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Evaluation of New Equipment to Measure Pressurized Crystallization Temperatures of High-Density Brines

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Abstract

A new and commercially available instrument for measuring Pressurized Crystallization Temperatures (PCT) of high-density brines is evaluated and compared to a legacy instrument that was manufactured in-house. The new instrument offers some advantages, such as more accurate and reliable results, and easier service, over other instruments that are used currently in the industry.

To evaluate the new instrument, a 11.3 ppg $CaCl_2$ brine was used for both Gage R&R and paired t-test. For the Gage R&R test, five brine samples were prepared by five different operators. PCT of these samples were measured with the new instrument by two operators, and the measurements were run in duplicate for each sample. For the paired t-test, a large batch of the 11.3 ppg $CaCl_2$ brine was used. PCT of this stock brine was measured on two different instruments, each repeated five times. The PCT for both tests was measured under two different pressures: 100 and 15,000 psi.

Gage R&R analysis showed that the measurement is both repeatable and reproducible. The paired t-test analysis conducted at both 100 and 15,000 psi demonstrated that, at the 95% confidence level, a statistically significant difference of the means of the PCTs from the two instruments could not be detected. Also, it was found that the variation in the data from the new instrument is much lower than that of the legacy instrument.

Introduction

High density clear brines, both monovalent and divalent, are commonly used in completion and workover operations. Typical monovalent brines include sodium chloride (NaCl), potassium chloride (KCl), sodium bromide (NaBr), and formate brines (sodium, potassium, and cesium formates), while divalent brines include calcium chloride ($CaCl_2$), calcium bromide ($CaBr_2$), and zinc bromide ($ZnBr_2$). These brines cover a density range from 9.5 to 19.2 ppg. The maximum density of each brine is governed by the salt density as well as the solubility in water. For instance, NaCl salt has a solubility of 26 wt% in water at room temperature and a maximum density of 10.0 ppg; while cesium formate has a solubility of 88% and can reach a density of 20.7 ppg at room temperature.

The actual maximum density of a clear brine that can be used in the field, however, depends on its true crystallization temperature (TCT). The TCT is the temperature where solids form and precipitate out from the saturated brine solution under atmospheric pressure. The TCT is also affected by the pressure, in which case it is called pressurized crystallization temperature (PCT). The PCT is generally higher than TCT, and the effect of pressure is generally more significant for divalent brines than monovalent brines. The effects of pressure can be significant in deepwater applications and cold climates where the brines can crystallize at a temperature higher than the measured TCT under atmospheric conditions. The crystallization can result in pressure control issues due to reduced brine density, as well as plugging leading to non-productive time (NPT).

While the measurement of TCT of clear brines is commonly run following an API procedure (API 13J, 2014), the measurement of PCT is not standardized and varies from user to user. Historically, the PCT is measured either by monitoring the change of heat flow (differential scanning calorimetry (DSC)), temperature, volume, pressure, or light intensity when the crystallization occurs under a certain pressure (Helmy et al. 2021; Freeman et al. 2000). Many of these instruments are home-made and not readily commercially available, which can make it very hard or even impossible for repair and maintenance, as the technical support is not always there, and the parts may not be available anymore. It could also make it difficult to compare results from different labs or suppliers because of the different instruments used.

To address this issue, a new commercially available instrument was purchased to replace the current home-made legacy instrument. Both instruments work the same way by measuring light intensity transmitted through the sample to detect the occurrence of crystallization under pressure. Two major questions occur when replacing an existing instrument with a new one:

1. Does the instrument give reliable results? In other words, is the measurement system of the new instrument acceptable?
2. Does the new instrument give the same results as the old one?

To answer these questions, both gage Repeatability and Reproducibility (R&R) and paired t-tests were conducted to evaluate the new instrument and compare with the legacy one. Test results and data analysis confirmed that the new instrument has better repeatability than the legacy instrument and therefore is acceptable and reliable in measuring PCT

PCT Instrument

The main part of the new PCT apparatus is a thermally insulated Hastelloy cell equipped with a magnetic stirrer and a Laser Detection System (LDS) with optical fibers. The cell is also connected to a chiller and a syringe pump for temperature and pressure control (Figure 1). The cell can be pressurized from atmospheric pressure up to 20,000 psi using the syringe pump. The temperature of the sample can be regulated from 100 °F (37.8 °C) to as low as -4 °F (-20 °C) with the chiller. The cell has vent tubing controlled by Valve #1 at the top to aid in sample injection and removal of air entrainment that could interfere with light transmission through the sample. Additionally, there is injection tubing controlled by Valve #2 at the bottom. A floating piston sits in the cell that separates the pump oil and the clear brine sample to prevent contamination of the brine. The piston is connected to the syringe pump controlled by Valve #3. A laser light beam passes through the brine sample and goes into the LDS that measures the light intensity. The PCT is determined by the sudden drop in light intensity when crystallization occurs. Furthermore, the liquid sample is continuously stirred throughout the process. Finally, the instrument is fully automated with computer-controlled temperature and pressure.

