sampling program confirmed the findings from the laboratory. A small amount of decomposition was found to have taken place in the bottom of one HPHT well after a very long exposure time (two years). The decomposition was limited to the very bottom section of the well, and did not significantly influence the bulk properties of the recovered brine. The local changes in the most decomposed samples did not have any adverse effect on critical fluid properties such as

pH, density, and buffer capacity.

The discovery that formate brines will reach equilibrium with bicarbonate has allowed us to design carbonate rich formate brine fluids, which will remain stable even at very high temperatures.

The most important lesson learned from testing in the gold hydrothermal cell is that traditional laboratory autoclaves operated with gaseous headspace are not suited for testing formate brines at high temperatures. In fact, test results generated in such autoclaves will be laboratory artifacts that do not reproduce what actually happens in HPHT wells.

Introduction

Formate brines were originally designed and developed for use as high-performance HPHT drilling and completion fluids [1-3] and have been deployed in more than 150 HPHT wells since 1996 [4]. Over this time they have been exposed for lengthy periods (typically 30 – 60 days, but sometimes for more than a year) to well temperatures of up to 225°C / 437°F without any observable change in composition or properties (i.e. no major build up of decomposition products, such as hydrogen or significant changes in density, pH, buffer level, etc).

Such resistance to thermal degradation or transformation under HPHT conditions is not intuitive, given that the technical literature contains many examples of laboratory experiments showing that formates in aqueous solutions can decompose appreciably at high temperatures.

It seems that there is no obvious correlation between field experience and results of laboratory tests using HPHT autoclaves. In other words, it appears that no researchers have yet managed to simulate or reproduce the conditions experienced by formate brines in HPHT wells. This is perhaps not surprising given that HPHT wells are effectively very long tubular hydrothermal reactors lined with a variety of catalytic surfaces.

In spite of the lack of evidence of any significant formate decomposition in HPHT wells, there has always been some concern in the industry about the risk of decomposition and its possible effect on the integrity of metals. The main concern is the potential for hydrogen that is generated by formate decomposition to enter into susceptible Corrosion Resistant Alloys (CRAs) and cause hydrogen embrittlement.

Before investigating what impact hydrogen generation from formate decomposition might have on the integrity of metallic material in real well operations, it is important to first understand how and to what extent such hydrogen generation will actually take place under realistic well conditions.

In this paper, the chemistry and dimensions of decomposition events observed in specialized laboratory test equipment at the Woods Hole Oceanographic Institution in USA are reviewed and compared with changes observed in formate fluids recovered from HPHT well construction operations. The importance of the carbonate / bicarbonate as a stabilizing additive for formate brines under HPHT conditions is reviewed. Through the judicious addition of carbonate and bicarbonate formate fluids can be formulated that will be chemically stable even under extreme HPHT conditions.

The effect of decomposition and decomposition products on corrosion is a topic of another paper, and will not be discussed here.

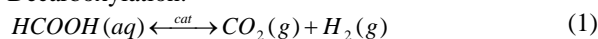
Theory of Formate Decomposition

The technical literature contains a number of reports on the thermal decomposition of formate salts under laboratory conditions. The majority of these address the decomposition of solid-phase (i.e. crystalline or powder) formate salts or formic acid [5–17]. Most of the experiments described in these papers are either carried out at very high temperatures or in the presence of a platinum catalyst. Results from these studies on crystalline formates and formic acid show that the decomposition mechanism, the products, and the rates are all dependent on the atmosphere (air, O₂, N₂, H₂, CO₂, vacuum) in which the tests are conducted, the amount of water in the test sample, and the nature of the cation. Results from these studies on solids, such as particular reaction rates, major decomposition products, and effect of counter ion, are not relevant to aqueous solutions of formates.

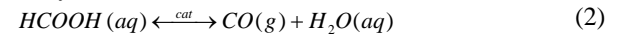
The aqueous phase decomposition of formate and formic acid is less extensively studied [18]. Most of the work that has been done on aqueous systems has looked at decomposition of low pH formic acid / formate solutions [18-21], often in the presence of a palladium catalyst. These studies conclude that the rate and mechanism of decomposition largely depends on the pH and the concentration of formic acid. These experiments were mainly carried out at pH values of less than 6.5. The pH of buffered formate brines that are used in the field can never drop much below 6.5, even after a large influx of CO₂.

Decomposition studies on formate brines with higher pH are even fewer in [number \[21-22\]](#). All studies done in aqueous formate / formic acid solutions do, however, agree that the major decomposition pathway is the reaction of formate and water to produce bicarbonate and hydrogen (decarboxylation), with the dehydration mechanism being the minor pathway. For formic acid the following reactions apply:

Decarboxylation:

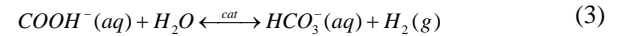


Dehydration:

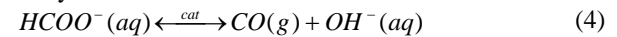


And the analogous reactions for formate are:

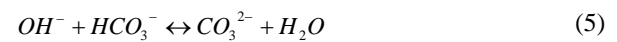
Decarboxylation:



Dehydration:



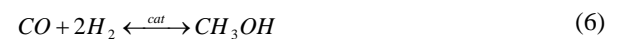
The hydroxide formed from reaction 4 will immediately react with bicarbonate to form carbonate:



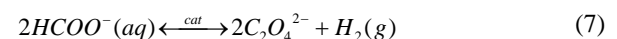
From the literature we find that when formic acid or formate is dissolved in water, the decarboxylation pathway strongly predominates, while dehydration is favored in the gas phase. All of these reactions are reversible so that formate and formic acid can be generated by reduction of dissolved CO₂ or HCO₃⁻ with hydrogen or by hydration of CO [22]. At equilibrium, the formate to CO₃²⁻/ HCO₃⁻ ratio depends on the pH of the solution. More formate / formic acid is favored at higher pH.

