CHEMICAL AND PHYSICAL PROPERTIES

SECTION A5
CRYSTALLIZATION TEMPERATURE

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VERSION 5 – 06/15

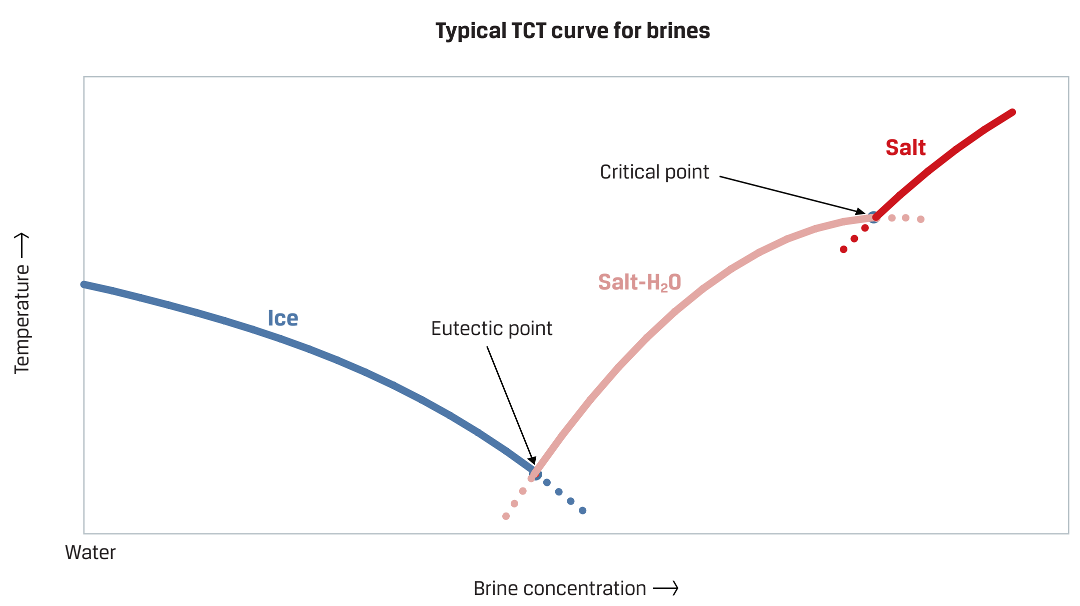


Figure 1 Typical TCT curve or phase diagram for brine, consisting of three phase-equilibrium lines, a eutectic point and a critical point. The phase-equilibrium lines represent conditions where different solid crystals exist in equilibrium with the brine. The eutectic point represents the brine composition (concentration) with the lowest TCT, and the critical point shows where phase-equilibrium lines of the two different salt structures join.

A5.1 Introduction

Crystallization temperature is an important property of well construction and intervention fluids used in cold weather conditions and / or under high pressure. True crystallization temperature (TCT) is one of the properties used to define the performance ceiling of oilfield brines and fluids.

Since formate brines were introduced in the oilfield in the 1990's, test laboratories have struggled to determine their True Crystallization Temperature (TCT). Standard API procedure for measuring TCT in halide brines simply does not work in some formate brines. Formate brines – especially potassium and cesium formate brines and their blends – behave very differently from halide brines due to strong kinetic effects that complicate TCT measurements. Factors that complicate TCT measurements in formate brines are a) TCT values can be very low, and may be lower than the cooling capability of the measuring equipment, b) an enormous amount of supercooling, and c) existence of metastable potassium formate crystals that form in potassium-rich formate brines. For concentrated potassium formate brine, for example, TCT data in literature vary from -18 to +7°C / -4 to +45°F. It is not uncommon to observe TCTs in formate brines reported as "too low to measure", even in cases where TCT is reportedly or reputedly well within measurable limits of the equipment.

Thanks to the same kinetic effects, formate brines are ideal fluids for use and storage at low temperatures because they can be cooled to temperatures significantly lower than their official TCT without crystallizing.

A5.2 Typical crystallization behavior in brines

A typical TCT curve for a brine system is shown in Figure 1. This is a phase diagram consisting of three phase-equilibrium lines, a eutectic point, and a critical point. To the very left on the curve is pure water with density of 0.999 g/cm^3 / 8.338 lb/gal and a crystallization (freezing) point of 0°C / 32°F. The phase equilibrium line to the left (in blue) represents the brine's freezing point. At conditions along this line, ice crystals are in equilibrium with the brine. The eutectic point represents the brine composition (concentration) with the lowest possible TCT. The center equilibrium line marked 'Salt·H_2O' in light red represents the concentration range of brine where a hydrated version of the salt crystallizes. Along this equilibrium line, hydrated salt crystals exist in equilibrium with the brine. The right equilibrium line (shown in dark red) represents the concentration range

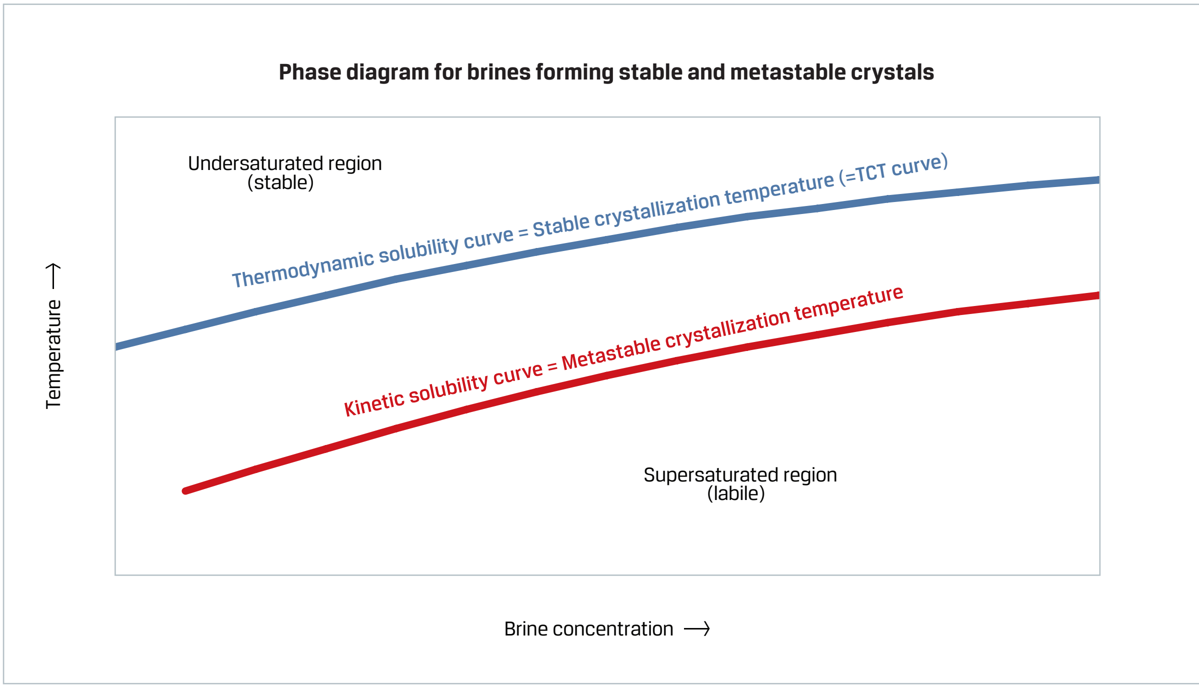


Figure 2 Phase diagram for brine that forms both stable and metastable crystals. Along the upper solubility curve stable crystals are in equilibrium with the brine, while along the lower solubility curve metastable crystals are in equilibrium with the brine.

where dry salt crystals precipitate from the brine. Along this equilibrium line, dry salt exists in equilibrium with the brine. This right portion of the plot doesn't exist for all brines or exists at temperatures so high that it is impractical to measure. This is the case for cesium formate brine.

Due to kinetic effects it is possible for crystal-free brines to exist below the phase-equilibrium (saturation) lines in Figure 1. This is because of a phenomenon called supercooling. When brine is cooled below its actual crystallization temperature, crystals may not form spontaneously due to lack of nucleation sites.

A5.3 TCT behavior in formate brines

The simple TCT curve shown in Figure 1 seems to be representative of the majority of brines used in well construction applications. However at least one exception to this is potassium formate brine, where a different type of crystal can form. This is a metastable crystal, i.e. a crystal that is not in its state of least energy. These metastable crystals form along a lower phase-equilibrium line as illustrated in Figure 2. For potassium formate, the crystallization temperature for these metastable crystals is significantly lower than TCT (about 20°C / 36°F). A stable-phase crystal cannot form spontaneously in this brine. However, metastable crystals can convert to stable crystals under favorable conditions.

Existence of metastable crystals in potassium formate brine gives an additional safety margin during field use and storage as the stable crystal with highest crystallization temperature cannot form before the metastable crystal has formed at a much lower temperature. However, this phenomenon means that measuring TCT in the laboratory is more complicated as there are two crystallization curves to consider. The complications are indeed so great that the standard API-recommended method for measuring TCT no longer works.

Formate brines – especially cesium – have also been shown to have enormous potential for supercooling. Addition of particles of certain nucleation materials such as barium oxide, barium hydroxide, calcium carbonate, and bentonite are usually effective in minimizing supercooling in traditional halide oilfield brines. However, these nucleation particles do not seem to have much effect on crystallization in formate brines. Supercooling up to 50°C / 90°F has been measured in cesium formate brine.

A5.4 TCT curves for formate brines

The three formate brines that are commonly used for well construction – sodium, potassium, and cesium formate – exhibit very different TCT behavior (Figure 3). Figure 4 to Figure 6 and Table 1 to Table 3 show the TCT curves for these three single-salt brines as measured with the sophisticated measuring technique described in A5.5. The figures also show some measured points representing supercooling. This is the temperature where the brine has been held successfully for at least two weeks in a freezer with and without traditional seeding material and other particles (barite, bentonite, rust, dust, etc.) without crystallizing.

