

CHEMICAL AND PHYSICAL PROPERTIES

SECTION A13

THERMAL STABILITY

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A13.1 Introduction

Formate brines were originally designed and developed for high-performance HPHT drilling and completion fluid applications (Downs, 1992; Downs, 1993; Howard, 1995) and have been deployed in hundreds of HPHT wells since 1996 (Downs et al., 2006). During this time they have been exposed for up to two years to well temperatures up to 225°C / 437°F without any substantial changes in composition or essential properties such as density, pH, etc.

Such resistance to thermal degradation or transformation under HPHT conditions is not intuitive, given that the technical literature contains several 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 some laboratory tests using HPHT autoclaves. In other words, it appears that most researchers are unable to simulate or reproduce the conditions experienced by formate brines in HPHT wells. This is perhaps not surprising given that HPHT wells are effectively long tubular hydrothermal reactors lined with a variety of catalytic surfaces.

In this section of the manual, the chemistry and dimensions of formate compositional changes observed in standard laboratory autoclaves are reviewed and compared with changes observed in formate fluids recovered from HPHT well construction operations. The variances in conditions and observed chemistry in these two different environments are explained. These explanations are supported by specialist testing conducted by scientists at the Woods Hole Oceanographic Institution in USA.

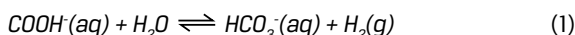
A13.2 Chemistry of formate brine at high temperature

The technical literature contains a number of reports on thermal decomposition of formate salts under laboratory conditions. The majority of these address decomposition of solid-phase, i.e. crystalline or powder, formate salts or formic acid (Baraldi; Barham and Clark, 1951; Canning and Hughes, 1973; Górski and Krasnica, 1987 a, b, c; Judd, Pope, and Wintrell, 1972; Meisel et al., 1975; Morando, Piacquadio, and Blesa, 1987; Muraishi et al., 1981; Patnaik and Maharana, 1981; Sinnarkar and Ray, 1975; Suoma et al.). Most experiments described in these papers are either carried out at very high temperatures or with a platinum catalyst. Results from these studies on

crystalline formates and formic acid show that the decomposition mechanism, products, and rates are all dependent on the atmosphere (air, O_2 , N_2 , H_2 , CO_2 , vacuum) in which the tests are conducted, the amount of water in the test sample, and the cation's nature. Results from these studies on solids, are not relevant to aqueous solutions of formates, i.e. formate brines.

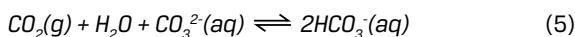
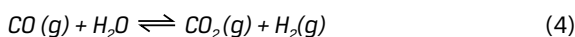
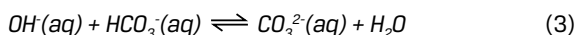
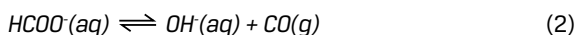
The thermal stability of aqueous solutions of formate is less extensively studied (Hill and Winterbottom, 1988). Most of the work completed on aqueous systems is on decomposition of low pH formic acid / formate solutions (Akiya and Savage, 1998; Hill and Winterbottom, 1988; research notes, 1992; Wakai et al., 2004), often with a palladium catalyst. These studies conclude that the compositional changes largely depend on the pH and the concentration of formic acid. These experiments were mainly carried out at pH values of less than 6.5. Buffered formate brines used in oilfield applications cannot drift to such low pH levels, even after a large influx of CO_2 . (See section A6 pH and buffering). Therefore, the results of these studies are also irrelevant to oilfield formate brines.

Thermal stability studies on formate brines with alkaline pH are even fewer in number (Maiella and Brill, 1998; McCollom and Seawald, 2003). All studies completed in aqueous formate solutions do, however, agree that the major reaction path in these fluids is the decarboxylation reaction that establishes equilibrium between formate and bicarbonate (**Equation 1**).



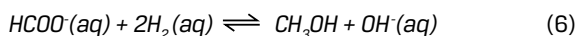
This reaction can lead to a small drop in pH.

A minor pathway that has been reported is the dehydration reaction (**Equation 2**). This is also an equilibrium reaction, but neither of the products can exist in buffered formate brines. They will react further to form carbonate and bicarbonate, according to **Equations 3 and 4**. Equation 4 is the water-gas shift reaction, which is an equilibrium that leans heavily towards the formation of CO_2 in the temperature range of interest (Twigg, 1989). CO_2 formed from the water-gas shift reaction instantly reacts with carbonate pH buffer to form bicarbonate (**Equation 5**).

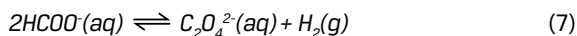


The net effect of dehydration equilibrium (Equation 2) and further conversion of products (Equations 3 to 5) is the conversion of a small amount of formate to carbonate, bicarbonate and hydrogen gas. A small increase in pH can be observed from these equilibria.

There are also some reduction reactions that may take place when formate brines are exposed to very high temperatures that can potentially form formaldehyde, methanol, methane, and solid carbon. The only one of these products that Cabot Specialty Fluids has observed in laboratory tests (up to 270°C) and field sampling is methanol, which has been seen in very small amounts. The reduction of formate to form methanol is shown in **Equation 6**.



Another minor equilibrium reaction mentioned in the literature is the reaction of formate and water to form hydrogen and oxalate according to the following equation (Górski and Krasnica, 1987c):



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 has only detected insignificant increases in oxalate levels in any brine samples returned from the field. More significant increases in oxalate levels have, however, been reported in laboratory tests run with a nitrogen gas cap (Javora et al., 2003). This can be considered an artifact of the inappropriate test configuration (see A13.3.1).

The above reactions can be catalyzed by certain metal surfaces. In chemistry and biology, catalysis is the acceleration 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 (Leth-Olsen, 2005).