As a buffered formate brine is almost always alkaline, and can only drop to a slightly acidic state of pH = 6.0 – 6.5 after a massive acid gas influx, only small amounts of protons and / or formic acid can ever be present in this brine system (pKa for formic acid = 3.75). As reactions 1, 2, and 4, shown above, require formic acid or an acidic environment they are never likely to dominate. This is supported by gas analyses and measurements of chemical constituents present in laboratory and field samples. The dominating reaction is therefore the decarboxylation of formate to bicarbonate and hydrogen gas (Equation 3).

The carbon monoxide formed from the dehydration reactions (Equations 2 and 4) can react further with hydrogen from the decarboxylation reactions (Equations 1 and 3) to form methanol:



Another minor decomposition pathway that is mentioned in the literature is the reaction of formate and water to form hydrogen and oxalate according to the following reaction [15]:



This is predominantly a gas-phase reaction and is not expected to take place to any large extent in autoclaves without headspace or in a downhole environment. Cabot Specialty Fluids has never detected any significant increase in oxalate levels in any brine samples that have been returned

from the field. Increased oxalate levels have, however, been reported in laboratory tests that have been run with a nitrogen gas cap [26].

All of the above decomposition reactions can be catalyzed by certain metal surfaces. In chemistry and biology, catalysis is the acceleration (increase in rate) of a chemical reaction by means of a substance, called a catalyst, which is not consumed by the overall reaction. Nickel, which is a common alloying component in Cr-steel oilfield tubulars, is known to be a good catalyst for formate decomposition [24].

The initial reaction rates of all of these decomposition reactions depend on the temperature and the catalyst surface area-to-brine volume ratio, as well as the type and condition of catalysts present. How reactions proceed and eventually stop depends on whether or not the catalysts become poisoned over time and when the reactions reach equilibrium.

There is only a small amount of information in the literature about formate decomposition reactions and equilibria under the hydrothermal conditions typical of those found in the lower reaches of HPHT wells. McCollom and Seewald [22] reported that at high temperatures and in the presence of certain catalysts bicarbonate could be reduced with hydrogen to form formate. This indicates that the major formate decomposition reaction could be counterbalanced by the opposite reaction under the appropriate conditions in HPHT wells. Fu and Seyfried [25] have reported that magnetite (common mill scale found on many oilfield tubulars) catalyses the reduction of CO₂ with hydrogen to create formate under hydrothermal conditions.

Experimental

When studying the thermal stability of formate brines in the laboratory environment it is vital to reproduce within the test cell the conditions found in the real down hole environment. Considering the fact that the formate decomposition reactions (Equation 1 – 6) are equilibrium reactions, it is important that both reactants and products of these reactions are allowed to build up to realistic levels. Especially when gaseous products are formed, it is important that the concentration of this gas, which is measured by its partial pressure, is allowed to build up to a realistic level. The faster this partial pressure is allowed to build up, the sooner the decomposition reaction will reach equilibrium and stop. Testing in a low pressure test cell or applying a large artificial gas cap into which the gas can escape are both very effective means of preventing such equilibria from establishing. Since hydrogen gas is a product of the main formate decomposition reaction (Equation 4), the only way of accurately reproducing what is happening downhole is to run the test in a high pressure test cell without a gas cap. The extent to which some of the most frequently reported decomposition reactions proceed depends not only on whether headspace is present, but also the type of gas contained in it [15].

Unfortunately all previous attempts by oil industry researchers to investigate the thermal stability of formate brines have used the wrong test equipment and procedures [26-28]. Not only have low pressure gas cap conditions

prevented equilibria from establishing so the reactions can stop, but the high-nickel Hastalloy autoclave walls have provided a perfect catalytic surface and thereby accelerated the decomposition reactions.

With the lack of literature data about formate decomposition reactions and equilibria under hydrothermal conditions, and the known shortcomings of the standard autoclave test environment, it was found necessary to search for a more realistic test environment, i.e. a high-pressure high-temperature test chamber without a gas-filled headspace that could interfere with the kinetics of the equilibrium reactions. Such a test environment was found at Woods Hole Oceanographic Institution in USA in the laboratory of Jeff Seewald, one of the world's leading experts on the hydrothermal reactivity of organic acids [22]. In this laboratory, the test fluid is contained in a flexible gold test cell immersed in a high-pressure high-temperature autoclave filled with water. The gold test cell, as shown in Figure 1, has the advantage of not being very catalytic and – due to the flexibility of gold pouch – experiments can be operated and sampled without the need for a gas cap.

The first set of experiments conducted with formate brines in this test cell has yielded very interesting results. These tests were conducted without any catalytic material added to the test cell. The test program was designed to identify where formate decomposition equilibria would establish. It is acknowledged that a variety of different catalytic materials might be present in real-life field situations, but the presence of such materials only affect the rates of the decomposition reactions; they will not shift the final equilibria. Consequently, these tests give a realistic picture of the equilibria that establish in formate brine after extended exposure to real well temperatures and pressures, regardless of the presence of catalytic material.

It is known [22] that the formate / bicarbonate equilibrium (Equation 3) is dependent on temperature. At higher temperatures more bicarbonate and hydrogen form, while at lower temperatures the equilibrium leans towards a higher concentration of formate. Likewise, we know that equilibria involving solubilized gas depend on the solubility of the gas and thereby on the pressure. As solubility of hydrogen gas increases with greater pressure, more hydrogen is present in solution to push the formate / bicarbonate equilibrium (Equation 3) back towards a higher formate concentration.