A5.4.1 TCT in single-salt sodium formate brine

Sodium formate behaves just like the salt in Figure 1. Its TCT curve has one critical point, where hydrated and dry salt are in equilibrium. The measured TCT curve of high-purity grade sodium formate single-salt brine is presented in Figure 4 and Table 1.

The figure also shows the extent of supercooling that typically takes place in sodium formate brine. The measured supercooling points shown in Figure 4 represent the temperature where the brine has been successfully kept for at least two weeks with common nucleation material such as bentonite, rust, and dust. The second set of supercooling points represents the temperature where the brine has been successfully kept for at least two weeks without any seeding material. The data represent a mixture of measurements completed by Shell [1], [2] and newer measurements taken by Cabot.

A5.4.2 TCT in single-salt potassium formate brine

Measured TCT curves for field-grade potassium formate single-salt brine are presented in Figure 5 and Table 2. All test results were obtained using the measuring technique described in this section [3]. Potassium formate also behaves like the salt in Figure 1 as both a eutectic and a critical point exist. However, experimental testing on pure potassium formate brine has shown that potassium formate can form metastable crystals. The two different potassium formate crystals are:

- A metastable crystal that in typical stock potassium formate brine (1.57 g/cm^3 / 13.1 lb/gal) gives low crystallization temperature of around –10°C / 12°F and is normally formed after a certain degree of supersaturation (supercooling) has been reached.
- A thermodynamically stable phase, which in typical stock brine (1.57 g/cm^3 / 13.1 lb/gal) gives a rather high TCT of around 7°C / 19°F and is formed from the metastable phase after some time in equilibrium with the brine.

The higher crystallization temperature, i.e. the one from the stable phase, is the thermodynamically correct definition of TCT for the brine. The metastable-phase crystallization temperature, on the other hand, is often more useful to oilfield engineers as it better corresponds with behavior of formate brine in the field and in storage. It is interesting to note that if a metastable crystal formed on or below the metastable phase-equilibrium line is heated, it is possible for this crystal to fully dissolve again without transforming to a stable crystal as shown at vimeo.com/130550929.

It is worth noting that this complex phase behavior is only observed in potassium formate brine. No similar effect has been observed in sodium, rubidium, or cesium formate brines. As potassium formate is commonly used in blends with sodium and cesium formate, difficulties relating to the formation of this metastable phase can be experienced over a large part of the formate brine density range.

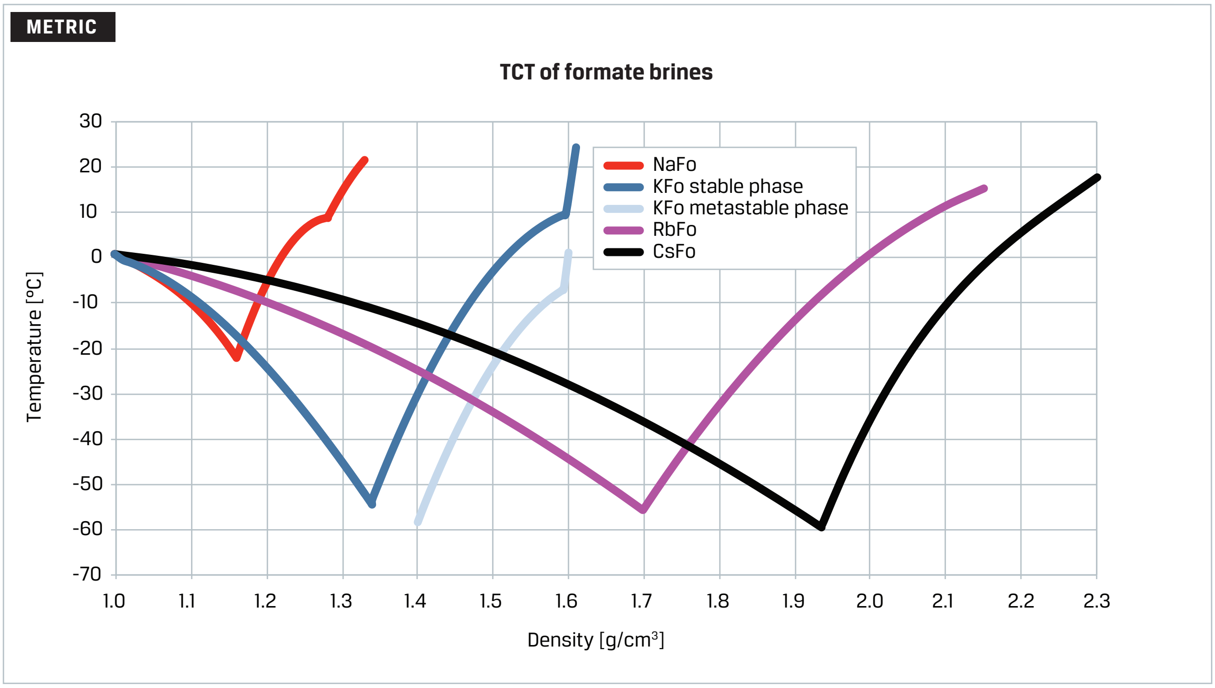
The measured supercooling points shown in Figure 5 represent the temperature where the brine has been successfully kept for at least two weeks with common nucleation material such as bentonite, rust, and dust. The second set of supercooling points represents the temperature where the brine has been successfully kept for at least two weeks without any seeding material.

A5.4.3 TCT in single-salt cesium formate brine

The measured TCT curve for field-grade cesium formate single-salt brine is presented in Figure 6 and Table 3. All test results were obtained using the measuring technique described [3][4]. The right-hand side of the TCT curve for cesium formate brine only shows the phase-equilibrium line for cesium formate monohydrate in equilibrium with cesium formate brine. The temperature of the critical point for cesium formate brine is so high that it is impractical to measure. Measured supercooling points shown in Figure 6 represent the temperature where the brine has been successfully kept for at least two weeks with common nucleation material such as bentonite, rust, and dust. The second set of supercooling points represents the temperature where the brine has been successfully kept for at least two weeks without any seeding material.

A5.4.4 TCT in blended cesium and potassium formate brines

TCT data for blends of potassium and cesium formate brines have been measured for a standard blend (1.57 g/cm^3 / 13.1 lb/gal potassium formate brine and 2.20 g/cm^3 / 18.3 lb/gal cesium formate brine). The TCT curves are shown in Figure 7. All test results were obtained using the measuring technique described [5]. It is difficult to measure consistent data for the low-density range, i.e. high concentration of potassium



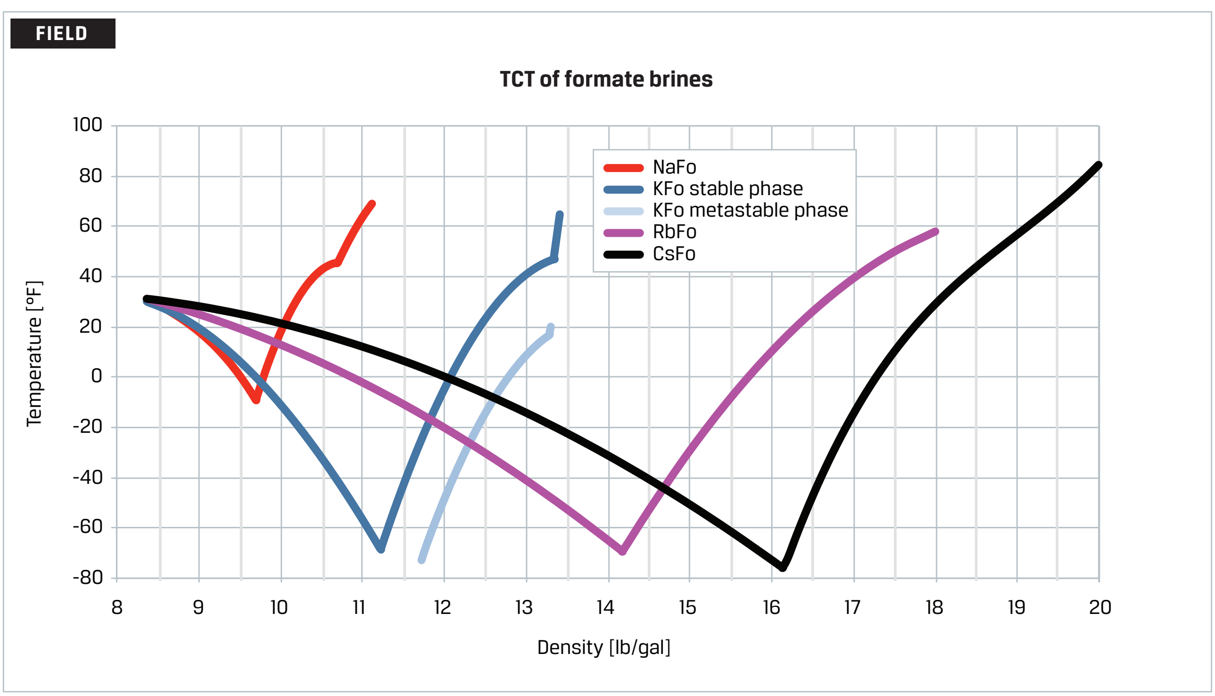
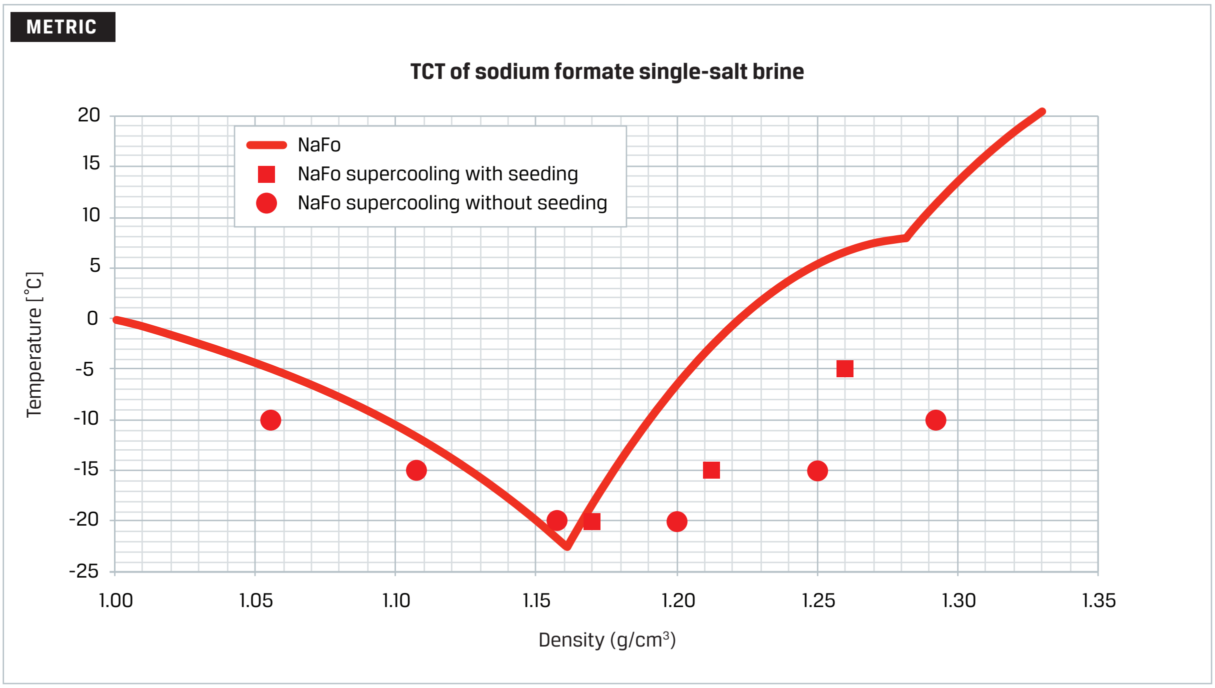