The initial reaction rates of all of these equilibrium 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 compositional changes taking place under hydrothermal conditions typical of those found in the lower reaches of HPHT wells. McCollom and Seewald (2003) reported that at high temperatures and in the presence of certain catalysts, bicarbonate could be reduced to form formate. This proves that the dominant reaction (Equation 1) is likely to establish equilibrium in a downhole environment. Fu and Seyfried (2003) further strengthened this theory by showing that magnetite (common mill scale found on many oilfield tubulars) catalyzes reduction of CO_2 with hydrogen to create formate under hydrothermal conditions.

A13.3 Laboratory experience versus field experience

With regard to formate stability, it is clear that results obtained in typical laboratory autoclaves do not replicate real HPHT well conditions or reproduce the relatively minor compositional changes seen in formate fluids recovered from HPHT wells. This suggests that laboratory test conditions, in some way, do not accurately simulate or reproduce the real downhole environment. The obvious differences are:

- **Pressure:** Laboratory testing is typically conducted at low-pressure conditions, up to about 50 bars (5 Mpa / 725 psi). In HPHT wells, pressures up to about 200 MPa / 30,000 psi are experienced.
- **Presence of headspace:** HPHT laboratory autoclaves are usually run with a rather large gas-filled headspace (the gases are typically nitrogen, air, or CO_2). Any gas cap present in a well is proportionally much smaller and located at least several kilometers away from the fluid experiencing the highest temperatures. Any gas present in formate brine at the bottom of an HPHT well is either solubilized or highly compressed in small gas bubbles. A gas cap in a laboratory autoclave shifts the point of equilibrium and thereby increases the degree and duration of formate-to-bicarbonate conversion.
- **Catalytic surfaces:** As HPHT autoclaves are commonly made out of Hastalloy, a high-nickel alloy with catalytic properties, unrealistic proportions of high-nickel alloys are often present in laboratory experiments. In the field, high-nickel alloys are normally only used in small amounts in certain specialized downhole equipment, such as packers, liner hangers, etc.
- **Catalyst poisoning:** Tubing and casing material used in the field is often coated with corrosion products, such as magnetite (mill scale from the tubular production process). In HPHT laboratory experiments using Hastalloy autoclaves, this is usually not the case.

A13.3.1 Laboratory testing of formate brines 'Standard' oilfield testing

In past years, quite a number of experiments have been carried out in oilfield laboratories to try to establish the operating ceiling for formate brines (Benton et al., 2003; Javora et al., 2003; Lo Piccolo and Scoppio, 2003). These experiments have typically been carried out in Hastalloy autoclaves with a large gas cap (typically N_2 or CO_2) at relatively low pressures. Decomposition testing has often been combined with corrosion testing, which means that the autoclave is typically loaded with large amounts of catalytic material, such as martensitic, duplex, and austenitic stainless steel. A screening study performed by Hydro Corporate Research Centre (Leth-Olsen, 2005) showed that all of these materials could be catalysts for formate decomposition, unless passivated by some film that screens off the catalytic sites.

Very high initial reaction rates have typically been reported from these 'standard' tests. One explanation for this is obviously the presence of unrealistically large amounts of catalytic material, including the Hastalloy autoclave wall. Another problem with these tests is the large gas cap above the fluid. Such gas caps not only hinder reactions to reach equilibrium by letting gaseous reaction products escape into the gas phase, but can also alter kinetics of decomposition reactions as some reactions preferentially take place in the gas phase. The extent of some of the most frequently reported reactions not only depends on whether headspace exists or not, but also the type of gas contained there (Górski and Krasnica, 1987c).

In spite of the unfavorable configurations used in these simplified laboratory experiments, all reported testing has shown that reactions taking place appear to stop, i.e the headspace pressure stops rising, before more than 30% of the formate is converted to bicarbonate (typically within 30 to 60 days).

In 2004, Hydro Corporate Research Centre confirmed the equilibrium theory using a simple laboratory test (Leth-Olsen, 2004) where a high-pressure hydrogen gas cap was used to simulate a situation where equilibrium would have been established in the liquid phase. Although such a gas cap would never exist downhole, this experiment provided realistic partial pressure of hydrogen in the formate brine where the decarboxylation reaction (Equation 1) would have reached equilibrium. The experiments were run using buffered formate brines with an alkaline pH level, and buffered formate brines where the buffer had been overwhelmed with CO_2 . In both cases, high partial pressure of hydrogen in the reactor