In order to simulate the most extreme temperature / pressure challenge likely to face formate brines, the first tests at Woods Hole were conducted at 270°C / 518°F. Equilibria were obtained at two rather moderate pressures, 34 MPa / 5,000 psi and 41 MPa / 6,000 psi. The formate brine under test was buffered with carbonate / bicarbonate at the level which Cabot Specialty Fluids recommends for fluids used in HPHT well construction operations (6 ppb potassium carbonate and 4 ppb potassium bicarbonate). The amount of decomposition measured in this brine at 270°C / 518°F is shown at two different pressures in Table 1. From this we can see that even under these severe conditions (very high temperature combined with moderate pressure) only a relatively small

amount of formate transforms to bicarbonate. At lower temperatures and / or higher pressures more formate is present at equilibrium and therefore less bicarbonate and hydrogen forms. The presence of catalytic metals in this test in this test would have shortened the time it took to establish this equilibrium, but would not have influenced the final brine composition.

These preliminary tests at Woods Hole have demonstrated the importance of testing formate brines under conditions that begin to reproduce the downhole well environment. Even at the extreme temperature of 270°C / 518°F and a moderate pressure of 34 MPa / 5,000 psi the formate decomposition reactions stopped after a moderate amount of formate conversion to bicarbonate and hydrogen. With a realistic temperature/pressure combination (lower temperature, higher pressure), one can expect significantly less decomposition to take place. In a standard laboratory test environment the presence of a headspace would have prevented the hydrogen, which forms from the initial decomposition, from playing the important role it does in this equilibrium and the formate decomposition would have continued unrestricted.

Future testing at Woods Hole will focus on the effect of pH on the equilibria reactions. More bicarbonate will be needed in order to establish equilibrium in a lower pH fluid. However, as the acid gas that is responsible for lowering the pH is mainly CO₂, a larger amount of bicarbonate is already naturally present in such brine. Any one CO₂ molecule that enters into the wellbore reacts with one carbonate ion from the pH buffer and forms two bicarbonate ions.

Field Experience

The knowledge gained by the Woods Hole experiments has contributed to a better understanding of why there have never been any signs of decomposition in formate brines that have been recovered from HPHT wells. Neither has hydrogen gas been detected above any well that has been suspended with formate brine. This means that if any decomposition has taken place, it has only been in a small volume of the brine present at the very bottom of the well.

In order to achieve a better understanding of any chemical changes that could take place locally down hole in formate brines when exposed to hydrothermal conditions, extensive fluid sampling has been conducted during the recovery of the cesium formate brine from two different HPHT wells after they had been suspended in formate brine for various periods of time.

Well A

Well A is located in the world's largest HPHT field development project in the North Sea. Over a period of about eight years, a total of seven wells have been suspended and worked over in this field with 2.18 s.g. / 18.2 ppg cesium formate brines [29]. Initial reservoir pressures were around 115 MPa / 16,700 psi, and maximum BHST was in the range of 190°C / 374°F to 205°C / 401°F. The 8.5" reservoir sections were drilled with synthetic oil-based mud (SBM) and completed with 7" liners before running production tubing.

Liners and production tubing were all made from 25Cr. Due to fabrication problems with some of the downhole production equipment, all seven wells had to be suspended and worked over. Two of the seven wells had already been perforated.

All of the seven wells have been exposed to 2.18 s.g. / 18.2 ppg cesium formate brine for various durations. In the last well, Well A, the cesium formate brine was left in the cased hole as a suspension fluid for a period of two years.

The cesium formate brines that went into these wells were all buffered with a standard amount of carbonate / bicarbonate buffer. No attempt was made to make the brines more thermally stable by increasing the amount of buffer.

When the brine was circulated out of Well A after 24 months (firstly from within the 25Cr production tubular, using CT, and later from the well annulus), samples were retrieved from various depths, and analyzed. The results of the analyses from inside the tubing are shown in Table 2 and Table 3. The analyses of the annular fluid showed similar levels of chemical transformations.

Since there had been no recorded influx of carbon dioxide during the well suspension period, the increase in the combined carbonate / bicarbonate in the brine could be used as an indicator of formate decomposition. Bicarbonate is a reaction product from formate decomposition via the decarboxylation mechanism (Equation 3), while the carbonate is a reaction product from the dehydration mechanism (Equations 4 and 5).

The formate brine sample recovered from the deepest section of Well A inside the 25Cr production tubular at 5,000 meters contained combined carbonate / bicarbonate levels that were 0.83 moles / liter higher than in the original brine before it was run in the hole (Table 2). This corresponds to the decomposition of about 8% of the formate brine in the sample taken at the bottom of the well. Test results from the Woods Hole laboratory (see Table 1) would suggest that the formate brine in Well A had reached decomposition equilibrium and that no further changes in chemical composition were occurring by the end of the suspension period.

A Dräger Pac III instrument was used to measure the level of combustible gases over the brine as it was circulated to surface (Table 2). Unfortunately, no instrument was available at the rig site that could measure the concentration of hydrogen gas alone.

Small amounts of methanol and acetate were measured in the retrieved formate brine samples. These may have originated from reactions between the products of the primary decomposition processes (Equation 6). The glycol that was found in the deepest samples is likely to originate from previous well treatments. A very low level of citrate was present in the top part of the well. It is uncertain how this was introduced, but it seems to have disappeared in the lower part of the well, possibly as a result of decomposition, during the exposure to the highest temperatures. Decomposition products from citrate decomposition are similar to decomposition from formate decomposition (bicarbonate and carbon monoxide). The measured oxalate levels do not increase with temperature (depth). Therefore, there is no evidence of formate

decomposition to oxalate in this well. A low level of oxalate exists in formate brine that has been exposed to daylight during storage.

