

The Effect of Pressure on the Crystallization Temperature of High Density Brines

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Abstract

Pressure has been found to effect the crystallization points of all of the brines tested. An increase is most pronounced in calcium chloride brines and brines containing large amounts of this salt, and at temperatures of 50°F or more. For calcium chloride brines (but not for sodium brines) the pressure changes resulting from the small volume changes of crystallization were dramatic and provided an excellent indicator of the onset of crystallization. Further work using a cell specifically designed to study the pressure effect on crystallization temperature is proceeding.

Introduction

History

Clear brine fluids have been commonly used for pressure control since the 1970's (1,2). The advantage of their non-damaging character is accepted and reflected by their common usage in completion fluids, perforating fluids, packer fluids, and in pay zone drill-in fluids. Early applications quickly exposed a significant drawback – untimely crystallization. In a ‘worst case’ scenario a rig was lost when crystallized solids formed in the work string concealing a gas bubble below. As the plugged lines were cleared, the well blew out (3). The practice of formulating ‘summer’ blends vs. ‘winter’ blends, and shortly later, the practice of specifying brines by crystallization temperature as well as by density became the normal industry practice.

The crystallizing solids are not the anhydrous materials sold in commerce, but are highly hydrated species. For

example, calcium chloride forms at least 4 different hydrated species at ambient temperature, with the most hydrated having six moles of water to form a crystal that is only slightly more dense than the concentrated liquid. Zinc halide hydrates include charged complexes, which increases the solubility of the alkaline metals (4).

Relation of Crystallization to Temperature and Pressure

Standard tests of chemical thermodynamics describe crystallization as the effect of temperature on the maximum solubility of a single component in a solution. The subject is treated from the perspective of equilibrium constants and related to the free energy of solution (5,6). Thus for ideal solutions of single salts, the equilibrium can be related to temperature. The formula is usually presented in the form(5):

$$(d \ln x / d T)_P = (a \text{ characteristic heat quantity}) / RT^2 \quad (1)$$

Despite its similarity to familiar equations, little use has been made of this approach, as the brines of commercial interest are rarely single salts and are never ideal solutions.

Most texts also make a passing reference to the effect of pressure on solubility, but then conclude that pressure effects are so small as to be negligible under most conditions (6). Free energy data and equilibria at high pressures are not found in the literature. Though empirical expressions for the crystallization of brines exist (7,8), the industry relies on experimentally measured crystallization temperatures. For the record, such an expression has the general form (5):

$$(d \ln x / d P)_T = (DV, a \text{ characteristic volume}) / RT(2)$$

The equation is not absolute for more than a single salt and ideal solutions. A simplified approach can assume a combination of species to reduce the number of components so that some insight can be gained.

Problem

Until recently, the pressure effect on crystallization has not presented a problem -- even in exceptionally high pressure work -- as the greatest pressures are encountered together with the highest temperatures. However, the combination of high pressure and low temperature does occur in two cases; 1.) when working in exceptionally deep waters where the hydrostatic pressure at the sea floor (mud-line) is combined with near freezing temperatures, and 2.) when conducting pressure tests of lines and similar equipment such as blow-out preventors in colder climates. Testing sub-sea blow-out preventors combines both conditions. For example, in 5,000

ft seas a 14.2 lb./gal brine would exert a hydrostatic pressure of 4,250 psi combined with temperatures near 30°F at the sea floor.

It has been found that most brines of commercial interest do crystallize at temperatures higher than expected when they are “pressurized”. In one case, this higher crystallization point was 15°F greater at 5,000 psi than the crystallization points at ambient temperature and pressure. Consequently, we have undertaken this study to measure the crystallization temperature of representative brines under increasing pressure, and report the results as a “Pressured Crystallization Temperature” (PCT).

Experimental Procedures

Testing – API RP 13J

In normal ambient pressure testing the onset of crystallization is visually observed. RP13J provides a clear procedure for the determination of the crystallization point, calling for a gradual cooling through the expected temperature range(9). The temperature at which crystals are first observed is the First Crystal to Appear (FCTA) temperature. The mixture is later warmed while observing the dissolution of the crystals. The temperature at which complete dissolution occurs is recorded as the Last Crystal to Dissolve (LCTD). Between the FCTA and LCTD is the True Crystallization Temperature (TCT). This temperature is most evident when some small amount of super cooling has occurred before the FCTA. Thus at the point of crystallization, an exotherm occurs which rapidly raises the temperature a few degrees in spite of the fact that the liquid is being cooled at that point.

There is then a short time period while crystallization (exotherm) and dissolution + cooling heats are in balance forming a shoulder to the curve. The first maximum of this temperature rise is the True Crystallization Temperature (TCT), provided the super cooling has not been excessive. RP 13J calls for the procedure to be repeated two additional times, particularly if the TCT is more than 3°C greater than the FCTA.

There are also instrumental methods of determining the TCT. These systems work off the cooling curve inflection by comparing the current temperature to the previous readings over a 3 to 20 second period. Thus the FCTA is usually detected, though there can be some problem with determining the TCT if the interval between it and the FCTA is too brief to be detected by the recorder.

Present Procedure

Obviously, visual observation of the crystallization under the conditions of high pressure is difficult.

We have used the FCTA exotherm, as described above, where possible and a second physical phenomenon – pressure changes with the crystallization, as suggested by equation 2. The significant difference between the densities of solids and liquids provides for a volume loss when comparing different phases of the same mass. Provided the test cell is a closed system containing only liquids, this volume change can effect the pressure significantly. Note that this is not a gas hydrate

evaluation cell. A pressurized system with any gas phase present at all – even in small amounts – would not permit detection of the small volume changes present on crystallization. However, with a sealed, all hydraulic system, pressure changes are significant, and can be even more discernible than the exotherm in the testing of some brines.