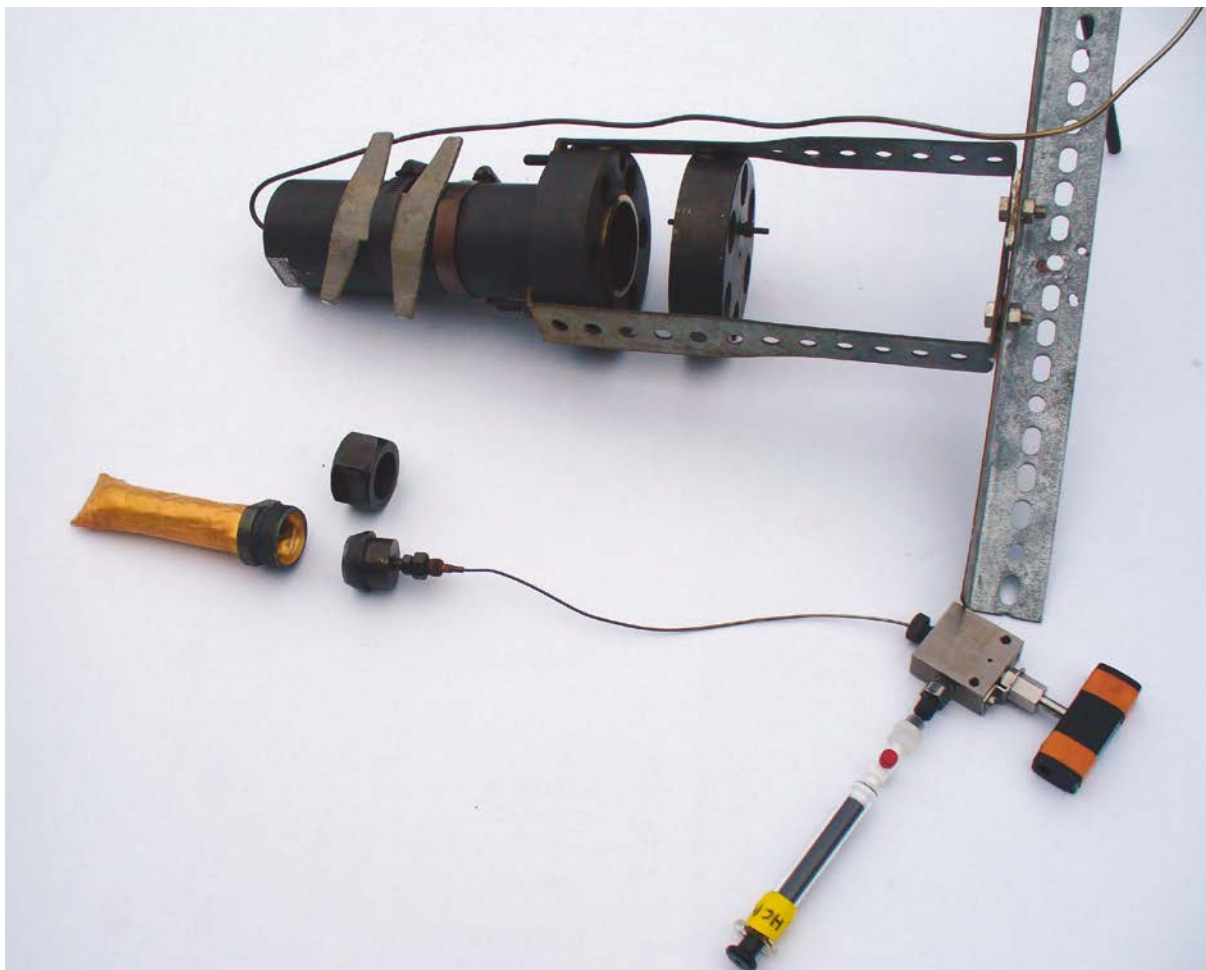


Figure 1 Gold test cell and holder used by Woods Hole Oceanographic Institution, USA for hydrothermal testing.

significantly increased the temperature threshold where decomposition of formate brine was initiated. For comparison, similar experiments with an identical pressure nitrogen gas cap resulted in significant conversion of formate to carbonate. Leth-Olsen's experiments prove that standard laboratory autoclaves are not suited for studying formate thermal stability.

'Specialized' testing by Woods Hole Oceanographic Institution

The test results from Hydro Corporate Research Centre motivated Cabot to search for a more realistic test environment, i.e. a high-pressure test environment with no headspace gases present to interfere with kinetics of the equilibrium reactions. Such a test environment was created at Woods Hole Oceanographic Institution in USA by Jeff Seewald, one of the world's leading experts on hydrothermal reactivity of organic acids (McCollom and Seawald, 2003). In this laboratory, the fluid is contained in a 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 flexibility of the gold pouch, experiments could be completed and sampled without a gas cap.

Experiments conducted with formate brines in this test cell have yielded very interesting results. These tests were conducted with and without catalytic material added to the test cell. The test program was designed to identify where formate decomposition equilibria would establish at 220°C / 428°F and 270°C / 518°F.

It is known (McCollom and Seawald, 2003) that the formate / bicarbonate equilibrium (Equation 1) is dependent on temperature. At higher temperatures more bicarbonate and hydrogen form, while at lower temperatures equilibrium leans towards a higher concentration of formate. Likewise, we know that equilibria involving solubilized gas depend on gas solubility 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 1) back towards a higher formate concentration at high pressure.

At Woods Hole, equilibria were obtained at two pressures of 34 MPa / 5,000 psi and 41 MPa / 6,000 psi. These pressures are high compared with standard oilfield laboratory testing, but low compared with pressures that can be found at the bottom of HPHT wells. The formate brine under test was buffered with around 17 kg/m³ / 6 lb/bbl potassium carbonate and 11 kg/m³ / 4 lb/bbl potassium bicarbonate. The amount of compositional changes measured in this brine at these two temperatures 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 more realistic downhole conditions (lower temperatures and / or significantly higher pressures) more formate is present at equilibrium and therefore less bicarbonate and hydrogen form.

Table 1 Amount of formate conversion taking place in a buffered cesium formate brine before equilibrium is established. Formate conversion is calculated from the decrease in formate concentration.

| Temperature | | Pressure | | Formate conversion [%] |
|-------------|------|----------|-------|------------------------|
| [°C] | [°F] | [MPa] | [psi] | |
| 220 | 428 | 35.2 | 5,100 | 8.2 |
| 270 | 518 | 34.5 | 5,000 | 15 |
| | | 41.4 | 6,000 | 13 |

These tests at Woods Hole demonstrate the importance of testing formate brines under realistic conditions. Even at the extreme temperature of 270°C / 518°F and relatively low pressure of 5,000 psi / 34 Mpa the equilibrium reactions reached equilibrium after a moderate amount of formate conversion to bicarbonate. In a standard laboratory test environment, presence of headspace would have prevented hydrogen, which forms from the initial decomposition, from playing the important role it does in this equilibrium, and conversion of formate to bicarbonate would have continued almost unrestricted.

The Woods Hole tests have also contributed to our understanding of how to formulate more stable formate brine systems for extreme temperature conditions. '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 a typical formate fluid. (See section A6 pH and Buffering).

A13.3.2 Field experience

Formate brines have been regularly used in HPHT applications since the 1990's in wells with downhole temperatures as high as 236°C / 457°F and pressures up to 96 MPa / 14,000 psi. During this time, there has been very little evidence of any compositional changes of formate fluids following exposure to hydrothermal conditions downhole. Examples of cesium formate brine use in HPHT well construction operations is shown in **Table 2**.

To achieve a better understanding of any minor chemical changes that can take place locally in formate fluids when exposed to hydrothermal conditions, extensive fluid sampling has been conducted during recovery of cesium formate brine from two different HPHT well suspensions.