Figure 3 True Crystallization Temperature (TCT) for sodium, potassium, rubidium, and cesium formate brines.

formate. It is probably related to the metastable-phase crystals that form when potassium formate is present in high concentrations. The measured supercooling points shown in Figure 7 represent the temperature where the brine has been successfully kept for at least two weeks with common nucleation material such as bentonite, rust, and dust. The second set of supercooling points represents the temperature where the brine has been successfully kept for at least two weeks without any seeding material.

As cesium / potassium formate brine blends supplied by Cabot may not have the exact composition as blends used for measurement in Figure 7, TCT may vary from the values shown.



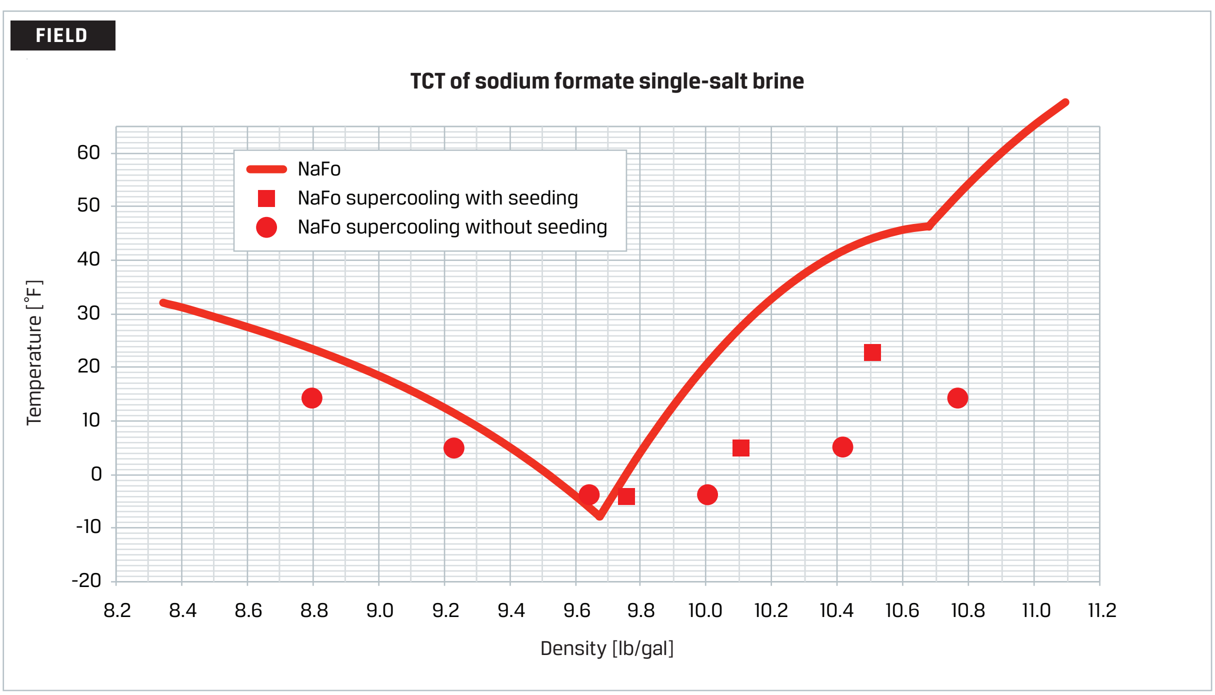
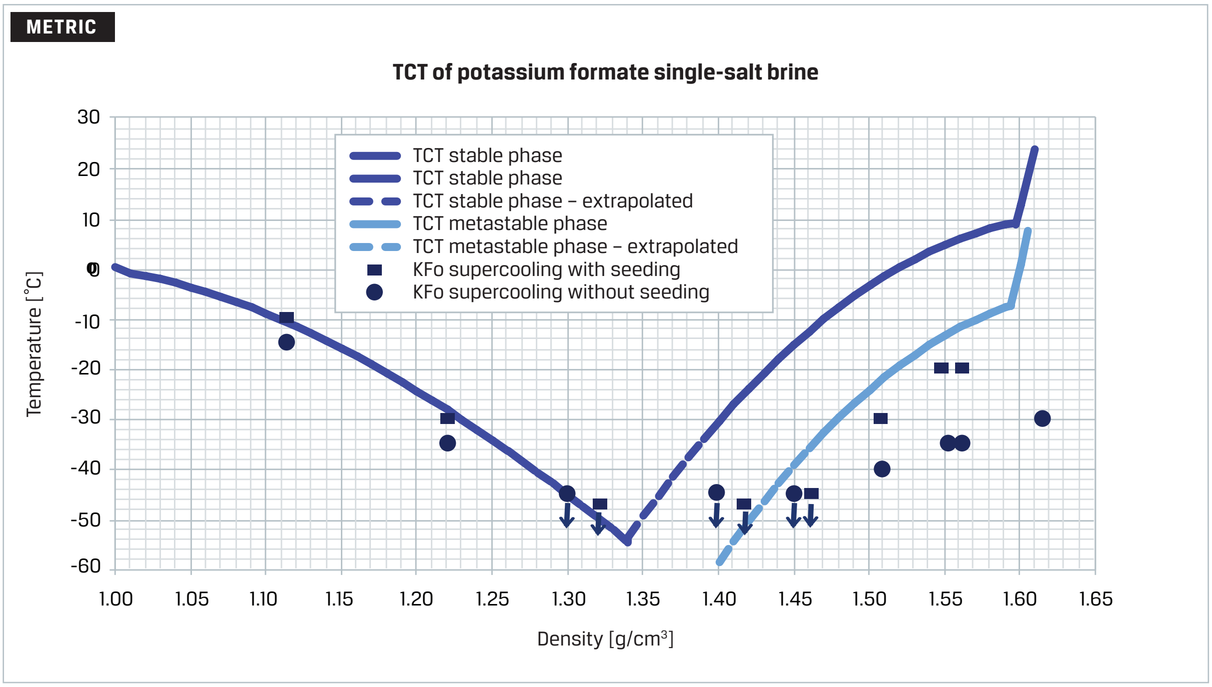


Figure 4 True Crystallization Temperature (TCT) for sodium formate single-salt brine. The supercooling points represent the temperature where the brine has been successfully kept for at least two weeks with and without standard seeding material present.

Table 1 True Crystallization Temperature (TCT) for sodium formate single-salt brine.

METRIC	
Density [g/cm^3]	TCT [°C]
1.00	0.0
1.01	-0.7
1.02	-1.6
1.03	-2.5
1.04	-3.4
1.05	-4.4
1.06	-5.4
1.07	-6.5
1.08	-7.8
1.09	-9.1
1.10	-10.6
1.11	-12.1
1.12	-13.9
1.13	-15.7
1.14	-17.8
1.15	-20.0
1.16	-22.5
1.17	-18.2
1.18	-13.9
1.19	-10.0
1.20	-6.4
1.21	-3.3
1.22	-0.5
1.23	1.9
1.24	3.9
1.25	5.5
1.26	6.7
1.27	7.6
1.28	8.0
1.29	10.7
1.30	13.6
1.31	16.2
1.32	18.6
1.33	20.7

FIELD	
Density [lb/gal]	TCT [°F]
8.34	32.0
8.40	31.2
8.50	29.4
8.60	27.5
8.70	25.5
8.80	23.3
8.90	21.0
9.00	18.4
9.10	15.5
9.20	12.3
9.30	8.8
9.40	4.9
9.50	0.6
9.60	-4.2
9.70	-5.9
9.80	3.8
9.90	12.5
10.00	20.2
10.10	26.9
10.20	32.7
10.30	37.4
10.40	41.2
10.50	44.0
10.60	45.7
10.70	47.6
10.80	54.2
10.90	60.0
11.00	65.2
11.10	69.8