Equipment

Work to date has been on a Fann 70 rheometer modified for use to evaluate drilling fluids at lower temperatures. The original instrument was designed as a high pressure rheometer for measuring fairly viscous fluids. The heater controls on the instrument were disabled, and the heating system was removed and replaced with internal by-pass tubing. The instrument was coupled with an external cooling bath and constant delivery circulating pump so that it was capable of reaching temperatures as low as 0°F and pressures up to 20,000 psi.

The thermocouple probe on the instrument is placed in a well outside the wetted area but not in the direct cooling fluid circulation. Thus, detected temperatures lead actual fluid temperatures by 2 to 4°F, depending upon the cooling rates and heat capacities of the fluid under test as runs at ambient pressures resulted in crystallization points by 2 to 4 degrees lower than those observed visually. For comparison, normal variance between tests by the same technician in measuring crystallization points is about +/- 2°F and about 4°F between different technicians. Thus the precision is similar, but the readings are lower.

Testing Procedures

On a typical experimental run, the pressure cell and manifold were loaded with the brine being tested while at room temperature. The hydraulic lines from the manifold back to the hand pump used to pressurize the cell were filled with hydraulic oil. After sealing the cell, the system was exhausted of air at the hand-pump vent. The cell was then brought to the test pressure and the cooling bath turned on. The bath cooled at a rate of about 2°F/minute after reaching a temperature 20°F lower than the temperature of the thermal probe. The cooling rate reached a “steady state” for a time under these conditions with the cooling bath temperature also approaching 2°F/minute. As the measured temperature reached 30°F (on those tests where it did) cooling rates declined due to limitations of the equipment to about 1.2°F/min. and to about 0.5°F at 23°F. The rheometer was run at a constant speed of 200 RPM throughout the tests to provide some stirring of the fluids.

During this time the pressure steadily fell as well, due to the normal thermal contraction of liquids. This was corrected for by periodically pressuring back up with the hand pump in units of 100 psi to 250 psi. The pressure was never allowed to fall any lower than 200 psi from the test pressure, and was usually maintained within +/- 120 psi of the target pressure.

The amount of pressure “added back” was recorded for some of these tests, and is included as “Sum of Pressure Additions” figures in the data. Thus the fluid contraction due to cooling, and the contraction due to crystallization could be

distinguished. In the discussion of further testing, plans are described to replace the hand pump with a screw driven piston, so that the volumes associated with these pressure changes might be known precisely. Finally, there were tests where first real sign of crystallization was a 'clattering' of the stirring mechanism. It was then found that the amounts of crystals in these cases was very small after the inevitable delay in opening the pressurized equipment.

Experimental Results and Discussion

While pressure sensitivity is less than thermal measurement sensitivity, pressure variations can be quite large in some cases when large differences in density between the liquid and crystal phases. Thus pressure variation can be an excellent guide in such cases. Tests with CaCl_2 and lower weight $\text{CaCl}_2/\text{CaBr}_2$ mixed brines at temperatures above 20°F fall into this class.

Conversely, mixed brines of NaCl and NaBr show very little or no pressure response, probably because of the relatively constant solubility of NaCl over wide temperature ranges and consequent small amount of new phase. Crystallization must be determined in these cases by thermal estimates. Two approaches to thermal estimates are 1.) Use of a heat of crystallization exotherm, if there is a significant one, or 2.) Observation of a change in the rate of cooling. This primarily results from the crystallization exotherm, but is determined by plotting the slope of the cooling curve (temperature vs. time).

NaCl/NaBr Brines

Mixed sodium halide brines were among the more difficult to evaluate as they showed no isotherm or significant pressure effect. However, there was a clear decrease in the rate of cooling which was used in estimating the pressure - temperature crystallization point. The actual pressure effect was less than that observed with the heavier brines as well. (Figures 1-3)

CaCl₂ Brines

Two of these were run. One was a 9.0 lb./gal brine which was also the only brine in the series that had a density less than the density of the same system at the eutectic point (the minimum crystallization temperature of any mixture of the same salt and water). This effectively means it is on the 'ice' side of the phase diagram; where ice, rather than salt, would be expected to come out of solution. However, no volume expansion was observed - either the precipitating crystal is not pure ice, or the effect is so small as to be undetected. (Figures 4-6).

The high density calcium chloride brine gave both the clearest exotherm and pressure drop observed in the testing. This is the standard stock calcium chloride brine of commerce in the United States. The brine gave a very pronounced exotherm at crystallization as well as a pressure drop. (Fig. 7,8).

CaBr₂ Brine

From an experimental standpoint, the 14.45 ppg single salt brine (CaBr_2) was the most interesting of the fluids tested. The 12,000 psi tests showed a remarkable pressure drop at $40 - 42^\circ\text{F}$. However, tests at lower pressures showed virtually no exotherm and very small changes in cooling slope, or pressure effects. The most plausible explanation of this is a change in the hydrated crystal coming out of solution. However this conclusion is tentative, in view of the limited testing. (Figures 4,9,10).

CaBr₂/CaCl₂ Brines

Three of these brines were tested, all had densities near 13 ppg. These included the brine mixture with the lowest crystallization point formulation tested during this project, and so there is a range of 40°F in the ambient TCT's of the three materials. These brines all showed both clear exothermic temperature increases and very large pressure effects in the region of crystallization. (Figure 11)

For the single salt brines of calcium chloride the crystal (precipitate) is known to be the hexahydrate at temperatures below 85°F . It is plausible to assume that primarily CaCl_2 hexahydrate comes out of a mixed $\text{CaCl}_2 - \text{CaBr}_2$ brine, particularly when large amounts of the chloride have been added, there is also the probability of a mixed precipitate forming. The precipitating solids have a propensity to dissolve before they can be separated from solution at ambient conditions.