Table 2 Typical HPHT field experience with Cabot formate brines.

| | | BP Rhum 3/29a | Shell Shear- water | Marathon Braemar | BP Devenick | Total Elgin/ Franklin | Statoil Huldra | Statoil Kvitbjørn |
|---------------------------|-------------------|---------------------------------------|--|-------------------------|---------------------|--|-----------------------------------|--|
| No. of wells | | 3 | 6 | 1 | 1 | 10 | 6 | 12 |
| Hydrocarbon | | Gas condensate | Gas condensate | Gas condensate | Gas condensate | Gas condensate | Gas condensate | Gas condensate |
| Max. temp (BHST) | °C | 149 | 182 | 135 | 146 | 204 | 149 | 155 |
| | °F | 300 | 360 | 275 | 295 | 400 | 300 | 311 |
| Tubing material | | S13Cr | 25Cr Duplex | 13Cr | 13Cr | 25Cr Duplex | S13Cr | S13Cr |
| Liner material | | S13Cr | 25Cr Duplex | 22Cr Duplex | VM110 | P110 | S13Cr | 13Cr |
| Packer material | | Alloy 718 | Alloy 718 | Alloy 718 | Alloy 718 | Alloy 718 | Alloy 718 | Alloy 718 |
| Brine density | g/cm ³ | 2.00 – 2.20 | 2.05 – 2.20 | 1.80 – 1.85 | 1.60 – 1.65 | 2.10 – 2.20 | 1.85 – 1.95 | 2.00 – 2.06 |
| Reservoir pressure | MPa | 84.8 | 105.6 | 74.4 | 72.4 | 115.3 | 67.5 | 81 |
| | psi | 12,300 | 15,320 | 10,800 | 10,500 | 16,720 | 9,790 | 11,700 |
| CO₂ | % | 5 | 3 | 6.5 | 3.5 | 4 | 4 | 2 – 3 |
| H₂S | ppm | 5 – 10 | 20 | 2.5 | 5 | 20 – 50 | 10 – 14 | Max. 10 |
| Exposure time | | 250 days | 65 days | 7 days | 90 days | 2 yrs | 45 days | 6 months 15 months |
| Application | | Perforation Completion Workover | Well kill CT Workover Perforation | Workover Perforation | Drill Completion | Workover Completion CT Well kill Perforation | Drilling Completion Screens | Drilling Completion Screens Liners Suspensions |

| | | Statoil Kristin | BP High Island A-5 | Devon West Cameron 165 A-7, A-8 | Devon West Cameron 575 A-3 | Walter O&G Mobile Bay 862 | TXM Hungary | Total Kessog |
|---------------------------|-------------------|-----------------------------------|-----------------------------------|--|-------------------------------------|-----------------------------------|----------------------------------|-----------------------|
| No. of wells | | 13 | 1 | 1 | 1 | 1 | 1 | 1 |
| Hydrocarbon | | Gas condensate | Gas | Gas condensate | Gas | Gas | Gas | Gas condensate |
| Max. temp (BHST) | °C | 171 | 163 | 149 | 135 | 216 | 235 | 170 |
| | °F | 340 | 325 | 300 | 275 | 420 | 455 | 305 |
| Tubing material | | S13Cr | S13Cr | 13Cr | 13Cr | G-3 | L80 | 25Cr Duplex |
| Liner material | | S13Cr | S13Cr | 13Cr | 13Cr | G-3 | P-110 | 25Cr Duplex |
| Packer material | | Alloy 718 | Alloy 718 | Alloy 718 | Alloy 718 | G-3 | 22Cr Duplex | Alloy 718 |
| Brine density | g/cm ³ | 2.09 – 2.13 | 2.11 | 1.03 | 1.14 | 2.11 1.49 packer | 2.15 | 2.14 |
| | MPa | 90 | 99 | 80 | 74 | 129 | 96 | 86 |
| Reservoir pressure | psi | 13,000 | 14,359 | 11,650 | 10,731 | 18,767 | 14,000 | 12,400 |
| | % | 3.5 | 5 | 3 | 3 | 10 | 30 | 6 |
| H₂S | ppm | 12 – 17 | 12 | 5 | 5 | 100 | 150 | 50 |
| Exposure time | | 57 days | 4 days 3 yrs packer | 2 yrs and 1.3 yrs | 1.4 yrs | 20 days 1.5 yrs packer | 38 days 35 days 9.5 months | 90 days |
| Application | | Drilling Completion Screens | Well kill Completion Packer | Packer | Packer | Well kill Completion Packer | Well test Suspensions | Extended well test |

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 g/cm³ / 18.2 lb/gal cesium formate brines (Brangetto et al., 2007). Initial reservoir pressures were around 115 MPa / 16,700 psi, and maximum BHST was between 190°C / 374°F and 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 Duplex. 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 were exposed to 2.18 g/cm³ / 18.2 lb/gal cesium formate brine for various durations. In the last well, Well A, cesium formate brine was left in the cased hole as a suspension fluid for two years.

The cesium formate brines that went into these wells were all buffered with a standard amount of carbonate / bicarbonate pH buffer.

When the brine was circulated out of Well A after two years (firstly from within the 25Cr Duplex production tubular, using CT, and later from the well annulus), samples were retrieved from various depths, and analyzed. Results from inside the tubing are shown in **Tables 3 and 4**. The analyzes 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 combined carbonate / bicarbonate in the brine could be used as an indicator of any conversion of formate to bicarbonate.

The formate brine sample recovered from the deepest section of Well A inside the 25Cr Duplex production tubular at 5,000 meters contained combined carbonate / bicarbonate levels that were 0.83 moles per liter higher than in the original brine before it was run in the hole (Table 3). This corresponds to decomposition of about 8% of the formate brine in the sample taken at the bottom of the well.

NMR analyzes show that formate concentration has dropped towards the bottom of the well. The drop in formate concentration corresponds to about 4% formate conversion. Test results from Woods Hole (see A13.3.1) suggest that the compositional changes in the formate brine in Well A had reached equilibrium and that no further changes in chemical composition had taken place 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 3). Unfortunately, there was no instrument available at the rig site that could measure hydrogen gas concentration alone.