No decomposition at all was experienced in the top part of the well. As some of the carbonate / bicarbonate detected further up the tubing could have diffused up from the bottom of the well, it is difficult to predict exactly at what depth / temperature decomposition first began to take place.

Despite decomposition, the recovered brine was in good condition and fit for further duty. The brine's pH had dropped slightly in the bottom samples (due to the decreased carbonate-to-bicarbonate ratio), and the density had increased a little. These bottom samples also had a higher buffer capacity than the original brine (because of increased carbonate content) and had become more thermally stable as a result of the increased carbonate and bicarbonate levels. The brine samples were all clear and free of any salt precipitation, even at room temperature.

Well B

An operator used 2.145 s.g. / 17.88 ppg cesium formate brine as a well control fluid during the appraisal of a basin-centered gas accumulation in Hungary. The appraisal activities involved fracturing various zones in an extreme HPHT well (Well B), which has a total depth in excess of 5,000 m / 16,400 ft, a BHT of 236°C / 457°F and pressures in excess of 96 MPa / 14,000 psi.

Various fluid displacements carried out for operational reasons allowed Cabot Specialty Fluids two opportunities for capturing samples of cesium formate brine that had been exposed to these exceptionally high pressures and temperatures inside a P110 carbon steel casing for periods of 34 and 39 days.

Well B – Suspension 1

In April 2007, Well B was killed with 60 m³ / 377 bbl of 2.145 s.g. / 17.88 ppg cesium formate brine by bullheading the frac fluid (calcium chloride brine) and spacer fluid (potassium formate brine) into the fracs and formation. After a 39-day suspension the cesium formate brine was displaced out of the hole with a KCl packer fluid. Samples of the formate brine were captured during the reverse circulation operation. The brine samples were analyzed to assess their physical and chemical condition after exposure to the extreme HPHT conditions.

The cesium formate brine that went into this well was buffered with a standard amount of carbonate / bicarbonate buffer. Again, no attempt was made to make this fluid more thermally stable by increasing the amount of buffer. The bottom of the column of cesium formate brine was at a depth of 5,300 m / 17,390 ft with a local temperature of 225°C / 437°F.

It should be noted that when the well was bullheaded at the start of operations it contained CaCl₂ brine and that a potassium formate spacer was employed to separate it from the cesium formate. As the well was live throughout the operation and a sump existed below the perforated interval the

possibility for fluid exchange existed, i.e. CaCl₂ and potassium formate could have co-mingled with the heavier cesium formate brine.

Additionally, while running the test, the string was over-displaced periodically to keep it full. Surface pressure control was exerted such that only half the displacement and fill volumes were taken to surface, the remainder going to the formation / frac. As a consequence the resident cesium formate brine in the well was 'contaminated' to some extent by 'new' fluids during this operation. Absolutely accurate correlation of sample depth with logged depths was therefore impossible, but bulk condition and trends in fluid properties should be observable. Properties and composition of the brine samples that were recovered are listed in Tables 4 and 5.

As can be seen from the brine sample properties in Table 4, only the two deepest samples showed any signs of increased bicarbonate levels that could be indicative of decomposition. The more affected of the two samples, taken from the deepest part of the well, had only suffered about 1.7% decomposition after more than a month of exposure at 222°C / 432°F. All of the recovered brine samples were in good condition without any significant change in density or essential properties. No precipitation was observed in any of the samples, even after they were cooled down. Some CO was detected in the brine when it was circulated out. This could have originated from formate decomposition (Equation 4). However, no acetate or methanol was measured, indicating that no further reactions involving CO occurred during this suspension. Also, no increased levels of carbonate were measured, which one would expect to be produced with CO from the dehydration reaction (Equations 4 and 5).

A very small increase in oxalate level was observed in the lowest sample, which could have originated from formate decomposition.

Well B – Suspension 2

In June 2007, Well B was killed again with cesium formate brine following completion of the well test. After a 34-day suspension the brine was displaced to fresh cesium formate brine following the appearance of low levels of H₂S gas at the wellhead. This gave Cabot Specialty Fluids another chance to assess the condition of the brine that, on this occasion, had experienced both extreme HPHT and a sour gas influx during service.

The cesium formate brine that went into Well B this time was the same brine that was used in Well suspension 1. Therefore, the fluid had a slightly increased bicarbonate level compared to the brine that was first sent out. No attempt was made to make this fluid more thermally stable by further increasing the amount of carbonate / bicarbonate buffer.

Nine brine samples were recovered during the displacement operation. The first was considered to be reasonably representative of the original brine pumped into the well (sample 0). The other samples were taken during the partial displacement operation at increasing well depths. It is estimated that the last four samples came from the deeper levels of the annulus, while samples 1 – 4 came from

progressively deeper horizons within the work string. Properties and composition of the brine samples that were recovered are listed in Tables 6 and 7. Both the annular and tubular samples had been exposed to CO₂ and H₂S under hydrothermal conditions. The fact that the brine was exposed to CO₂ makes it difficult to use the bicarbonate level increase to calculate the degree of decomposition. As CO₂ dissolves it forms carbonic acid, which pushes the carbonate / bicarbonate equilibrium towards bicarbonate. When carbonic acid comes in contact with buffered formate brine, one carbonate ion reacts with one carbonic acid molecule and forms two bicarbonate ions. Based on this mass balance an attempt has been made to calculate the degree of decomposition using the increase in the bicarbonate concentration combined with the decrease in the carbonate concentration. This is shown in the last two columns of Table 6. There is some uncertainty in these calculations as sample 0 might not have been representative as a start fluid for all of the samples taken.