Three salt (CaCl₂/CaBr₂/ZnBr₂) Brines.

Three different formulations in the 15.3 - 15.5 ppg weight range were run. Two higher temperature formulations showed a very clear exotherm between 68 and 76°F , as well as a pronounced pressure drop.

The remaining brine, blended for a 30°F lower crystallization range, did not show a significant exotherm or pressure loss in the region of apparent crystallization. Determination was made by estimation from the change in temperature decline slopes in the region of 30°F . Figure 12 and 13, included for illustrative purposes, shows the tests run at 12,000 psi. The most probable explanation for this is a change in the crystal coming out of solution. There were little increase in the crystallization temperature of this brine compared to the two other three-salt brines. (Fig. 14)

Joule-Thomson Heating on Compression

Being non-ideal fluids, these brines do exhibit Joule-Thomson (or Joule Kelvin) heating on compression. However, it is felt that the rapid cooling present in most sub-sea applications rules this phenomenon out in most cases. As the Joule Thomson coefficient is related to the thermal expansion and compression coefficients, it should vary little in brines of this type. Joule Thomson heating on compression was about 4°F . (Fig. 5)

Also, as indicated in the procedures discussion, efforts were made to exclude any gas from the system. These results

should not be confused with gas hydrate formation.

Proposed Equipment Modifications

The equipment used was not completely satisfactory – it had not been designed for this application. Instrumentation to more carefully evaluate the phenomenon is being constructed, but was not used for this work. Specifically, the large mass present in the pressure cell of the rheometer serves as a heat sink with a large and indefinite heat exchange surface. The instrument was cooled with separate cold bath; but this combination limited to work above 10°F and more practically to work above °F. The pressure applied by the Fann 70 is a hydraulic hand pump and the transducers are relatively less precise at higher pressures (though still good to about 1% of the total applied pressure).

The most fortunate advantage of the Fann 70 is a very sensitive temperature sensor, reporting temperature changes of 0.1°F. However, the placement of the sensor is actually outside of the pressurized cell, and so it is monitoring some average of the cooling fluid and the total stainless steel cell – not the actual fluid temperature. Thus recorded data leads the actual temperature in the pressurized cell by some function of the conductivity of the cell.

The equipment being constructed has temperature sensors in the fluid itself, in the mass of the pressure container, and in the surrounding cooling bath. The bath will be cooled at a constant rate. In addition, the cell will be pressurized mechanically with precise volume measurements noted to maintain the pressure. This may allow some thermodynamic interpretation not presently possible.

Conclusions

The effect of pressure raising the apparent crystallization temperature on high density brines has been established. Drilling in deep waters, and particularly subsea completions provide the conditions that can raise the crystallization points of heavy brines significantly. As the effect is not universal, the pressurized crystallization temperature behavior of specific brines should be known before proceeding in deep water applications or colder climates. Some basic observations we have learned so far include:

- 1.) Sodium halide brines appear to show the effect the least. This is thought to be due to the relatively constant solubility of NaCl.
- 2.) Near saturated CaCl₂ brines and mixed brines including significant amounts of CaCl₂ show pronounced pressurized crystallization temperature (PCT) behavior.
- 3.) Generally, CaCl₂ containing brines showed both a greater crystallization exotherm and a greater pressure - volume effect on crystallization than bromide brines alone.
- 4.) Modifications of existing equipment will be required for more definite determination of pressure effects where the crystallization exotherm and/or volumetric effect is small.
- 5.) The operational dangers – plugged lines and associated hazards of untimely crystallization - are present when using high density brines under conditions of combined cold and

high pressure. These can be overcome with proper selection of the brine based upon its pressurized crystallization temperature.