Small amounts of methanol and acetate were measured in the retrieved formate brine samples. The methanol is likely to have originated from the formate reduction equilibrium (Equation 6). Although from analyzes of samples taken from Well A it may appear that there is more acetate in the warmest part of the well, there is no evidence from literature, laboratory testing, or other field sample analyzes that acetate is formed downhole. A very low level of citrate was present in the top part of the well. It is uncertain how this was introduced. Citrate forms similar products to formate when exposed to hydrothermal conditions. As measured oxalate levels do not increase with temperature (depth), there is no evidence of formate reacting to form oxalate in this well. A low level of oxalate exists in formate brine after exposure to daylight during storage.

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

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

Table 3 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples recovered from within the 25Cr Duplex production tubular of Well A after two years' exposure to hydrothermal conditions. The amount of formate conversion was estimated from the increase in carbonate / bicarbonate levels.

| Sample # | Depth [m] | Temperature | | Density at 15.6 [g/cm ³] | pH | Titration | | | | |
|----------|-----------|-------------|------|--------------------------------------|-------|---------------|-----------------|---------------|------------------------------|----------------------------------|
| | | [°C] | [°F] | | | Carb. [mol/L] | Bicarb. [mol/L] | Total [mol/L] | Change from original [mol/L] | Estimated formate conversion [%] |
| 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 | 290 | 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 4 Composition of cesium formate brine samples recovered from within the 25Cr Duplex production tubular of Well A after two years' exposure to hydrothermal conditions. The amount of formate conversion is estimated from the decrease in cesium formate concentration.

| Sample # | Depth [m] | Temperature | | Gas ¹⁾ [ppm] | Ion analysis | | | NMR [wt%] | | | | | Estimated formate conversion [%] |
|----------|-----------|-------------|------|-------------------------|---------------------------------|-----------------|----------------|-----------|---------|----------|-----------------------|---------|----------------------------------|
| | | [°C] | [°F] | | Acetate (as acetic acid) [mg/L] | Oxalate [% v/v] | Cesium formate | Water | Unknown | Methanol | Citrate ²⁾ | Acetate | |
| Orig. | - | - | - | - | 1,346 | 0.08 | 79.4 | 20.6 | 0.00 | 0.00 | 0.000 | 0.002 | 0.0 |
| 1 | 0 | 5 | 41 | 125 | 837 | 0.19 | 78.6 | 21.0 | 0.00 | 0.00 | 0.005 | 0.002 | 1.1 |
| 2 | 1,554 | 65 | 148 | 165 | 1,288 | - | 78.4 | 21.0 | 0.00 | 0.00 | 0.005 | 0.002 | 1.3 |
| 3 | 1,937 | 80 | 177 | 205 | 1,239 | 0.25 | 78.1 | 21.3 | 0.00 | 0.00 | 0.003 | 0.002 | 1.6 |
| 4 | 2,320 | 96 | 205 | 580 | 1,666 | 0.19 | 78.5 | 20.8 | 0.00 | 0.00 | 0.006 | 0.002 | 1.2 |
| 5 | 2,704 | 112 | 233 | 225 | 598 | 0.16 | 78.4 | 20.7 | 0.00 | 0.01 | 0.000 | 0.002 | 1.3 |
| 6 | 3,087 | 128 | 261 | 325 | 1,007 | 0.07 | 78.4 | 20.6 | 0.00 | 0.04 | 0.000 | 0.003 | 1.3 |
| 7 | 3,470 | 143 | 290 | 490 | 1,298 | 0.07 | 77.7 | 20.6 | 0.03 | 0.14 | 0.000 | 0.004 | 2.1 |
| 8 | 3,854 | 153 | 307 | 1,240 | 703 | 0.06 | 76.0 | 21.3 | 0.10 | 0.57 | 0.000 | 0.005 | 4.3 |
| 9 | 4,237 | 162 | 324 | 1,590 | 1,000 | 0.04 | 75.8 | 21.4 | 0.14 | 0.59 | 0.000 | 0.005 | 4.5 |
| 10 | 4,620 | 171 | 340 | 1,320 | 183 | - | 76.1 | 21.3 | 0.10 | 0.38 | 0.000 | 0.005 | 4.2 |
| 11 | 5,000 | 180 | 357 | >2,000 | 138 | 0.28 | 76.2 | 21.5 | 0.15 | 0.47 | 0.000 | 0.005 | 4.1 |

1) Combined combustible gases. Measured at surface with a Dräger Pac III Instrument. Background 25 ppm.

2) Citrate that was present in the brine could have decomposed at the highest temperatures.

Well B

An operator used 2.145 g/cm³ / 17.88 lb/gal cesium formate brine as well control fluid during 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 total depth of over 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 three 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 38 days, 35 days, and almost ten months.

Well B – suspension 1

In April 2007, Well B was killed with 60 m³ / 377 bbl of 2.145 g/cm³ / 17.88 lb/gal cesium formate brine by bullheading the frac fluid (calcium chloride brine) and spacer fluid (potassium formate brine) into the fractures and formation. After a 38-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 and analyzed to assess their physical and chemical condition after exposure to extreme HPHT conditions.

The cesium formate brine used in this well was buffered with a standard amount of carbonate / bicarbonate buffer. The bottom of the column of cesium formate brine was at a depth of 5,300 m / 17,390 ft with local temperature of 225°C / 437°F.

It should be noted that when the well was bullheaded at the start of operations it contained *CaCl*₂ brine and 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. *CaCl*₂ and potassium formate could have co-mingled with the heavier cesium formate brine.

Additionally, during running of 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 with the remainder going to the formation / fracture. 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 depth is therefore impossible, but bulk condition and trends in fluid properties should be observable. Properties and composition of the brine samples recovered are listed in **Tables 5 and 6**.