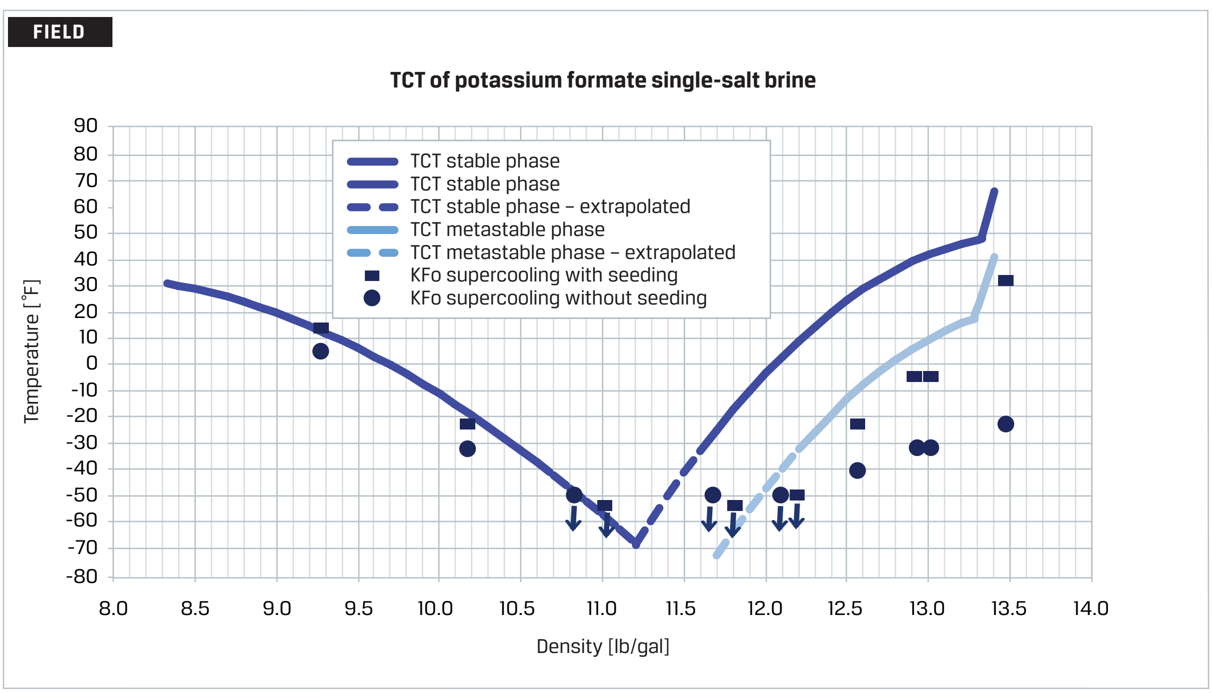


Figure 5 True Crystallization Temperature (TCT) for potassium formate single-salt brine. The stable-phase TCT is measured by seeding with stable-phase potassium formate crystals. The metastable-phase TCT is measured by seeding with metastable-phase potassium formate crystals. The supercooling points indicate the temperature where the brine has been successfully kept for at least two weeks with and without standard seeding material present.

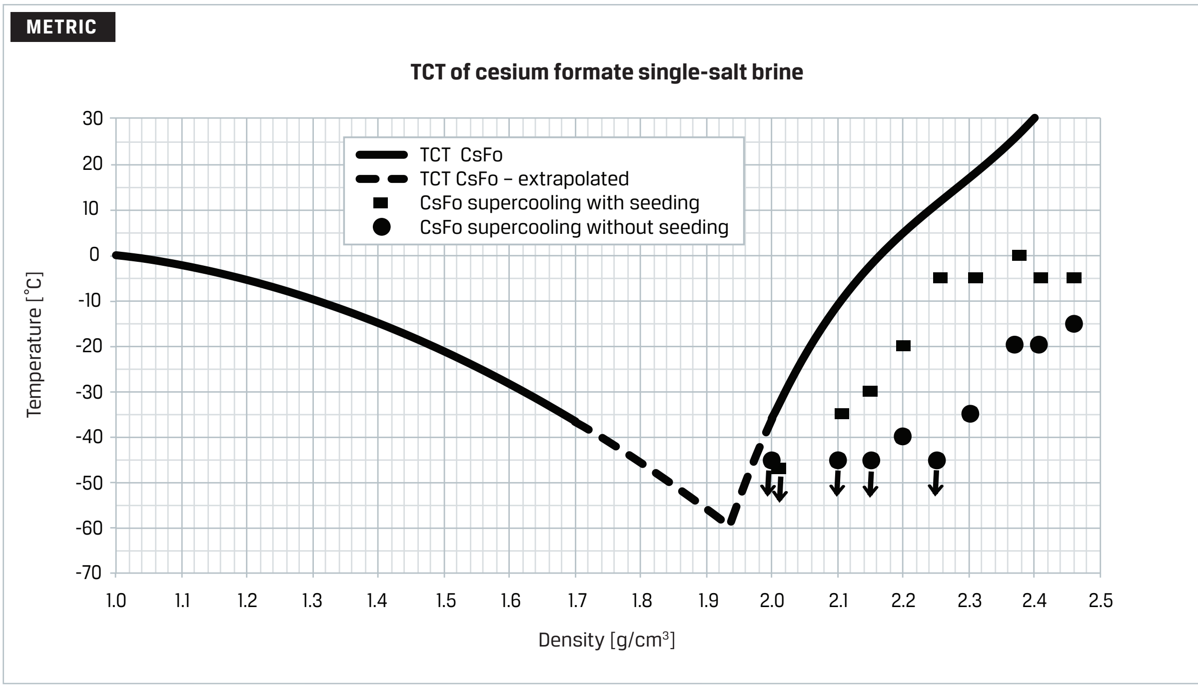
Table 2 True Crystallization Temperature (TCT) for potassium formate single-salt brine.

METRIC

Density [g/cm³]	TCT (stable) [°C]	TCT (metastable) [°C]
1.00	0.0	
1.01	-1.2	
1.02	-1.7	
1.03	-2.4	
1.04	-3.1	
1.05	-3.9	
1.06	-4.8	
1.07	-5.8	
1.08	-6.8	
1.09	-7.9	
1.10	-9.1	
1.11	-10.4	
1.12	-11.7	
1.13	-13.1	
1.14	-14.6	
1.15	-16.1	
1.16	-17.7	
1.17	-19.3	
1.18	-21.0	
1.19	-22.7	
1.20	-24.6	
1.21	-26.4	
1.22	-28.3	
1.23	-30.3	
1.24	-32.3	
1.25	-34.4	
1.26	-36.5	
1.27	-38.6	
1.28	-40.8	
1.29	-43.0	
1.30	-45.3	
1.31	-47.5	
1.32	-49.9	
1.33	-52.2	
1.34	-54.6	
1.35	-52.1	
1.36	-47.8	
1.37	-43.6	
1.38	-39.6	
1.39	-35.7	
1.40	-32.0	-58.6
1.41	-28.5	-54.4
1.42	-25.1	-50.3
1.43	-21.8	-46.5
1.44	-18.8	-42.8
1.45	-15.9	-39.3
1.46	-13.1	-36.0
1.47	-10.5	-32.8
1.48	-8.1	-29.8
1.49	-5.8	-27.0
1.50	-3.7	-24.3
1.51	-1.7	-21.8
1.52	0.1	-19.5
1.53	1.8	-17.3
1.54	3.3	-15.4
1.55	4.6	-13.5
1.56	5.8	-11.9
1.57	6.8	-10.4
1.58	7.7	-9.1
1.59	8.4	-8.0
1.60	12.4	0.4
1.61	23.4	14.2

FIELD

Density [lb/gal]	TCT (stable) [°F]	TCT (metastable) [°F]
8.34	30.8	
8.40	30.1	
8.50	28.9	
8.60	27.5	
8.70	25.9	
8.80	24.1	
8.90	22.1	
9.00	20.0	
9.10	17.7	
9.20	15.2	
9.30	12.5	
9.40	9.7	
9.50	6.7	
9.60	3.5	
9.70	0.2	
9.80	-3.3	
9.90	-6.9	
10.00	-10.7	
10.10	-14.7	
10.20	-18.8	
10.30	-23.0	
10.40	-27.4	
10.50	-31.9	
10.60	-36.6	
10.70	-41.3	
10.80	-46.3	
10.90	-51.3	
11.00	-56.5	
11.10	-61.8	
11.20	-67.2	
11.30	-58.6	
11.40	-49.4	
11.50	-40.7	
11.60	-32.3	
11.70	-24.3	-71.9
11.80	-16.8	-63.0
11.90	-9.6	-54.5
12.00	-2.9	-46.4
12.10	3.4	-38.8
12.20	9.3	-31.6
12.30	14.8	-24.9
12.40	19.9	-18.6
12.50	24.6	-12.7
12.60	28.9	-7.3
12.70	32.8	-2.4
12.80	36.2	2.2
12.90	39.3	6.3
13.00	42.0	9.9
13.10	44.2	13.1
13.20	46.0	15.9
13.30	47.4	22.8
13.40	65.6	41.2
13.50	89.3	59.7