Acknowledgements

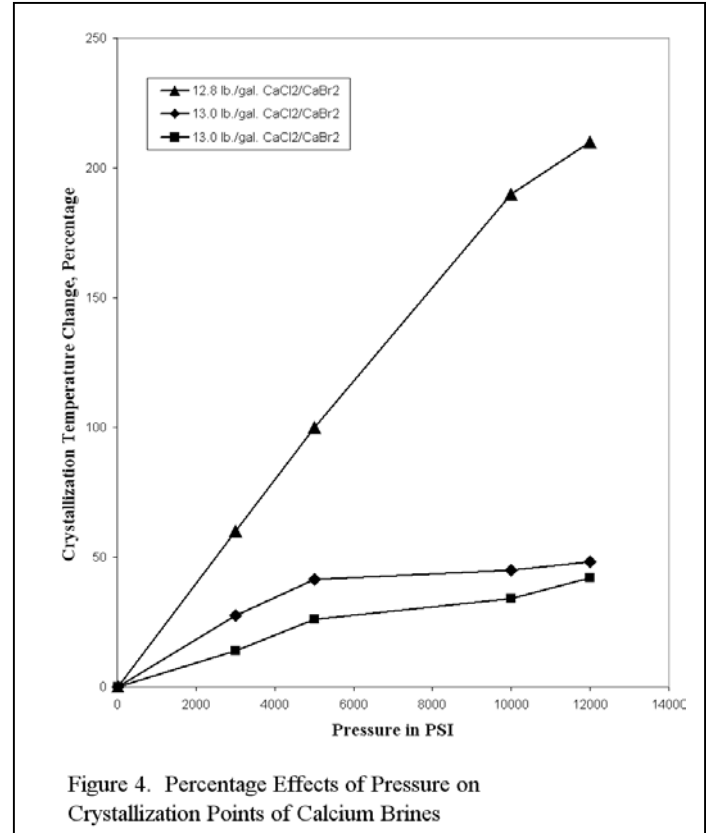
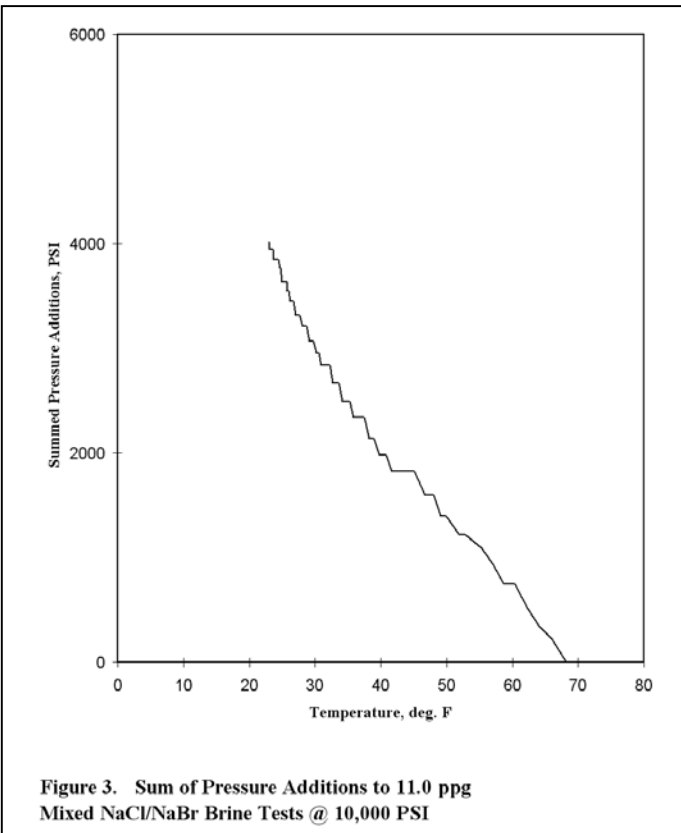
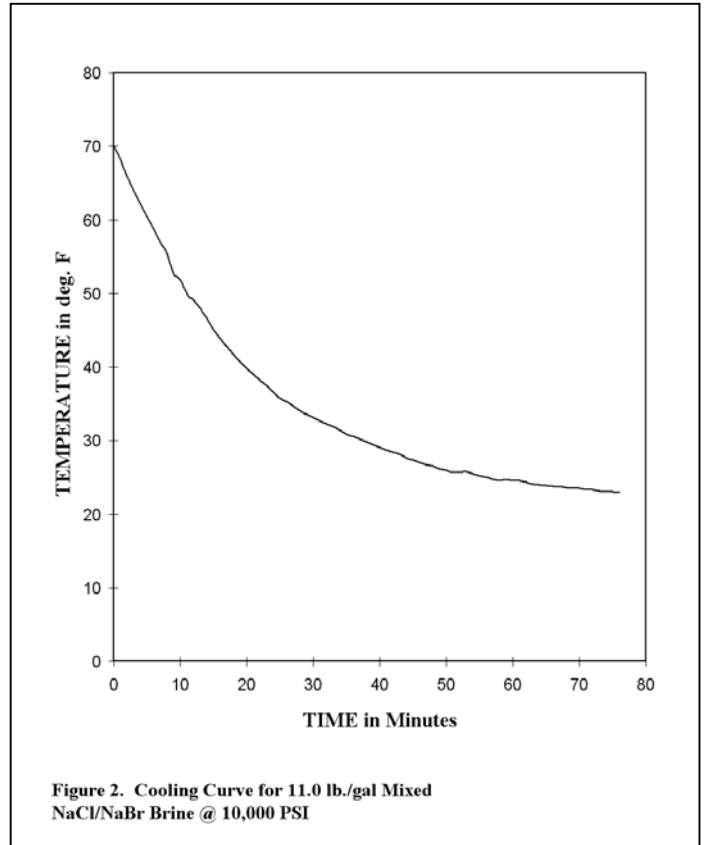
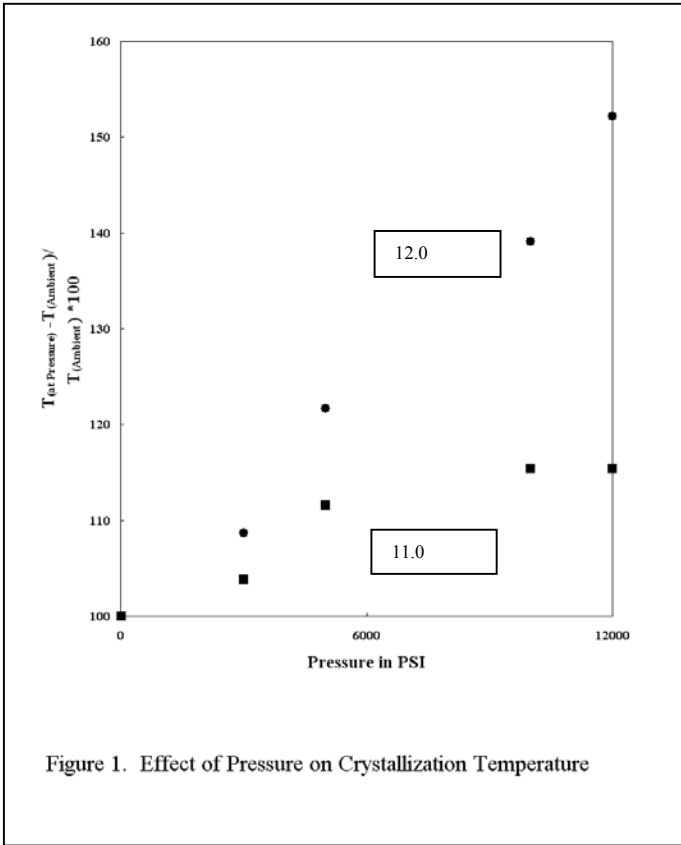