As can be seen from the brine sample properties in Table 5, only the two deepest samples showed any signs of increased bicarbonate levels. The more affected of the two samples, taken from the deepest part of the well, had only suffered about 1.3% to 1.7% formate conversion after more than a month of exposure. 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 positive readings were detected on a *CO*-detector when the brine was circulated out. A subsequent investigation of *CO*-detectors on a different well has shown that these instruments are not capable of differentiating between *CO* and *H*₂. What was reported as *CO* gas was in reality *H*₂ gas. This is also likely to have been the case as detectable levels of *CO* cannot exist in buffered formate brines, due to the water-gas shift reaction (Equation 4).

A very small increase in oxalate level was observed in the lowest sample, which could have originated from formate conversion (Equation 7).

Table 5 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples recovered from Well B after 38 days' exposure to carbon steel casing at temperatures up to 225°C / 437°F. The amount of formate conversion was estimated from the increase in carbonate / bicarbonate levels.

| Sample # | Depth [m] | Temperature | | Density [g/cm ³] | pH | Titrations | | | | |
|-----------------|-----------|-------------|------|------------------------------|-------|---------------|-----------------|---------------|------------------------------|----------------------------------|
| | | [°C] | [°F] | | | Carb. [mol/L] | Bicarb. [mol/L] | Total [mol/L] | Change from original [mol/L] | Estimated formate conversion [%] |
| 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 | -0.1 |
| 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 ¹⁾ | 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 |

1) Sample 8 appears to have been exposed to a slight water influx.

Table 6 Composition of cesium formate brine samples recovered from Well B after 38 days' exposure to carbon steel casing at temperatures up to 225°C / 437°F. The amount of formate conversion was estimated from the decrease in cesium formate concentration.

| Sample # | Depth [m] | Temperature | | Ion analysis | | NMR [wt%] | | | | | Estimated formate conversion [%] |
|-----------------|-----------|-------------|------|---------------------------------|----------------|----------------|-------|----------|---------|---------|----------------------------------|
| | | [°C] | [°F] | Acetate (as acetic acid) [mg/L] | Oxalate [mg/L] | Cesium formate | Water | Methanol | Citrate | Acetate | |
| Original | - | - | - | - | 0.0015 | 81.8 | 17.3 | 0.00 | 0.00 | 0.006 | 0.0 |
| 1 | 1,586 | <130 | <266 | - | - | 81.4 | 17.8 | 0.00 | 0.00 | 0.004 | 0.5 |
| 2 | 1,900 | <130 | <266 | 980 | 0.0014 | 81.6 | 18.0 | 0.00 | 0.00 | 0.008 | 0.2 |
| 3 | 2,250 | <130 | <266 | - | - | 81.3 | 17.9 | 0.00 | 0.00 | 0.005 | 0.7 |
| 4 | 2,564 | <130 | <266 | 1,910 | 0.0013 | 81.6 | 17.5 | 0.00 | 0.00 | 0.005 | 0.2 |
| 5 | 2,885 | <130 | <266 | - | - | 81.6 | 17.5 | 0.00 | 0.00 | 0.006 | 0.2 |
| 6 | 3,195 | 134 | 273 | 1,470 | - | 81.4 | 17.8 | 0.00 | 0.00 | 0.006 | 0.6 |
| 7 | 3,529 | 148 | 298 | - | - | 81.5 | 17.6 | 0.00 | 0.00 | 0.006 | 0.4 |
| 8 ¹⁾ | 3,839 | 160 | 320 | 1,600 | - | 80.0 | 18.6 | 0.00 | 0.00 | 0.005 | - |
| 10 | 4,496 | 185 | 365 | - | - | 80.6 | 17.7 | 0.00 | 0.00 | 0.006 | 1.4 |
| 11 | 4,496 | 222 | 432 | 1,180 | 0.0032 | 80.7 | 17.6 | 0.00 | 0.00 | 0.008 | 1.3 |

1) Sample 8 appears to have been exposed to a slight water influx.

Well B – suspension 2

In June 2007, Well B was killed again with cesium formate brine following completion of the well test. After a 35-day suspension the brine was displaced to fresh cesium formate brine following the appearance of low levels of H_2S gas at the wellhead. This gave Cabot 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.

On this occasion, the cesium formate brine that went into Well B was the same brine used in suspension 1. Therefore, the fluid had a slightly increased bicarbonate level compared to the brine that was first sent out.

This batch contained nine samples. 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 to 4 came from progressively deeper horizons within the work string. Properties and composition of the brine samples recovered are listed in **Tables 7 and 8**. Both the annular and tubular samples were exposed to CO_2 and H_2S . The fact that the brine was exposed to CO_2 makes it difficult to use the bicarbonate level increase to calculate the degree of compositional changes.

As CO_2 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. This is shown in the last two columns of Table 7. There is some uncertainty in these calculations, as there seems to have been some dilution, possibly due to influx of reservoir fluids.

Table 8 also shows results of other chemical analyzes 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 oxalate levels in brines exposed to the highest temperatures are no greater.

Based on the analyzes completed on the samples from this well exposure, it is difficult to estimate the amount of formate conversion. However, there is no indication from the analyzes that any significant amount of

decomposition has taken place. There is also no increase in the concentrations of methanol or acetate, which indicates that it is unlikely that any significant formate decomposition took place from dehydration (Equation 2).

The retrieved brine was in good condition and fit for further duty.