Table 7 also shows results of other chemical analyses that were conducted on these samples. A small amount of oxalate was measured in all samples. There is no indication that oxalate is formed downhole during this second exposure period as there is no higher oxalate level in the brines that were exposed to the highest temperatures.

Based on the analyses completed on the samples from this well exposure it is difficult to accurately estimate the amount of decomposition, but the indications are that if any decomposition did take place it was negligible. There was no increase in the concentrations of methanol or acetate, which indicated that it is unlikely that any significant formate decomposition took place via the dehydration route (Equations 4 and 5). The retrieved brine was in good condition and fit for further duty.

Conclusions and Recommendations

New users of formate brines are often concerned about the possibility of hydrogen evolution from formates held under hydrothermal conditions in HPHT wells for long periods. Their concern is driven by a fear of massive transformation of formate to bicarbonate and hydrogen as is often reported from standard laboratory autoclave testing with gaseous headspaces. Experimental work at Woods Hole Oceanographic Institution combined with a thorough field sampling program has proven that such massive transformation of formate to bicarbonate and hydrogen gas is a laboratory artifact, and will not happen under realistic downhole conditions.

- In the absence of a gas headspace, the formate decomposition reactions at high temperature and high pressure will eventually reach an equilibrium state, at which point they do not progress any further.
- The rapidity with which equilibrium is reached depends on the temperature, the pressure, the amount of carbonate/bicarbonate buffer in the brine, and the presence of reaction catalysts.
- The analysis of cesium formate brines exposed to hydrothermal conditions for long periods in two different

HPHT wells have validated the findings of the experimental study. Only minor levels of formate decomposition products were measured in the brine samples, and even then were restricted to samples taken from the deeper sections of the wells.

- The Woods Hole test has also contributed to our understanding of how to make formate fluid formulations that equilibrate and stabilize quicker under the hydrothermal conditions found in HPHT wells. 'Thermally stable' formate brines can be formulated by increasing the amount of carbonate and bicarbonate in the formulation. Carbonate and bicarbonate are already present as pH buffer in typical formate fluid formulations.
- The Woods Hole test has provided clear evidence that **standard laboratory autoclaves with gaseous headspaces are not suited for testing of formate brines at hydrothermal conditions**. Any property changes that might be influenced by decomposition products will be affected by the fact that the equilibria are not allowed to establish in such a test environment.

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Nomenclature

HPHT = High Pressure High Temperature
CRA = Corrosion Resistant Alloy

References

1. Downs, J.D.: "Formate Brines: New Solutions to Deep Slim-Hole Drilling Fluid Design Problems," SPE 24973, Cannes, November 1992.
2. Downs, J.D.: "Formate Brines: Novel Drilling and Completion Fluids for Demanding Environments," SPE 25177, New Orleans, March 1993.
3. Howard, S.K.: "Formate Brines for Drilling and Completion: State of the Art," SPE 30498, Dallas, October 1995.
4. Downs, J.D., Blaszczyński, M., Turner, J., Harris M.: "Drilling and Completing Difficult HPHT Wells with the Aid of Cesium Formate Brines – A Performance Review", SPE99068, February 2006.
5. Patnaik, S.K. and Maharana, P.K.: "Reaction Kinetics of Non-isothermal Decomposition of Sodium Formate and Sodium Oxalate and the Effect of Gamma Radiation", Radiochem. Radioanal. Letters (1981) 46/5, 271 – 284.
6. Canning, R. and Hughes, M.A.: "The Thermal Decomposition of Alkaline Earth Formates", Thermochemica Acta, Elsevier Scientific Publishing Company (1973) 6, 399 – 409.
7. Baraldi, P.: "Thermal Behaviour of Metal Carboxylates: Metal formates", Spectrochimica Acta, Pergamon Press 35a, 1003 – 1007.
8. Meisel, T., Halmos, Z., Seybold, K. and Pungor, E.: "The Thermal Decomposition of Alkali Metal Formates", Journal of Thermal Analysis (1975) 7, 73 – 80.
9. Morando, P.J., Piacquadio, N.H. and Blesa, M.A.: Thermochemica Acta (1987) 117, 325 – 330.