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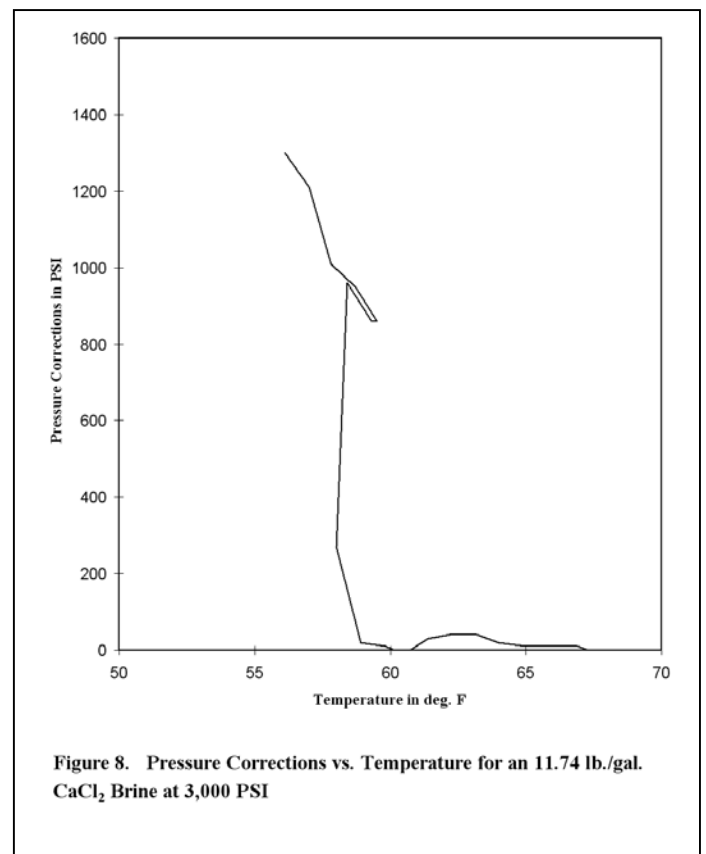
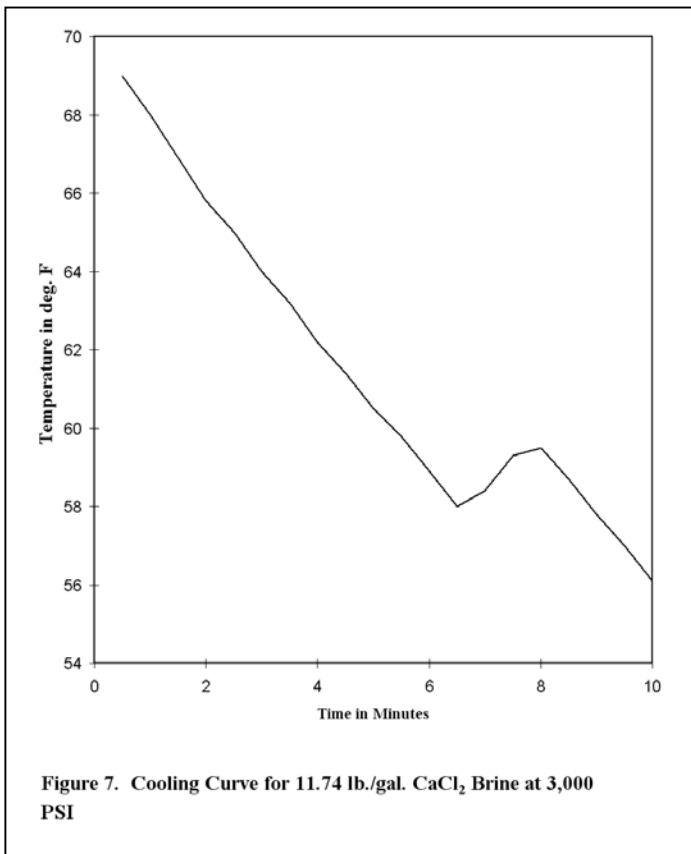
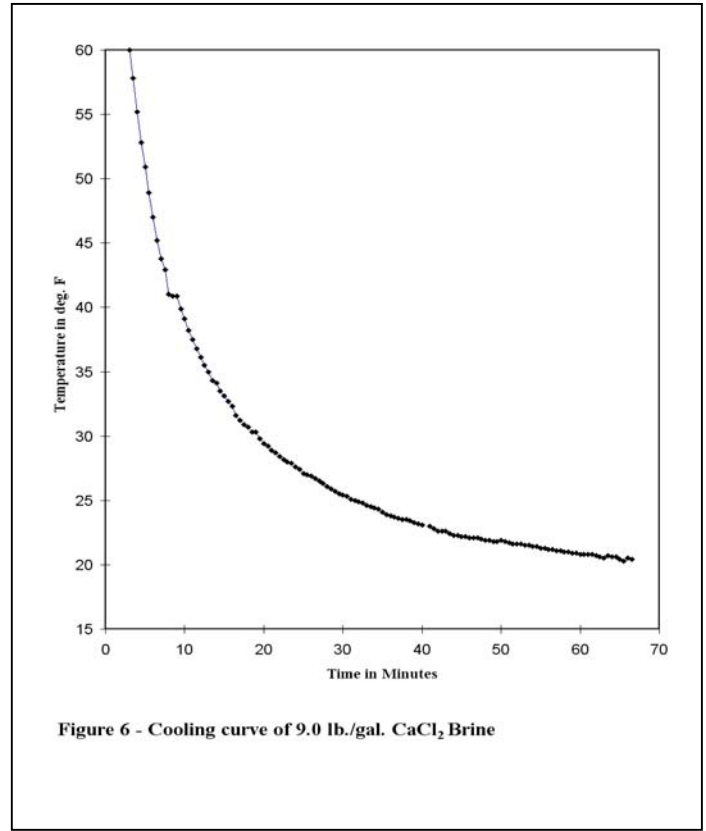