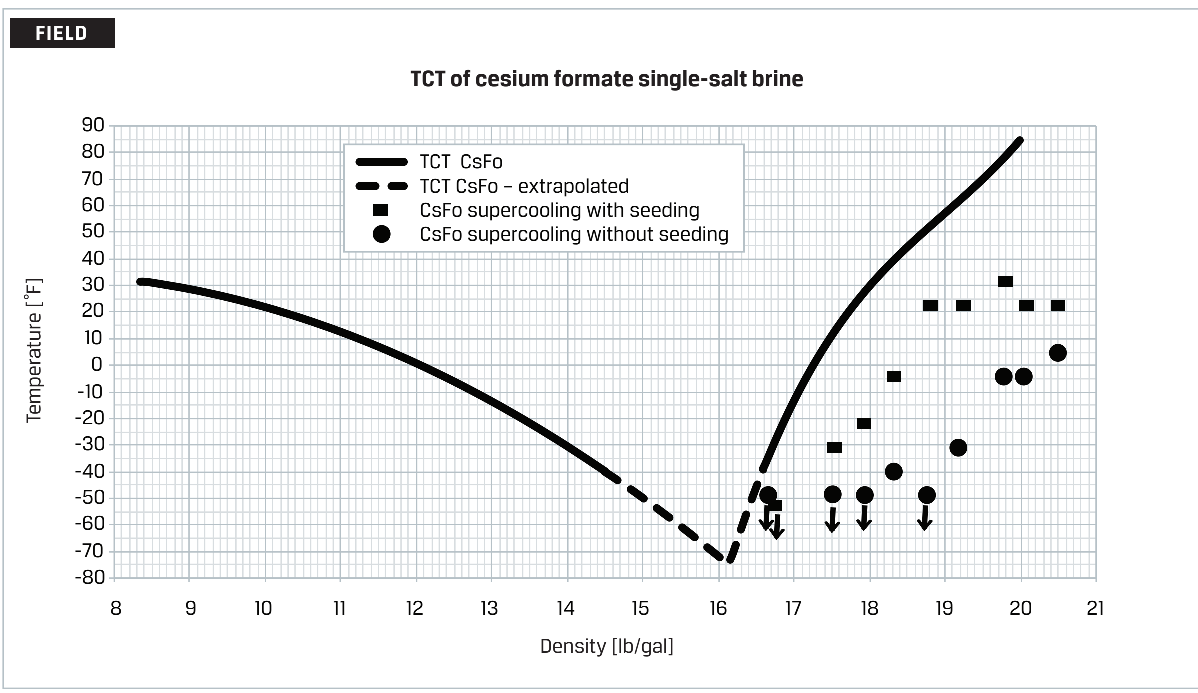


Figure 6 True Crystallization Temperature (TCT) for cesium formate single-salt brine. The supercooling points indicate the temperature where the brine has been successfully kept for at least two weeks with and without standard seeding material present.

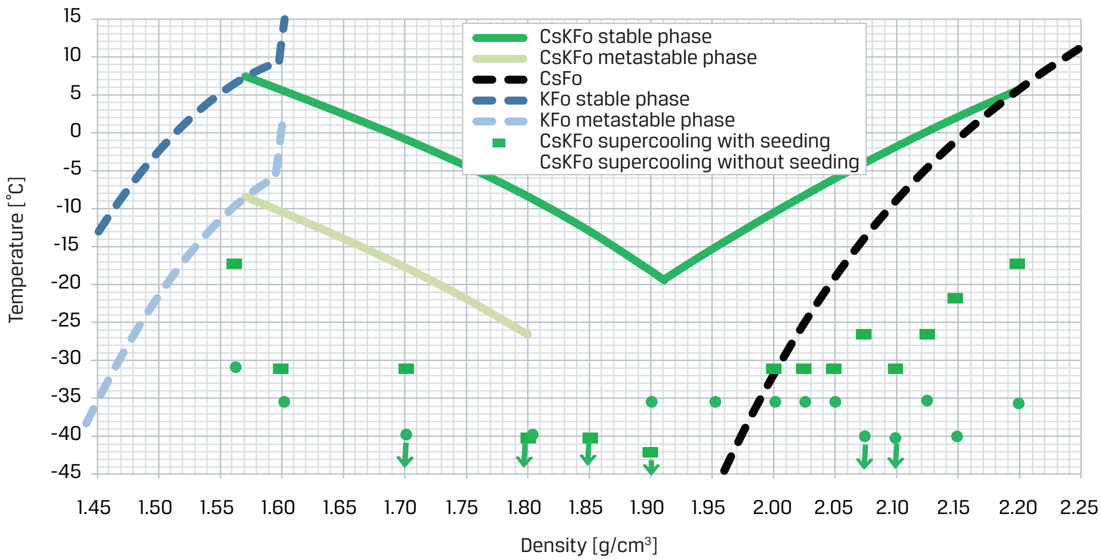
Table 3 True Crystallization Temperature (TCT) for cesium formate single-salt brine.

METRIC	
Density [g/cm³]	TCT [°C]
1.00	0.0
1.05	-1.0
1.10	-2.3
1.15	-3.8
1.20	-5.5
1.25	-7.5
1.30	-9.8
1.35	-12.3
1.40	-15.0
1.45	-18.0
1.50	-21.2
1.55	-24.7
1.60	-28.4
1.65	-32.4
1.70	-36.6
1.75	-41.0
1.80	-45.7
1.85	-50.6
1.90	-55.8
1.92	-58.0
1.94	-57.4
1.96	-49.6
1.98	-42.5
2.00	-35.9
2.02	-30.0
2.04	-24.5
2.06	-19.6
2.08	-15.1
2.10	-11.0
2.12	-7.2
2.14	-3.8
2.16	-0.7
2.18	2.2
2.20	4.9
2.22	7.4
2.24	9.9
2.26	12.2
2.28	14.5
2.30	16.9
2.32	19.2
2.34	21.7
2.36	24.3
2.38	27.1
2.40	30.1

FIELD	
Density [lb/gal]	TCT [°F]
8.34	32.0
8.5	31.4
9.0	29.0
9.5	25.9
10.0	22.2
10.5	17.8
11.0	12.8
11.5	7.2
12.0	1.0
12.5	-5.9
13.0	-13.4
13.5	-21.6
14.0	-30.4
14.5	-39.8
15.0	-49.8
15.5	-60.5
16.0	-71.8
16.2	-70.4
16.3	-61.9
16.4	-53.9
16.5	-46.2
16.6	-38.9
16.7	-32.0
16.8	-25.5
16.9	-19.3
17.0	-13.5
17.1	-8.0
17.2	-2.8
17.3	2.1
17.4	6.8
17.5	11.2
17.6	15.3
17.7	19.3
17.8	23.0
17.9	26.5
18.0	29.9
18.1	33.1
18.2	36.2
18.3	39.1
18.4	41.9
18.5	44.7
18.6	47.3
18.7	49.9
18.8	52.4
18.9	55.0
19.0	57.5
19.1	60.0
19.2	62.5
19.3	65.0
19.4	67.6
19.5	70.3
19.6	73.1
19.7	75.9
19.8	78.9
19.9	82.0
20.0	85.2

METRIC

TCT and supercooling data for blended cesium and potassium formate brine



FIELD

TCT and supercooling data for blended cesium and potassium formate brine

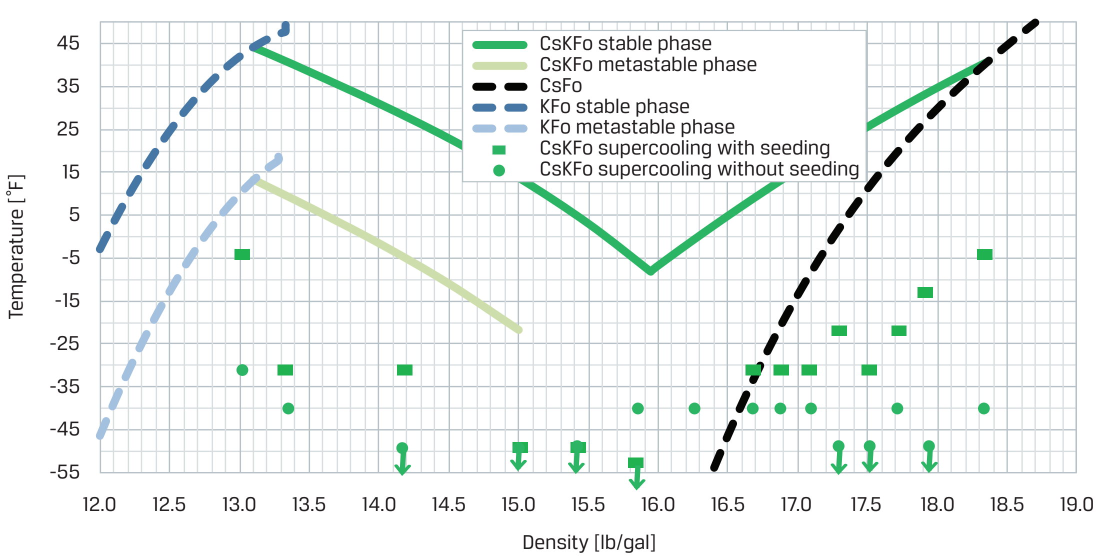


Figure 7 True Crystallization Temperature (TCT) for a blend of 1.57 g/cm³ / 13.10 lb/gal potassium formate and 2.20 g/cm³ / 18.36 lb/gal cesium formate brine. The stable-phase TCT is measured by seeding with stable-phase potassium and cesium formate crystals, while the metastable-phase TCT is measured by seeding with metastable potassium formate crystals.