Well B – suspension 3

After the second well suspension, the well was again left with cesium formate brine, this time for almost ten months. This provided a third opportunity for Cabot to sample and analyze the cesium formate brine that had been left in this very hot well for a very long time. During this suspension it became apparent that there was a leak in the packer and reservoir fluids had entered the brine. As no risk could be taken that the carbonate buffer in the bottom of the well would be overwhelmed and H_2S exposed to the C-steel casing in the top of the well during circulation, the fluid was reverse circulated out. A total of 16 samples were taken from different locations in the well and analyzed. The results of the analyzes are shown in **Tables 9 and 10**. As can be seen, two of the samples (7 and 8) had been contaminated with an influx of reservoir fluids, which means that these samples could not be used to determine the amount of formate conversion. The two deepest samples from the well seemed to be in good condition, and formate conversion levels of these were estimated at up to 5.7%. However, this is difficult to estimate as bicarbonate levels had also increased from CO_2 influxes. The analyzes show glycol in most of the samples. This is believed to be a contaminate as there is no evidence from literature or laboratory testing that formate can be converted to glycol. If it was a decomposition product, a concentration gradient would exist from the top to the bottom of the well. Increasing levels of oxalate were detected in the bottom of the well, but only in insignificant amounts. The low levels of acetate detected are not believed to be products from any formate reactions. In spite of the very high CO_2 and H_2S levels in the reservoir gas, the buffer was not overwhelmed in any part of the well, which confirms the power of this unique pH buffer.

Table 7 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples recovered from Well B after 35-days' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The last four samples came from the deeper levels of the annulus, while samples 1 to 4 came from progressively deeper horizons within the work string. The amount of formate conversion was estimated from the increase in carbonate / bicarbonate levels.

| Sample # | Depth [m] | Temperature | | Density @ 15.6 g/cm ³ | pH | Titrations | | | | |
|-----------------|--------------------|-------------|-------|----------------------------------|-------|---------------|-----------------|---------------|------------------------------|----------------------------------|
| | | [°C] | [°F] | | | Carb. [mol/L] | Bicarb. [mol/L] | Total [mol/L] | Change from original [mol/L] | Estimated formate conversion [%] |
| 0 | - | - | - | 2.219 | 10.49 | 0.24 | 0.08 | 0.32 | 0.00 | 0.0 |
| 1 | Inside work-string | - | - | 2.209 | 10.13 | 0.17 | 0.13 | 0.30 | -0.10 | -1.1 |
| 2 | | - | - | 2.215 | 8.85 | 0.02 | 0.20 | 0.22 | -0.33 | -3.5 |
| 3 ¹⁾ | | - | - | 2.028 | 8.64 | 0.05 | 0.87 | 0.92 | 0.40 | 4.3 |
| 4 | | ~ 225 | ~ 437 | 2.221 | 9.01 | 0.09 | 0.69 | 0.78 | 0.31 | 3.3 |
| 5 | Bottom of annulus | ~225 | ~437 | 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 |

1) Sample 3 appears to have been exposed to a water influx.

Table 8 Composition of cesium formate brine samples recovered from Well B after 35-days' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The last four samples came from the deeper levels of the annulus, while samples 1 to 4 came from progressively deeper horizons within the work string.

| Sample # | Depth [m] | Temperature | | Ion analysis | | NMR [wt%] | | | | |
|-----------------|--------------------|-------------|-------|---------------------------------|----------------|----------------|-------|----------|---------|---------|
| | | [°C] | [°F] | Acetate (as acetic acid) [mg/L] | Oxalate [mg/L] | Cesium formate | Water | Methanol | Citrate | Acetate |
| 0 | - | - | - | <0.10 | 0.0033 | 82.9 | 15.8 | 0.00 | 0.00 | 0.03 |
| 1 | Inside work-string | - | - | - | - | 82.8 | 16.6 | 0.00 | 0.00 | 0.04 |
| 2 | | - | - | - | - | 82.5 | 16.5 | 0.00 | 0.00 | 0.02 |
| 3 ¹⁾ | | - | - | 0.32 | 0.0015 | 74.7 | 24.6 | 0.00 | 0.00 | 0.02 |
| 4 | | ~ 225 | ~ 437 | 0.34 | 0.0038 | 80.8 | 17.1 | 0.00 | 0.00 | 0.02 |
| 5 | Bottom of annulus | ~ 225 | ~ 437 | 0.39 | 0.0038 | 79.8 | 17.9 | 0.00 | 0.00 | 0.02 |
| 6 | | - | - | 0.87 | 0.0051 | 82.2 | 16.4 | 0.00 | 0.00 | 0.01 |
| 7 | | - | - | <0.10 | 0.0041 | 82.8 | 16.5 | 0.00 | 0.00 | 0.01 |
| 8 | | - | - | - | - | 83.1 | 16.2 | 0.00 | 0.00 | 0.01 |

1) Sample 3 appears to have been exposed to a water influx.

Table 9 Properties and carbonate / bicarbonate concentrations of cesium formate brine samples recovered from Well B after almost ten months' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The fluid was present all the way to the bottom of the well. However, due to the well configuration, fluid at the very bottom was not circulated out. Samples 9 and 10 came from the deepest portion that was sampled.

| Sample | Depth [m] | Temperature | | Density [g/cm ³] | pH | Titrations | | | | Estimated formate conversion ²⁾ [%] |
|-----------------|-----------|-------------|------|------------------------------|-------|---------------|-----------------|---------------|---------------------------------|--|
| | | [°C] | [°F] | | | Carb. [mol/L] | Bicarb. [mol/L] | Total [mol/L] | Change from top of well [mol/L] | |
| 1 | 207 | 23 | 73 | 2.204 | 9.98 | 0.158 | 0.127 | 0.285 | 0.000 | 0.0 |
| 2 | 828 | 35 | 95 | 2.216 | 10.00 | 0.165 | 0.127 | 0.292 | 0.007 | 0.1 |
| 3 | 1,449 | 65 | 149 | 2.216 | 10.01 | 0.160 | 0.120 | 0.280 | -0.005 | 0.0 |
| 4 | 1,863 | 81 | 178 | 2.217 | 10.02 | 0.172 | 0.126 | 0.298 | 0.013 | 0.1 |
| 5 | 2,318 | 99 | 210 | 2.210 | 9.81 | 0.172 | 0.200 | 0.372 | 0.088 | 0.8 |
| 6 | 2,932 | 123 | 253 | 2.233 | 9.56 | 0.185 | 0.373 | 0.558 | 0.273 | 2.4 |
| 7 ¹⁾ | 4,160 | 171 | 339 | 2.114 | 9.21 | 0.206 | 0.893 | 1.099 | 0.814 | - |
| 8 ¹⁾ | 4,467 | 183 | 361 | 2.120 | 8.89 | 0.098 | 0.859 | 0.957 | 0.672 | - |
| 9 | 4,941 | 201 | 394 | 2.235 | 9.39 | 0.240 | 0.703 | 0.943 | 0.658 | 5.7 |
| 10 | 4,826 | 197 | 386 | 2.220 | 9.36 | 0.222 | 0.694 | 0.916 | 0.631 | 5.4 |
| 11 | 4,711 | 192 | 378 | 2.241 | 9.35 | 0.209 | 0.667 | 0.876 | 0.591 | 5.1 |
| 12 | 4,596 | 188 | 370 | 2.243 | 9.34 | 0.196 | 0.640 | 0.836 | 0.551 | 4.8 |
| 13 | 4,021 | 165 | 330 | 2.232 | 9.55 | 0.170 | 0.350 | 0.519 | 0.234 | 2.0 |
| 14 | 3,446 | 143 | 289 | 2.226 | 9.7 | 0.158 | 0.234 | 0.391 | 0.107 | 0.9 |
| 15 | 2,814 | 118 | 245 | 2.223 | 9.79 | 0.156 | 0.190 | 0.346 | 0.061 | 0.5 |
| 16 | 1,806 | 79 | 174 | 2.208 | 9.62 | 0.137 | 0.243 | 0.380 | 0.095 | 0.8 |