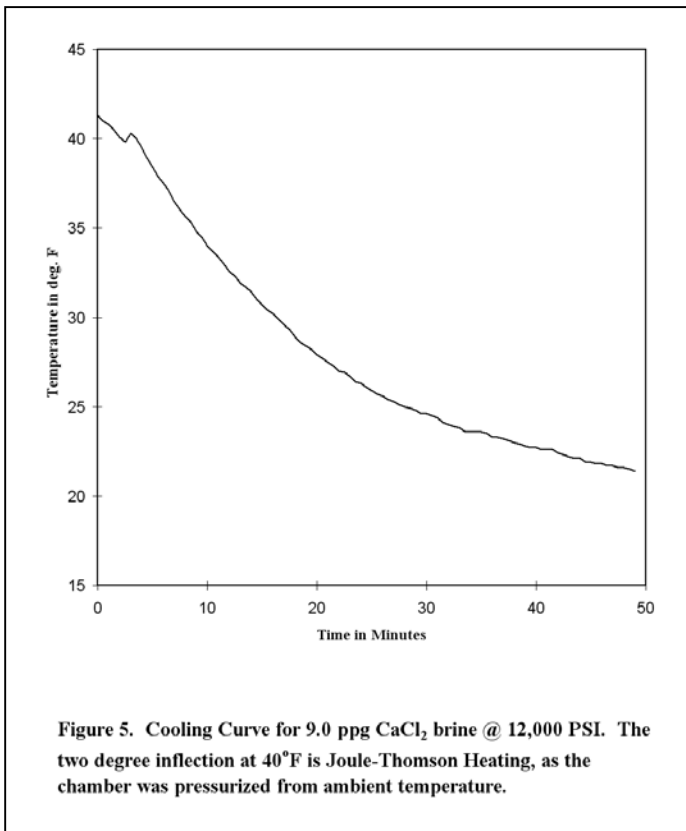
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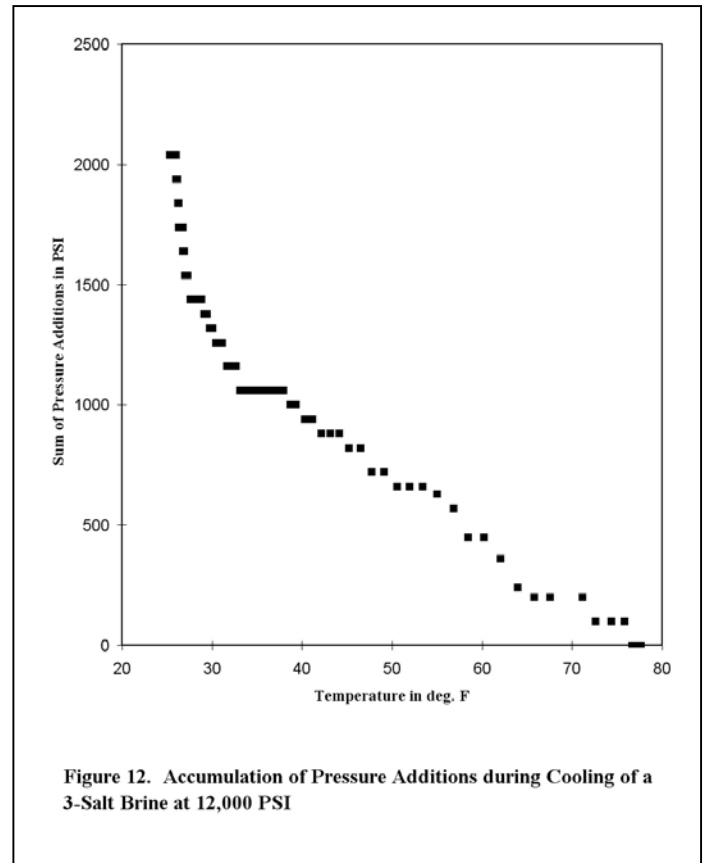
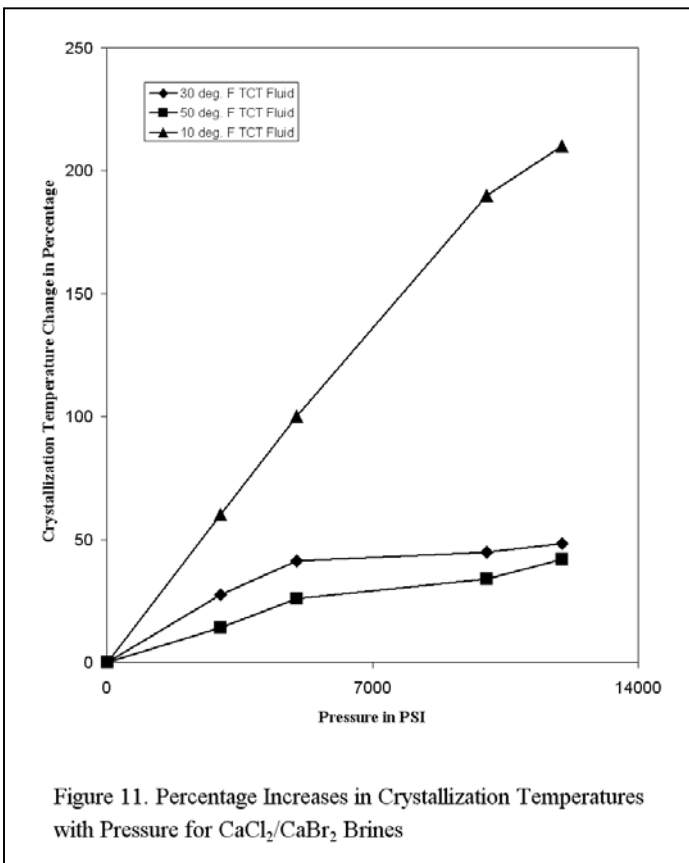