10. Muraishi, K. et al.: *J. Inorg. Nucl. Chem.* (1981) 43, 2293 – 2297.
11. Sinnarkar, N.D. and Ray, M.N.: “Kinetics of Thermal Decomposition of Barium Formate”, *Indian J. Chem.* (September 1975) 13, 962 – 964.
12. Souma, Y., Negi, Y.S., Sano, H. and Iyoda, J., Ishii, E.: “Studies on the Storage of Hydrogen by Potassium Bicarbonate-Potassium Formate System”.
13. Górski, A., Krasnica, A.D.: “Influence of the Cation on the Formation of Free Hydrogen and Formaldehyde in the Thermal Decomposition of Formates”, *Journal of Thermal Analysis* (1987) 32, 1345 – 1354.
14. Górski, A., Krasnica, A.: “Origin of Organic Gaseous Products Formed in the Thermal Decomposition of Formates”, *Journal of Thermal Analysis* (1987) 32, 1243 – 1251.
15. Górski, A., Krasnica, A.: “Formation of Oxalates and Carbonates in the Thermal Decompositions of Alkali Metal Formates”, *Journal of Thermal Analysis* (1987) 32, 1895 – 1904.
16. Judd, M.D., Pope, M.I. and Wintrell, C.G.: “Formation and Surface Properties of Electron-emissive Coatings. XI Thermal Decomposition of The Alkaline Earth Formates”, *J. Appl. Chem. Biotechnol.* (1972) 22, 679 – 688.
17. Barham, H.N. and Clark, L.W.: “The Decomposition of Formic Acid at Low Temperatures”, *Jrl. Am. Chem. Soc.* (1951) 73, 4638 – 4640.
18. Hill, S.P. and Winterbottom, J.M.: “The Conversion of Polysaccharides to Hydrogen Gas. Part 1: The Palladium Catalysed Decomposition of Formic Acid / Sodium Formate Solutions”, *J. Chem. Tech. Biotechnol.* (1988) 41, 121 – 133.
19. Research notes: “Thermal decomposition of Dilute Aqueous Formic Acid Solutions”, *Ind. Eng. Chem. Res.* (1992) 31, 1574 – 1577.
20. Wakai, C. et al.: “Effect of Concentration, Acid, Temperature, and Metal on Competitive Reaction Pathways for Decarbonylation and Decarboxylation of Formic Acid in Hot Water,” *Chemistry Letters* Vol. 33, No. 5, 2004.
21. Akiya, N., Savage, P.E.: “Role of Water in Formic Acid Decomposition” *AICHe Journal*, 1998, Vol. 44, No. 2, 405 – 415.
22. McCollom, T.M. and Seawald, J.: Testal Constraints on the Hydrothermal Reactivity of Organic Acids anions: I: Formic Acid and Formate”, *Geochemica et Cosmochimica Acta*, Vol. 67, No. 19, 3625 – 3644, 2003.
23. Maiella, P.G., Brill, T.B.: “Spectroscopy of hydrothermal reactions. Evidence of wall effects in decarboxylation kinetics of 1.00 m H CO₂X (X = H, Na) at 280 – 330°C and 275 bar”. *J. Phys. Chem. A*, vol. 102, 1998, 5886 – 5891.
24. Leth-Olsen, H.: “Decomposition of Potassium Formate: A Parameter Study.” *Hydro Corporate Research Centre*, Report # 05S_AF4, 2005.
25. Fu, Q., Seyfried, W.E.: “Hydrothermal Reduction of Carbon Dioxide at 250°C and 500 bar”. *American Geophysical Union*, Fall Meeting 2003, abstract #OS31C-0216.
26. Javora, P.H., et al.: “The Chemistry of Formate Brines at Downhole Conditions.” *SPE 80211*, Houston, February 2003.
27. Lo Piccolo, E., Scoppio, L.: “Corrosion and Environmental Cracking Evaluation of High Density Brines for Use in HPHT Fields”, *SPE 97593*, February 2003.
28. Benton, W. et al.: “Chemistry of Formate Based Fluids”, *SPE 80212*, Houston, February 2003.
29. Leth-Olsen, H.: “Decomposition of 75% potassium formate at high pressure.” *Hydro Corporate Research Centre Report # 04S_BD6*, 2004.
30. Brangetto, M. et al: “Cesium formate brines used as workover, suspension fluids in HPHT field development”, *Drilling Contractor*, May / June 2007.

Tables

Table 1 Formate decomposition testing at Woods Hole Oceanographic Institution, USA. Amount of formate decomposition taking place in a buffered cesium formate brine before equilibrium is established at 270°C / 518°F.

[MPa]	Pressure		Formate decomposition [%]
		[psi]	
34.5		5,000	15
41.4		6,000	13

Table 2 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples that were recovered from within the 25Cr production tubular of Well A after two years' exposure to hydrothermal conditions. The amount of decomposition was estimated from the increase in carbonate / bicarbonate.

Sample #	Depth [m]	Temperature		Density @ 15.6	pH	Titration				
		[°C]	[°F]			Carb. [mol/L]	Bicarb. [mol/L]	Total [mol/L]	Change from original [mol/L]	Estimated Decomposition [%]
Original				2.17	10.47	0.16	0.07	0.22	0.00	0.0
1	0	5	41	2.17	10.43	0.16	0.06	0.22	-0.01	-0.1
2	1,554	65	148	2.17	10.47	0.16	0.06	0.22	-0.01	-0.1
3	1,937	80	177	2.17	10.49	0.16	0.06	0.22	-0.01	-0.1
4	2,320	96	205	2.18	10.46	0.17	0.07	0.24	0.02	0.2
5	2,704	112	233	2.18	9.97	0.17	0.18	0.35	0.13	1.3
6	3,087	128	261	2.18	9.84	0.18	0.25	0.43	0.21	2.1
7	3,470	143	390	2.19	9.73	0.23	0.32	0.55	0.33	3.3
8	3,854	153	307	2.19	9.94	0.42	0.47	0.89	0.67	6.7
9	4,237	162	324	2.19	9.88	0.45	0.51	0.96	0.74	7.4
10	4,620	171	340	2.19	9.74	0.36	0.61	0.97	0.75	7.5
11	5,000	180	357	2.19	9.68	0.36	0.69	1.05	0.83	8.3

Table 3 Composition of cesium formate brine samples recovered from within the 25Cr production tubular of Well A after two years' exposure to hydrothermal conditions.