1) Samples 7 and 8 appear to have been heavily contaminated by influx of water and CO₂.

2) The degree of decomposition is difficult to estimate due to the large amount of reservoir fluids that entered the well.

Table 10 Composition of cesium formate brine samples recovered from Well B after almost ten months' exposure to carbon steel casing and a low-alloy steel work string at temperatures up to 225°C / 437°F. The fluid was present all the way to the bottom of the well. However, due to the well configuration, fluid at the very bottom was not circulated out. Samples 9 and 10 came from the deepest portion of the well.

| Sample | Depth [m] | Temperature | | Ion analysis (oxalate) [mg/L] | NMR [wt%] | | | |
|-----------------|-----------|-------------|------|-------------------------------|-----------|----------------|--------|---------|
| | | [°C] | [°F] | | Water | Cesium formate | Glycol | Acetate |
| 1 | 207 | 23 | 73 | <0.0001 | 16.7 | 83.3 | 0.0 | 0.00 |
| 2 | 828 | 35 | 95 | <0.0001 | 15.6 | 83.7 | 0.7 | 0.02 |
| 3 | 1,449 | 65 | 149 | <0.0001 | 15.5 | 83.5 | 1.0 | 0.03 |
| 4 | 1,863 | 81 | 178 | <0.0001 | 15.3 | 84.2 | 0.6 | 0.03 |
| 5 | 2,318 | 99 | 210 | <0.0001 | 15.4 | 83.9 | 0.6 | 0.04 |
| 6 | 2,932 | 123 | 253 | <0.0001 | 15.6 | 83.7 | 0.7 | 0.03 |
| 7 ¹⁾ | 4,160 | 171 | 339 | 0.0023 | 22.7 | 77.0 | 0.3 | 0.06 |
| 8 ¹⁾ | 4,467 | 183 | 361 | 0.0031 | 22.4 | 77.1 | 0.4 | 0.05 |
| 9 | 4,941 | 201 | 394 | 0.0009 | 17.6 | 81.9 | 0.6 | 0.01 |
| 10 | 4,826 | 197 | 386 | <0.0001 | 16.8 | 82.5 | 0.7 | 0.04 |
| 11 | 4,711 | 192 | 378 | <0.0001 | 16.6 | 82.7 | 0.6 | 0.04 |
| 12 | 4,596 | 188 | 370 | <0.0001 | 16.4 | 82.9 | 0.7 | 0.03 |
| 13 | 4,021 | 165 | 330 | <0.0001 | 16.1 | 83.1 | 0.7 | 0.03 |
| 14 | 3,446 | 143 | 289 | <0.0001 | 16.0 | 83.3 | 0.7 | 0.02 |
| 15 | 2,814 | 118 | 245 | <0.0001 | 16.1 | 83.1 | 0.8 | 0.03 |
| 16 | 1,806 | 79 | 174 | <0.0001 | 16.5 | 82.8 | 0.8 | 0.02 |

1) Samples 7 and 8 appear to have been heavily contaminated by influx of water and CO₂.

A13.4 Conclusions and recommendations

Deep oil and gas wells are, in essence, HPHT tubular reactors lined with catalytic surfaces. As such, they make an excellent environment for creating hydrothermal chemical reactions. There is evidence from both the laboratory and the field that formate can undergo some slight compositional changes at high temperature.

To what extent formate brines actually undergo any degree of compositional changes when exposed to realistic downhole conditions is dependent on temperature, pressure, pH, presence of catalytic surfaces, and brine composition. Based on results from laboratory testing and field experience, the following is concluded:

- It is only rarely and then only under the most demanding conditions that any discernible changes are detected in buffered formate brines after field use. In the exceptional cases of Well A (high temperature, very long duration) and Well B (extreme temperature, long duration) it was possible to detect low levels of formate compositional changes over time, but these had no obvious adverse effect on the brine properties.
- Research by Woods Hole Oceanographic Institution, USA has demonstrated that a) chemical reactions taking place in formate brines, studied under realistic hydrothermal conditions in special laboratory test cells, eventually reach equilibrium, b) this equilibrium point is reached only after minor levels of compositional changes and, c) conventional laboratory autoclaves and reactors, as currently used by the oil industry, are incapable of simulating true downhole conditions, and cannot predict what might or might not happen to formate brines in real HPHT well construction operations.

Although the exact mechanisms of the observed compositional changes in formate brine might still not be fully understood, all field and laboratory observations indicate that a small portion of formate is converted to carbonate and bicarbonate. Considering that cesium carbonate and cesium bicarbonate are brines with the same density as cesium formate brine, one can understand why no significant changes in brine density have been observed in the laboratory or in the field.

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