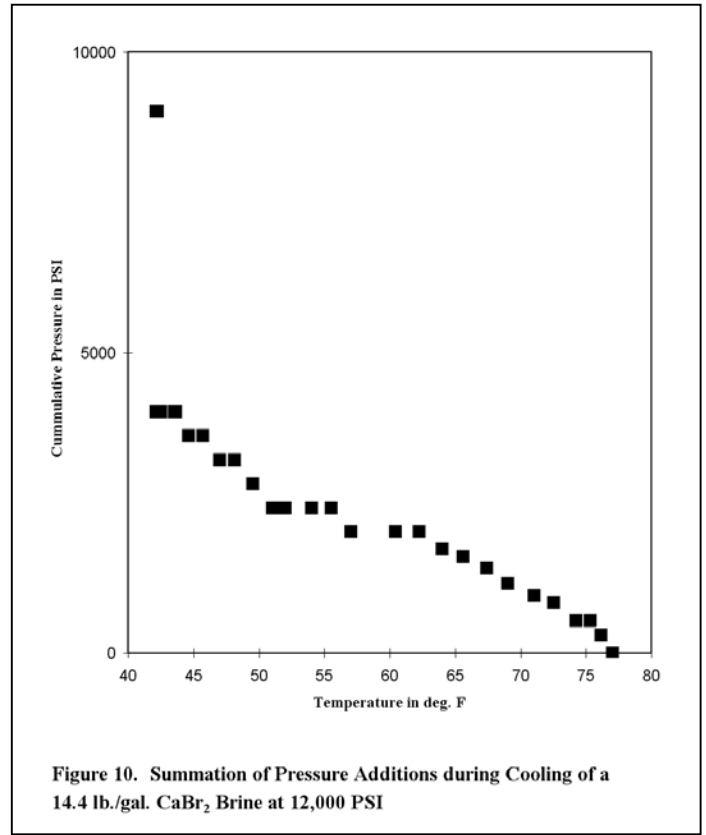
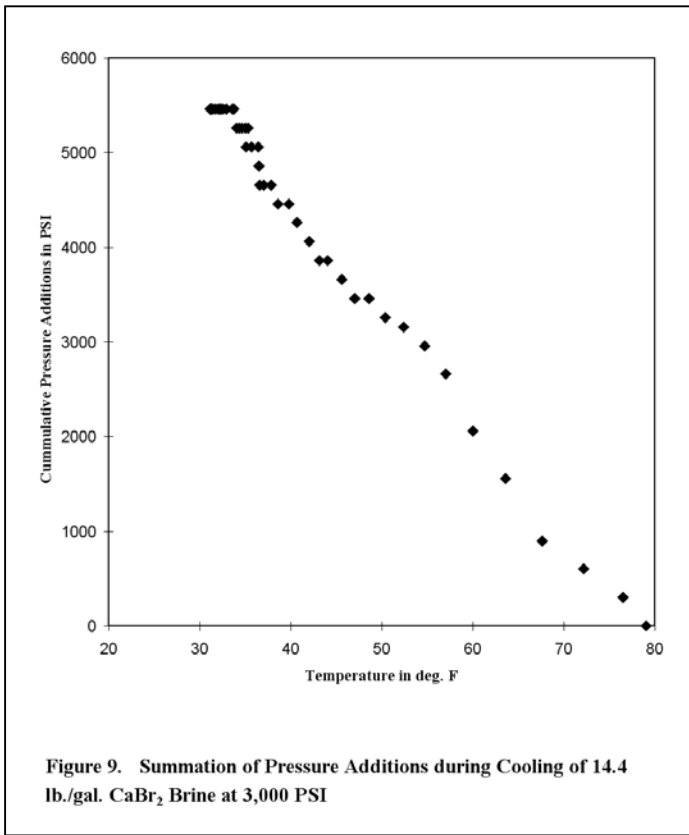
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SI Metric Conversion Factors