Sample #	Depth [m]	Temperature		Gas ⁽¹⁾ [ppm]	Ion analysis		NMR [wt%]						
		[°C]	[°F]		Acetate [mg/l]	Oxalate [%w/v]	Cesium formate	Water	Glycol ⁽²⁾	Unknown	Methanol	Citrate ⁽³⁾	Acetate
Original					1,346	0.09	79.42	20.57	0.02	0.000	0.000	0.000	0.002
1		5	41	125	837	0.19	78.55	20.97	0.01	0.000	0.000	0.005	0.002
2	0	65	148	165	1,288		78.39	20.95	0.01	0.000	0.003	0.005	0.002
3	1,554	80	177	205	1,239	0.25	78.12	21.30	0.01	0.000	0.000	0.003	0.002
4	1,937	96	205	580	1,666	0.19	78.49	20.83	0.01	0.000	0.000	0.006	0.002
5	2,320	112	233	225	598	0.16	78.49	20.67	0.01	0.000	0.005	0.000	0.002
6	2,704	128	261	325	1,007	0.07	78.39	20.60	0.03	0.000	0.040	0.000	0.003
7	3,087	143	390	490	1,298	0.07	77.73	20.55	0.03	0.069	0.144	0.000	0.004
8	3,470	153	307	1240	703	0.06	76.01	21.32	0.02	0.233	1.569	0.000	0.005
9	3,854	162	324	1590	1,000	0.04	75.81	21.37	0.03	0.332	1.594	0.000	0.005
10	4,237	171	340	1320	188	0.28	76.11	21.27	0.04	0.237	0.380	0.000	0.005
11	4,620	180	357	>2,000	138	0.28	76.16	21.50	0.04	0.146	0.471	0.000	0.005

(1) Combined combustible gasses. Measured at surface with a Dräger Pac III instrument. Background 25 ppm

(2) Glycol – Likely to be picked up downhole from previous well treatment

(3) Citrate that was present in the brine could have been decomposed to bicarbonate and CO.

Table 4 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples that were recovered from Well B after 39 days' exposure to carbon steel casing at temperatures up to 225°C / 437°F. The amount of decomposition was estimated from the increase in carbonate / bicarbonate.

Sample #	Depth [m]	Temperature		Density @ 15.6	pH	Titration				
		[°C]	[°F]			Carb. [mol/L]	Bicarb. [mol/L]	Total [mol/L]	Change from original [mol/L]	Estimated Decomposition [%]
Original				2.150	10.88	0.24	0.04	0.29	0.00	0.0
1	1,586	<130	<266	2.139	10.53	0.20	0.07	0.27	-0.01	-0.1
2	1,900	<130	<266	2.141	10.55	0.20	0.06	0.26	-0.03	-0.3
3	2,250	<130	<266	2.143	10.60	0.22	0.06	0.28	-0.01	-0.1
4	2,564	<130	<266	2.143	10.53	0.22	0.06	0.27	-0.01	-0.1
5	2,885	<130	<266	2.144	10.62	0.23	0.05	0.28	0.00	0.0
6	3,195	134	273	2.142	10.63	0.22	0.05	0.28	-0.01	-0.1
7	3,529	148	298	2.144	10.63	0.23	0.06	0.29	0.00	0.0
8	3,839	160	320	2.138	10.59	0.22	0.06	0.28	0.00	0.0
10	4,496	185	365	2.144	10.40	0.23	0.09	0.32	0.04	0.4
11	5,198	222	432	2.148	9.98	0.23	0.22	0.45	0.16	1.7

Table 5 Composition of cesium formate brine samples recovered from Well B after 39 days' exposure to carbon steel casing at temperatures up to 225°C / 437°F.

Sample #	Depth [m]	Temperature		Ion analysis		NMR [wt%]					
		[°C]	[°F]	Acetate [mg/l]	Oxalate	Cesium formate	Water	Glycol ⁽¹⁾	Methanol	Citrate	Acetate
Original					0.15	81.81	17.32	0.87	0.00	0.00	0.006
1	1,586	<130	<266			81.37	17.76	0.87	0.00	0.00	0.004
2	1,900	<130	<266	980	0.14	81.63	17.97	0.78	0.00	0.00	0.008
3	2,250	<130	<266			81.26	17.87	0.86	0.00	0.00	0.005
4	2,564	<130	<266	1,910	0.13	81.62	17.50	0.87	0.00	0.00	0.005
5	2,885	<130	<266			81.64	17.50	0.86	0.00	0.00	0.006
6	3,195	134	273	1,470		81.36	17.78	0.86	0.00	0.00	0.006
7	3,529	148	298			81.50	17.63	0.86	0.00	0.00	0.006
8	3,839	160	320	1,600		79.98	18.56	0.77	0.00	0.00	0.005
10	4,496	185	365			80.64	17.67	0.76	0.00	0.00	0.006
11	5,198	222	432	1,180	0.32	80.73	17.56	0.71	0.00	0.00	0.008

(1) Glycol – Likely to be picked up downhole from previous well treatment

Table 6 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples that were recovered from Well B after 34 days' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The last two samples came from the deeper levels of the annulus, while samples 1 – 4 came from progressively deeper horizons within the work string.

Sample #	Depth [m]	Temperature		Density @ 15.6	pH	Titration				
		[°C]	[°F]			Carb. [mol/L]	Bicarb. [mol/L]	Total [mol/L]	Change from original [mol/L]	Estimated Decomposition [%]
0	Inside work-string	~225	~437	2.219	10.49	0.24	0.08	0.32	0.00	0.0
1				2.209	10.13	0.17	0.13	0.30	-0.10	-1.2
2				2.215	8.85	0.02	0.20	0.22	-0.33	-3.5
3				2.028	8.64	0.05	0.87	0.92	0.40	4.3
4	Bottom of annulus	~225	~437	2.221	9.01	0.09	0.69	0.78	0.31	3.3
5				2.209	8.91	0.08	0.80	0.88	0.40	4.3
6				2.223	9.98	0.16	0.17	0.33	-0.07	-0.8
7				2.225	9.75	0.16	0.26	0.42	0.02	0.2
8				2.220	10.15	0.18	0.13	0.31	-0.07	-0.8

Table 7 Composition of cesium formate brine samples that were recovered from Well B after 34 days' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The last two samples came from the deeper levels of the annulus, while samples 1 – 4 came from progressively deeper horizons within the work string.