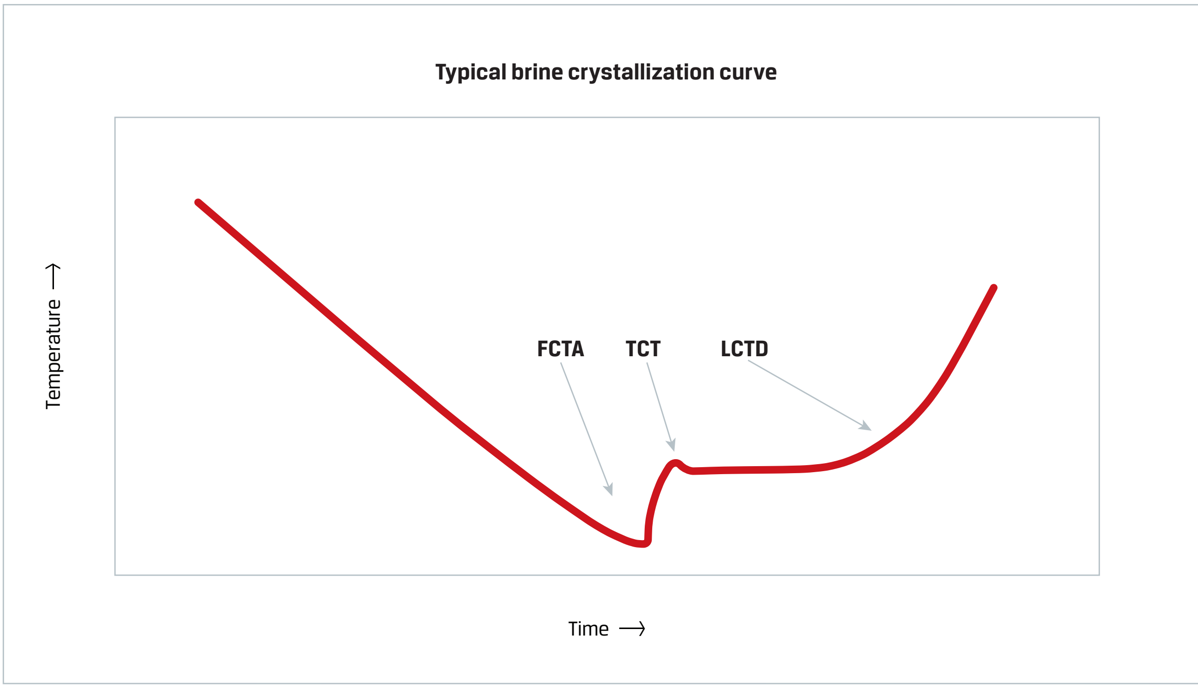


Figure 8 Typical crystallization curve for brines showing recorded temperature points recommended by API. True Crystallization Temperature is abbreviated to TCT, First Crystal to Appear is abbreviated to FCTA, and Last Crystal to Dissolve is abbreviated to LCTD.

A5.5 Recommended method for TCT determination in formate brines

The most commonly used procedure for measuring TCT in oilfield brines is the API 13J method [6]. The method involves several cycles of alternately cooling and heating brine. The brine sample is cooled at a set rate until onset of precipitation. Once precipitation starts, a small rise in temperature is usually seen due to the exothermic nature of crystallization. After precipitation has been noted, the sample is heated until all crystals have redissolved. Data recorded during this procedure (see Figure 8) include:

- First Crystal to Appear (FCTA) temperature. This corresponds to a minimum inflection point in the temperature plot during cooling, or the temperature at which visible crystals start to form. FCTA generally includes some supercooling effect.
- True Crystallization Temperature (TCT). This corresponds to the maximum temperature reached following the supercooling minimum. In a temperature plot during the cooling cycle, TCT is the maximum temperature reached following the supercooling minimum, or the inflection point in cases with no supercooling.
- Last Crystal to Dissolve (LCTD) temperature. This corresponds to the point on the temperature plot where crystals disappear. LCTD is the measured crystallization temperature nearest the temperature where formed crystals will re-dissolve.

From a thermodynamic viewpoint, FCTA, TCT, and LCTD should be the same; in practice kinetic considerations imposed by the method cause discrepancies. API recommends that if significant supercooling occurs, i.e. TCT exceeds FCTA by 3°C / 5°F or more, measurements should be repeated at a lower cooling rate. It also recommends that maximum temperature after LCTD should not exceed 1.0°C / 2.0°F above LCTD.

API identifies control of supercooling as the biggest challenge with the method. The API method attempts to overcome supercooling by introducing a requirement for slow cooling rates and nucleation of crystals with selected seeding solids. API has identified certain generic types of seeding particles to serve as nucleation sites for brines. Typical examples are barium oxide, barium hydroxide, calcium carbonate, and bentonite. Calcium carbonate is recommended for organic brines. Problems identified with the API method when used with formate brines are:

- Although supercooling can be overcome by low cooling rates, this still requires that the brine sample doesn't supercool to temperatures lower than the lowest temperature setting of the measuring equipment. In formate brines such extreme supercooling is often the case. This typically results in failure to measure TCTs, with TCT reported as 'too low to measure'.

- Generic seeding materials are ineffective in formate brines. API provides the following definition for TCT: "The actual crystallization temperature of brine is that temperature at which a solid will begin to form from the solution if given sufficient time and proper nucleating conditions." Yet its recommended method doesn't provide 'proper nucleation conditions' for all brines.
- API advises adding seeding material to the sample before the onset of cooling. This is only suitable when insoluble salt crystals are used for seeding.
- API does not provide any guidance for handling brines that form metastable crystals. Slow cooling rates simply mean that measured crystallization temperature may drift from the metastable to stable phase during the temperature cycle, but there is no guarantee this will happen. The operator has no means of knowing if they are measuring stable or metastable crystallization temperature.

Over the last years, Cabot has evaluated various procedures for determining TCT in formate brines. Testing has shown that it is critical to seed formate brines with appropriate (effective) seeding material and that this seeding material is added to the brine sample at the right time, something that is not addressed in the API guidelines. The key recommendations in the Cabot method as opposed to the API method are:

- A seeding crystal prepared from the brine sample itself should be used.
- The seeding crystal should not be added before onset of cooling, but rather when a temperature slightly lower than the expected TCT is reached.
- Stirring at the right times during cooling and heating cycles is important.
- Cooling and heating rates appear not to be so critical as API states.

Without proper seeding the large degree of supercooling in formate brines, especially cesium formate brine, makes it difficult to even cool the sample far enough to obtain crystallization in the first place. Furthermore, when potassium formate is considered, it is impossible to know whether crystallization is metastable or stable. To perform good TCT measurements in formate brines, it is critical for the operator to understand the basics of crystallization behavior and precipitation mechanisms for the brine being tested.

The method developed by Cabot consists of four steps. The last step corresponds to the API-recommended method, but has much stricter rules for seeding and stirring, and is less strict for cooling and heating rates.

A5.5.1 Recommended four-step TCT measurement technique

Based on many years of research into measuring methods for TCT in formate brines, Cabot recommends the following four-step method.

Step 1: Preparation of seeding material

The recommended seeding material for formate brines is a crystal from the brine being tested. This is obtained by keeping the brine in a freezer at low temperature or cooling the sample on either a cold plate or in the TCT-measuring equipment. For potassium formate, it is possible to produce both metastable and stable crystals.

- Metastable crystals can be produced from a concentrated potassium formate sample if it is placed in a freezer at its lowest setting (-40°C / -40°F) and allowed to crystallize spontaneously. These crystals generally remain metastable when kept in the freezer. However, there is a slight risk that they will convert to stable crystals.
- Stable crystals are readily produced by removing crystallized potassium formate brine (with metastable crystals) from the freezer and stirring at a temperature around metastable TCT. This is easiest achieved in the TCT-measuring equipment described in Step 2. Patience is often required, as transformation does not always take place easily.

With the following seeding material in the freezer, TCT can be measured in all formate single-salt and blended brines:

- Cesium formate crystals
- Potassium formate stable crystals
- Potassium formate metastable crystals
- Sodium formate crystals

It is a good idea to test the metastable potassium formate crystals against brine with known TCT before use, as there is a small chance that they could have converted to stable crystals during storage. The TCT curves for single-salt potassium formate brine, shown in Figure 5, can be used to verify if a crystal is stable or metastable.

Step 2: Selection of seeding material

Seeding material should be selected based on knowledge about brine compositions. Figure 4 to Figure 7 can be used as guidance.

- In very diluted brines, i.e. in brines where water crystallizes as ice (the left equilibrium curve in Figure 1), seeding is not required.
- In concentrated single-salt brines, seed with a crystal of the brine itself. For potassium formate,

the seeding crystal depends on whether stable or metastable crystallization temperature will be measured.

- In very highly concentrated brines, i.e. in the region to the right in Figure 1 where dry salt crystallizes out of solution, seeding might not be required. As TCT is high in this region, it should not be difficult to form crystals.
- In blended brines, a crystal of the predominant salt should be used. If it is uncertain which salt will crystallize first, add a crystal of each one.

Step 3: Determination of approximate TCT

An approximate TCT is needed for programming the temperature controller used in Step 4 below and also to determine when the seeding crystal should be added. The approximate TCT is determined based on knowledge about the brine sample. In single-salt brines, density is a good indicator of TCT. Use the measured brine TCT curves (see Figure 4 to Figure 6) to estimate TCT.

It is harder to approximate TCT in blended brines. If it is a straight blend of cesium formate and potassium formate stock brines with no water added or removed, TCT can be predicted from a standard measured TCT curve (see Figure 7). Otherwise, if it is believed that the brine could contain some extra water, a few degrees should be subtracted. Equally, if water could have been removed from the blend, for example by evaporation or addition of dry salt, approximate TCT should be adjusted up a few degrees.

Step 4: Accurate determination of TCT

The method used for this step is based on the API-recommended method [6]. Cabot uses a Grant GR-150 cooling bath, which is controlled by Labwise™ software. A liquid-cooled sample cup with stirrer is attached to the bath. The test brine is added directly to the sample cup and the stirrer turned on. The cup should be covered with a plastic film to eliminate the brine's water absorption from air.

The temperature controller is programmed to set the first target temperature to approximately 8°C / 14°F below approximate TCT determined in Step 1. Cooling rate is not critical when brine is seeded with a salt crystal. The seeding crystal should be added approximately 1°C / 2°F below approximate TCT determined in Step 3. This is simply done by touching a needle or spatula to the seed crystal sample and then inserting this in the test sample. Even if the crystals cannot be seen they will still be there. It is neither necessary nor desirable to add a large amount of seeding crystals. Watch carefully for crystallization. If crystallization does not take place, lower approximate TCT with 5°C / 9°F and try again. Cooling should be turned off after the temperature peak (TCT) has been reached. The second target temperature should be set some degrees higher than expected LCTD (exact value is less critical when a proper seeding crystal is used). The heating rate is also not critical. As soon as LCTD is reached, the stirrer should be turned off. This cooling / heating cycle should be repeated three times, or until measured TCT no longer changes. Please note that the sample only needs to be seeded once. For the second and third cycle, no seeding is required, and the stirrer should first be turned on when TCT (maximum peak) is reached. For each cycle, the target temperature should be adjusted to 8°C / 14°F below TCT (maximum peak) measured in the previous cycle. Figure 9 shows the sequence of three such cycles, indicating the various steps required for measurement.