dynes/cm	x	1	E-03	=	N/m
(F-32)	x	5.555	E-01	=	°C
ppg	x	1.198	E+02	=	kg/m ³
PSI		6.89	E-00	=	kPa







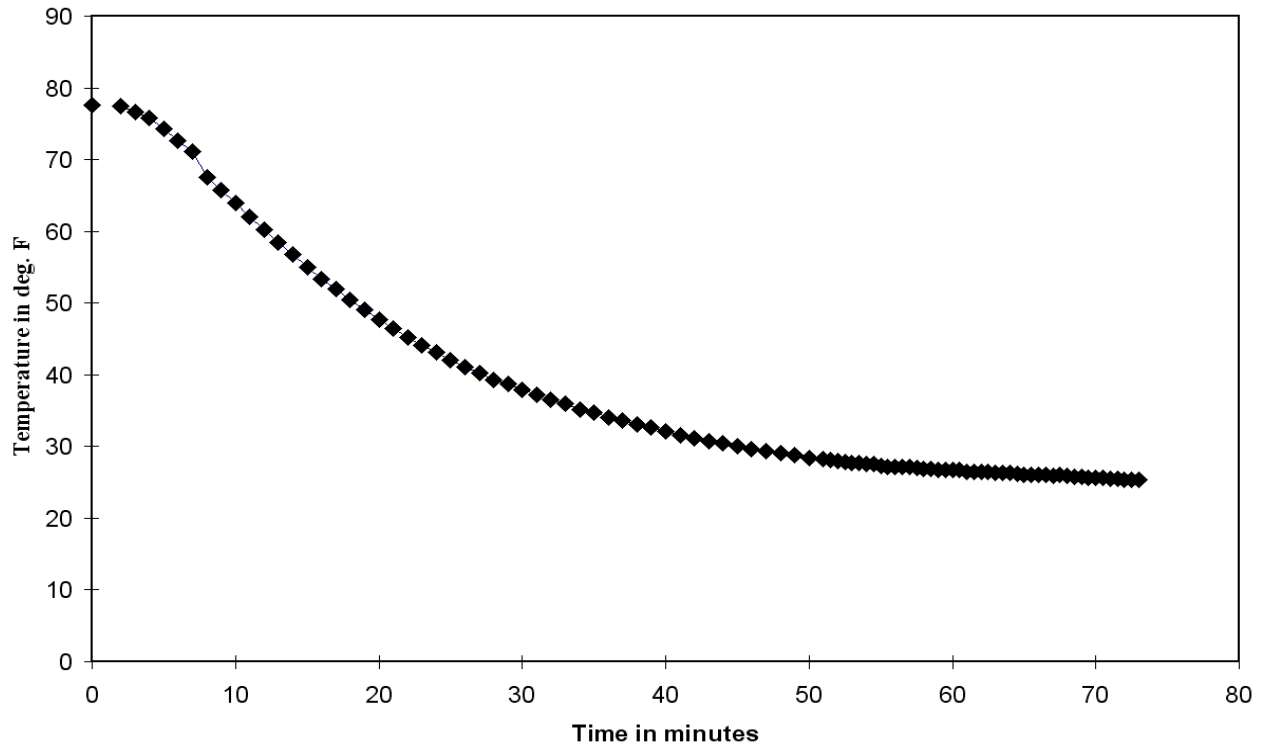


Figure 13. Cooling Curve for 15.41 lb./gal. Three-Salt Brine at 12,000 PSI

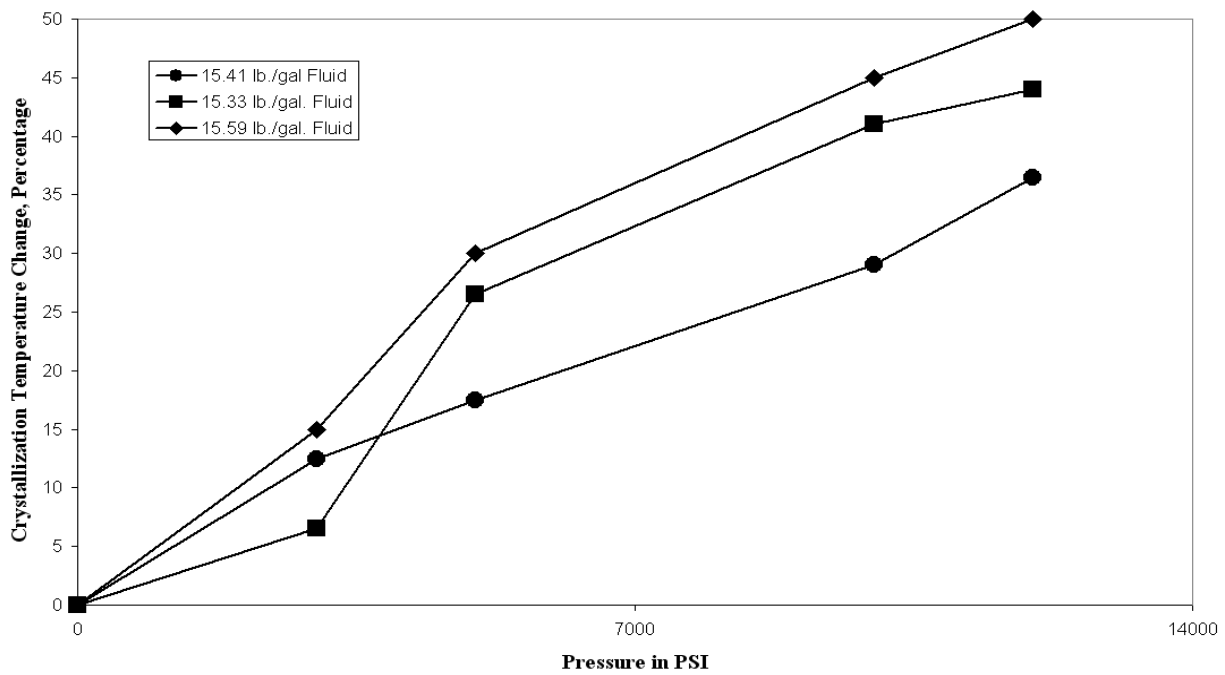


Figure 14. Percentage Effect on Crystallization Temperature of Pressure for Three-Salt Brines (ZnBr₂/CaBr₂/CaCl₂)