Sample #	Depth [m]	Temperature		Ion analysis		NMR [wt%]					
		[°C]	[°F]	Acetate [mg/l]	Oxalate	Cesium formate	Water	Glycol ⁽¹⁾	Methanol	Citrate	Acetate
Original	Inside work-string	~225	~437	<0.10	0.33	82.92	15.83	0.69	0.00	0.00	0.03
1				82.77	16.57	0.62	0.00	0.00	0.04		
2				82.52	16.54	0.69	0.00	0.00	0.02		
3				0.32	0.15	74.74	24.64	0.59	0.00	0.00	0.02
4	Bottom of annulus	~225	~237	0.34	0.38	80.75	17.11	0.69	0.00	0.00	0.02
5				0.39	0.38	79.79	17.87	0.70	0.00	0.00	0.02
6				0.87	0.51	82.21	16.40	0.70	0.00	0.00	0.01
7				<0.10	0.41	82.75	16.53	0.71	0.00	0.00	0.01
8				83.08	16.22	0.69	0.00	0.00	0.01		

(1)Glycol – Likely to be picked up downhole from previous well treatment

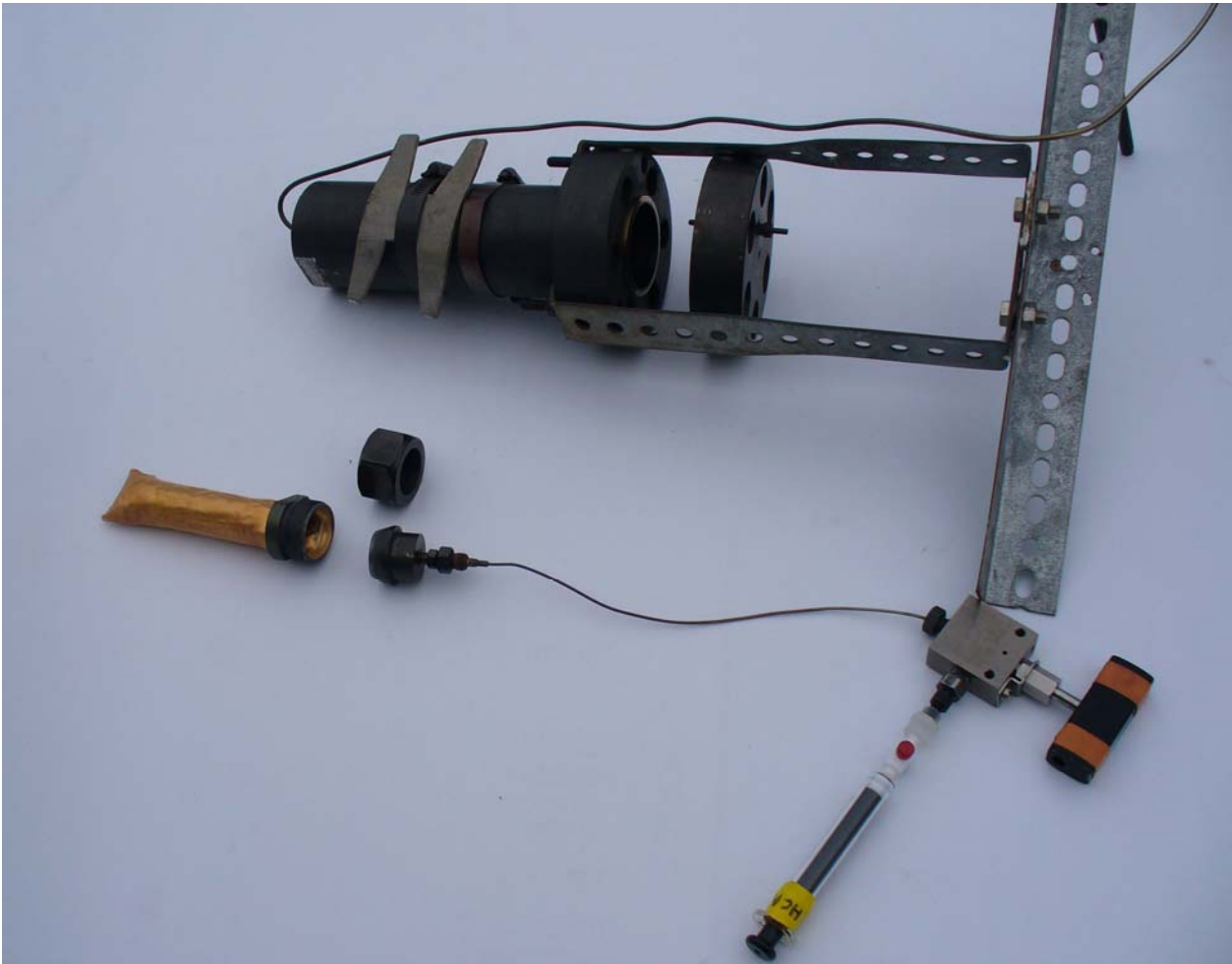
Figures

Figure 1 Gold test cell and holder used by Woods Hole Oceanographic Institution, USA for hydrothermal testing.