If appropriate seeding material has been used, the three TCT values (FCTA, TCT, LCTD) should be very similar. If no seeding material was used, the first TCT is likely to be much too low because of supercooling. For potassium formate, if either a metastable crystal is applied or no seeding material at all is used, the recorded TCT value might drift upwards with time as precipitated crystals transform from the metastable phase to the stable phase. This is illustrated in Figure 10. Following API guidelines and reporting FCTA (First Crystal to Appear) and LCTD (Last Crystal to Dissolve) are recommended.

Care should be taken when measuring TCT at or around the eutectic or critical points. It is better to measure on both sides of these points and extrapolate the measured TCT curves.

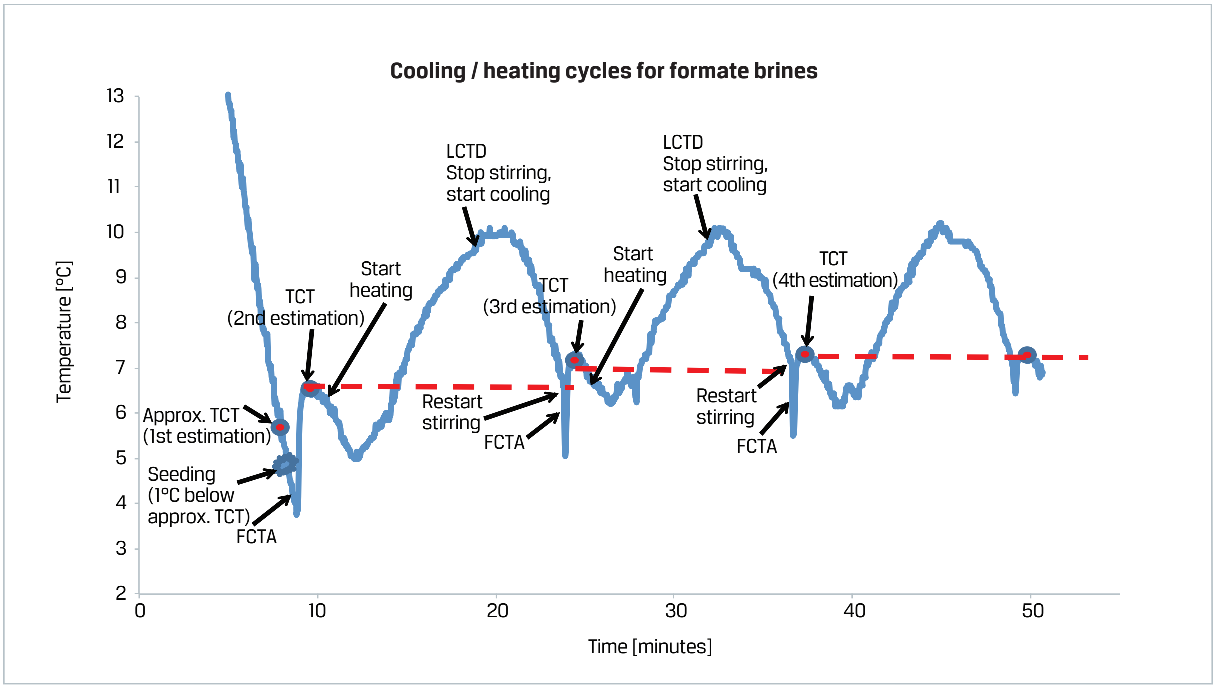


Figure 9 Typical plot of temperature versus time during cooling / heating cycles when measuring TCT in formate brines. The required steps are shown. True Crystallization Temperature is abbreviated to TCT, First Crystal to Appear is abbreviated to FCTA, and Last Crystal to Dissolve is abbreviated to LCTD.

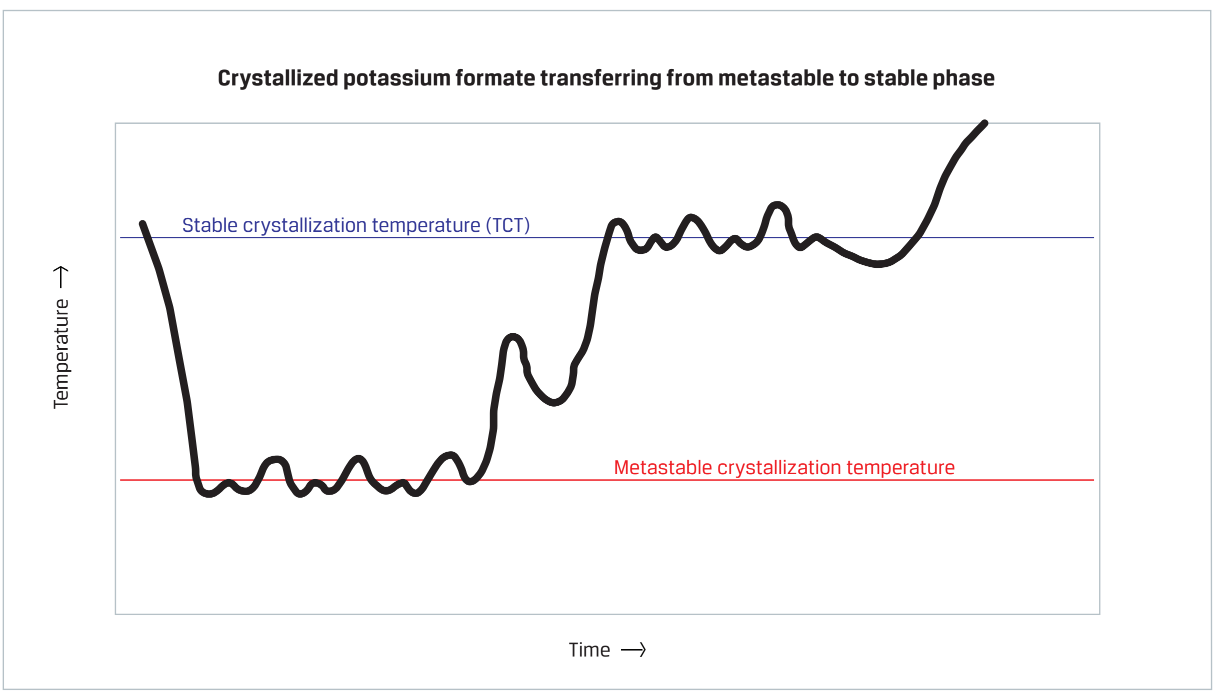


Figure 10 Temperature as a function of time during a TCT measuring test where crystallized potassium formate transfers from a metastable crystal to a stable crystal.

A5.6 Pressurized crystallization temperature (PCT)

A5.6.1 Introduction

In deep-water environments, crystallization can become a serious problem. High pressure and low temperature (HPLT) can cause salts in high-density brine solutions to become more susceptible to crystallization. Extremely high pressure and low temperatures are normally encountered at the mud line and during pressure testing of equipment.

Therefore, it is very important to know fluid crystallization temperature at realistic pressure conditions. There are two major problems associated with PCT measurements in general. The first is lack of a dependable standardized method. The second problem is poor availability of high-pressure testing equipment to measure TCT under dynamic pressure and temperature conditions. For formate brines, with additional difficulties of extreme supercooling and the existence of metastable phases, these measurements become increasingly complicated.

A5.6.2 Methods for determining PCT in formate brines

PCT measurements of formate brines have been carried out at two test laboratories: Westport Technology Center International and Baroid. The test methods used to determine PCT in formates are:

Westport Technology Center International: Acoustic method
Westport has chosen an acoustic method for determination of PCT due to serious limitations in standard determination techniques, such as visual detection, temperature time-plot, and volume change. The equipment can measure down to -30°C / -22°F. Pressure is from 0.07 to 140 MPa / 10 to 20,000 psi, and sample volume from 5 to 350 mL. Both arrival time of the acoustic wave and attenuation of wave amplitude are functions of the number of solid particulates in the brine solution.

To ensure temperature and composition homogeneity, the cell is rocked back and forth, which also helps reduce supercooling effects. The acoustic cell sits in a controlled temperature chamber with a circulation system that provides uniform temperature distribution and cooling rates.

Baroid (Halliburton): Fiber-optic technique
Baroid uses the following methods for determining crystallization:

- Visual (fiber optics)
- Volume change
- Temperature inflection point

The 70mL-volume cell is equipped with a stir disk. Testing starts at 10,000 psi and decreases to the base line of 100 psi in 2,500 psi increments. The test includes four cycles at each pressure stage to check for supercooling effects. Each test takes 16 to 21 hours with 0.05g of five-micron marble used as seeding agent.

A5.6.3 PCT data for formate brines

By using the two measurement methods described above, some limited PCT values have been determined.

PCT data for 2.195 g/cm³ / 18.3 lb/gal cesium formate brine with and without 5% *KCl*
TCT was measured as a function of pressure for 2.195 g/cm³ / 18.3 lb/gal buffered cesium formate brine with and without addition of 5% *KCl*, which was added to lower TCT. The tests were completed at Westport Technology Center according to its acoustic technique described on this page. Results are listed in Table 4 and plotted in Figure 11.

PCT data for various formate brines and blends
Baroid has carried out a number of PCT tests on formate fluids by using its fiber-optic detection technique mentioned above.

TCT as a function of pressure (up to 20,000 psi) was measured on buffered, saturated cesium formate brine (2.18 g/cm³ / 18.18 lb/gal). Test results are shown in Table 5 and plotted in Figure 11.

Similar tests were carried out on several buffered formate brines: 1.32 g/cm³ / 11.01 lb/gal sodium formate, 2.18 g/cm³ / 18.18 lb/gal cesium formate, 2.20 g/cm³ / 18.34 lb/gal cesium formate, and 1.52 g/cm³ / 12.67 lb/gal potassium / cesium formate. Figure 11 shows excellent consistency between the two PCT measurement methods. Also, by comparing TCTs with no applied pressure, it is found that those measured with these instruments are similar to the ones measured in standard TCT tests.

For cesium formate and cesium / potassium formate blends, the following rule of thumb applies:

> ***Cesium and cesium / potassium formate:***
> **Increase in TCT ~ 1°F per 1,000 psi pressure increase.**

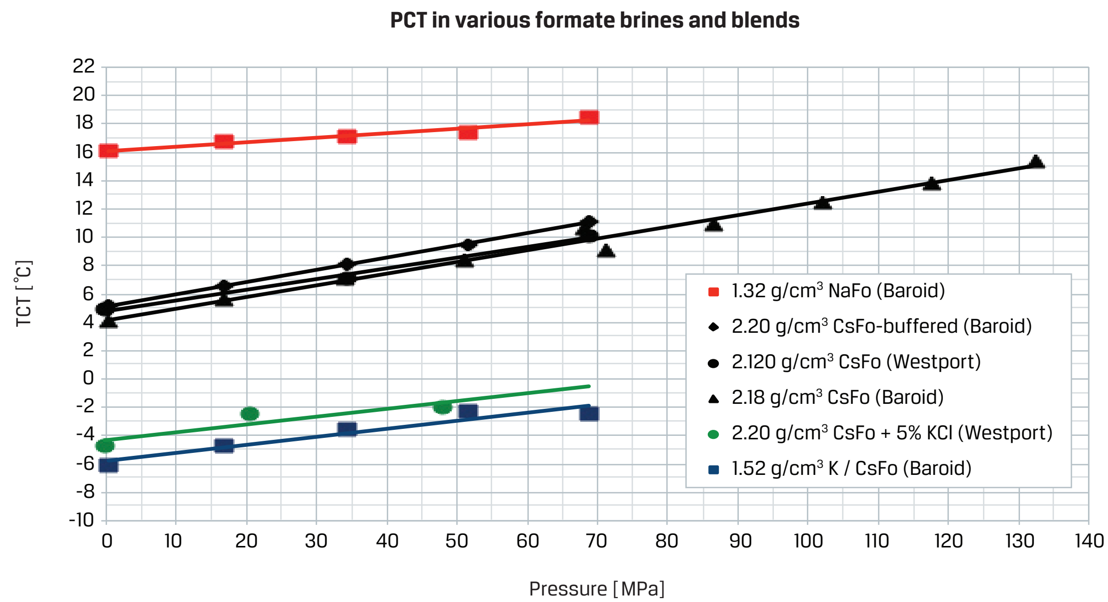
Table 4 TCT as a function of pressure for buffered 2.195 g/cm³ / 18.3 lb/gal cesium formate brine with and without 5% *KCl*. Measured at Westport Technology Center International.

Pressure		PCT 2.195 g/cm³ / 18.3 lb/gal CsFo		PCT 2.195 g/cm³ / 18.3 lb/gal CsFo + 5% KCl	
[MPa]	[psi]	[°C]	[°F]	[°C]	[°F]
0.14	21	7.2	41.0	-4.7	23.6
20.7	3,000	–	–	-2.3	27.8
34.5	5,000	7.5	42.0	–	–
48.3	7,000	–	–	-1.9	28.6
68.9	10,000	10.2	50.4	-0.33	31.4

Table 5 TCT as a function of pressure for a variety of formate brines and blends. The measurements have been carried out by Baroid. The 1.52 g/cm³ / 12.7 lb/gal potassium / cesium formate blend has been designed specifically to lower TCT / PCT.

Brine	Pressure		PCT	
	[MPa]	[psi]	[°C]	[°F]
1.32 g/cm³ / 11.0 lb/gal NaFo	0.69	100	10.39	61.2
	17.24	2,500	12.78	62.3
	34.47	5,000	12.33	63.0
	51.71	7,500	16.28	63.5
	68.95	10,000	17.06	65.5
1.52 g/cm³ / 12.7 lb/gal K / CsFo	0.69	100	-6.03	21.2
	17.24	2,500	-4.67	23.6
	34.47	5,000	-3.42	25.9
	51.71	7,500	-2.18	28.1
	68.95	10,000	-2.40	27.7
2.20 g/cm³ / 18.3 lb/gal CsFo buffered	0.69	100	5.3	41.5
	17.24	2,500	6.7	44.0
	34.47	5,000	8.2	46.7
	51.71	7,500	9.6	49.3
	68.95	10,000	11.2	52.2
2.18 g/cm³ / 18.2 lb/gal CsFo	132.5	19,221	15.5	59.9
	117.8	17,086	13.9	57.1
	102.2	14,830	12.6	54.7
	86.7	12,574	11.0	51.8
	71.4	10,352	9.2	48.5
	68.2	9,888	10.8	51.4
	51.2	7,433	8.4	47.2
	34.3	4,969	7.2	44.9
	17.1	2,476	5.7	42.3
	0.56	81	4.2	39.6

METRIC



FIELD

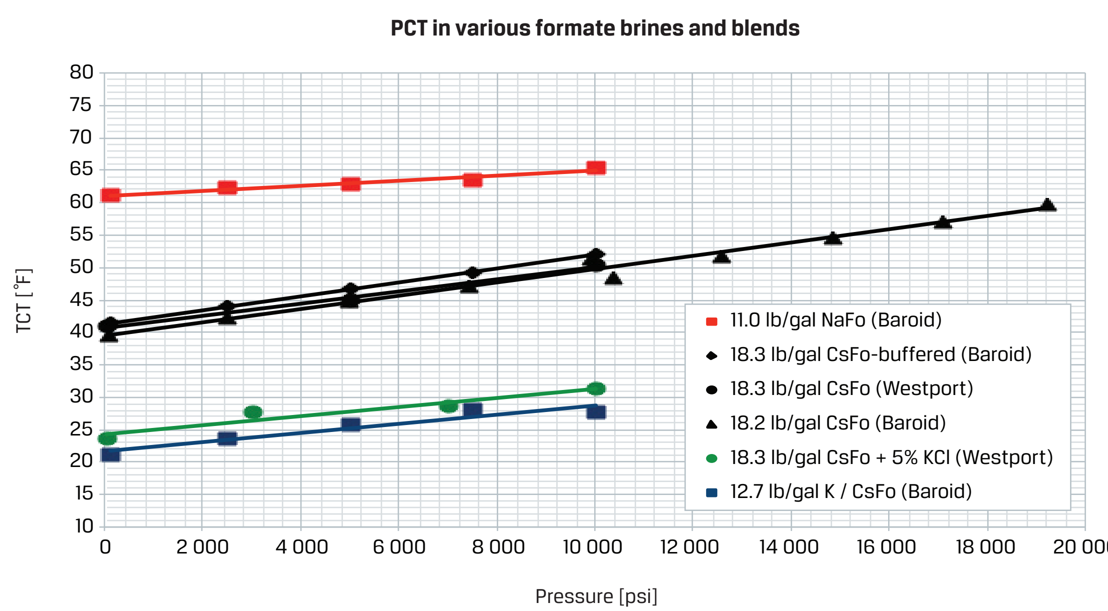


Figure 11 TCT as a function of pressure for a variety of formate brines and blends. The 1.52 g/cm³ / 12.7 lb/gal potassium / cesium formate blend is a heavier potassium / cesium formate blend cut back with water to lower PCT.

A5.7 How to apply TCT / PCT data in the field

Although the scientifically correct fluid TCT is the thermodynamically stable one, i.e. the highest one measured, this might not be the most suitable TCT value to use when formulating drilling and completion fluids. As formate brines – especially cesium formate brine – supercool more than other brines, and potassium formate brines and its blends precipitate metastable crystals with lower TCT, there is significant discrepancy between actual TCT (PCT) and the temperature where crystallization problems may occur.

Storage of potassium formate brine and formate blends with high potassium formate content in tanks is a good example of this. Without a stable potassium formate seeding crystal, a thermodynamically stable crystal cannot form before metastable crystals exist in the fluid. Therefore, this fluid can be stored safely at temperatures down to TCT of the metastable phase, or even lower due to supercooling. In periods when temperatures outside the tank go beyond metastable-phase TCT, metastable crystals may form locally at tank sides, although the fluid's bulk temperature inside the tank is significantly above this temperature. The extent of this crystallization is limited, but within a few hours transformation to thermodynamically stable crystals can occur. These stable crystals seed formation of thermodynamically stable crystals in the whole storage tank, assuming bulk temperature inside the tank is below TCT of the stable crystal. Crystallization is substantial as the fluid is effectively heavily supersaturated for this crystallization type. In order to dissolve these crystals again, the temperature obviously needs to be above the LCTD value of the stable crystal, which is significantly higher than the LCTD temperature of the metastable crystal.

Therefore, potassium formates can safely be stored down to the lower TCT of the metastable crystal, and even lower due to supercooling. However, it should be kept in mind that localized cooling and crystallization at the tank wall can have drastic consequences for the extent of crystallization and the ability to dissolve crystals afterwards.

A5.8 How to lower crystallization temperature of formate brines

In some applications, it might be desirable to lower crystallization temperature of formate brines and blends.

A5.8.1 Lowering TCT in single-salt formate brines

It is well known that when two brines are blended, TCT is often lower than the individual brines' TCTs. An example of this is shown in Figure 7, where stock cesium formate and potassium formate brines are blended. It should also be noted that adding potassium chloride can lower sodium formate brine TCT. Lowering TCT by adding 15% and 20% potassium chloride to sodium formate brine has been demonstrated by Shell [2]. Similarly, adding some potassium chloride can lower pure cesium formate brine TCT.

A5.8.2 Lowering TCT in blended formate brines

In certain deep-water applications there is need for formate brine with typical density of single-salt potassium formate brine, but with lower TCT than can be obtained from this single-salt brine alone. In this case, a blended potassium / cesium formate brine can be formulated by adding additional water.

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