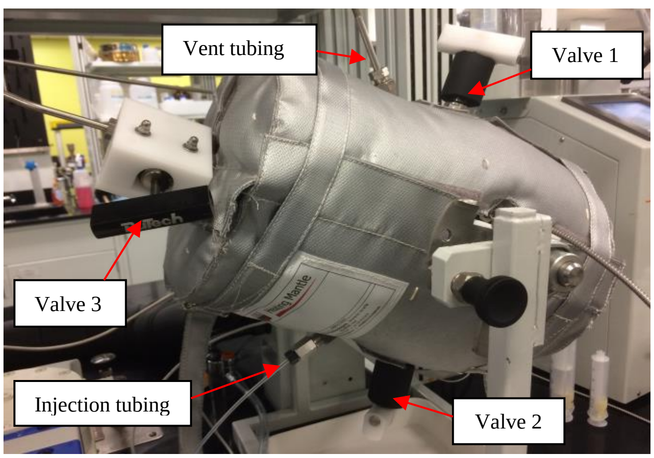

Figure 1. Hastelloy cell of the new PCT instrument

To run the PCT test, the piston in the Hastelloy cell is first pushed to the bottom. The cell is then vacuumed from the vent tubing with Valve #1 open and other valves closed. After that, close Valve #1, and inject the clear brine sample (with a small amount of diatomaceous earth as the seeding material) into the cell from the injection tubing by opening Valve #2. Open Valve #1 of the vent tubing and purge out possible remaining air bubbles that are trapped in the cell. Close Valve #1, open Valve #2, and inject the clear brine sample to push the piston upward until around 50 mL of the brine is injected into the cell. After introducing the brine, the light intensity is monitored while adjusting the mixing rate of the magnetic stirrer. If the light intensity changes erratically, that means there are still air bubbles trapped in the cell. Keep injecting the clear brine and purge out the air bubbles until the light intensity remains stable at different mixing rates. Once finished, close both Valve #1 and #2 and open Valve #3 and start the testing following a pre-determined testing schedule.

Figure 2 shows an example of the PCT test results of a 11.3 ppg $CaCl_2$ brine at 15,000 psi. As can be seen from the figure, the whole cooling and heating cycle was repeated for four times (red line for temperature). The light intensity (%, black line) dropped from 46% down below 10% each time the crystallization occurred. The PCT measured during the first cycle is generally lower than the other three likely due to supercooling effect. Once supercooling is overcome, the subsequent three cycles generally give very close PCT values and are used to calculate the PCT value as the average of the three readings.

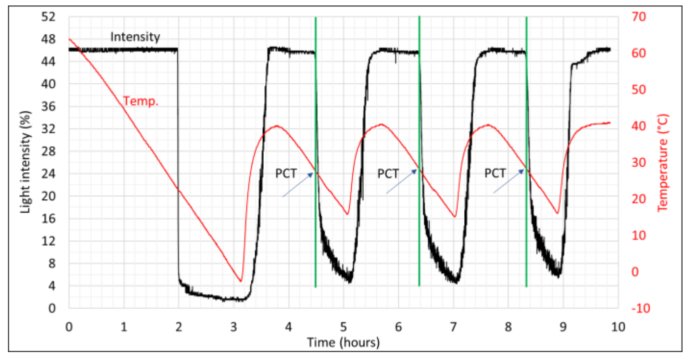

Figure 2. PCT measurement results by the new instrument

Gage R&R Test

Gage R&R test is used to evaluate the new instrument to see if it is a reliable instrument. For this test, five samples of 11.30 ppg $CaCl_2$ brine were prepared by five different operators. The brine samples were made by slowly adding 248.7 g of $CaCl_2$ salt (anhydrous) into 427.0 g of DI water, while cooling the container in an ice-water bath. The actual densities of these samples were measured using a pycnometer with an analytical balance, and the results are shown in Table 1.

Table 1. 11.30 ppg $CaCl_2$ brine

Samples	Density (ppg)	Operators
Sample A	11.27	1
Sample B	11.27	2
Sample C	11.29	3
Sample D	11.26	4
Sample E	11.27	5

The PCT of each of the five samples was measured by two operators on the new instrument at 15,000 and 100 psi, respectively. The measurements were run in duplicate for each sample, which added up to a total of 40 measurements for the gage R&R study. The cooling rate was set to be 0.4 °F/minute. The test was run following the same procedure as shown in Figure 2 and the results are shown in Table 2.

Table 2. PCT measurement of the 11.30 ppg $CaCl_2$ brine samples for Gage R&R

Operators	1				2			
Runs	#1	#2	#1	# 2	#1	#2	#1	# 2
Pressure, psi	15,000		100		15,000		100	
Sample A, °F	27.2	27.4	10.7	10.3	27.8	27.8	9.3	9.5
Sample B, °F	27.1	26.7	7.8	7.5	26.8	26.9	7.5	7.7
Sample C, °F	25.6	26.2	7.4	6.7	28.7	28.2	10.2	9.6
Sample D, °F	25.3	25.1	6.9	5.8	23.5	22.5	3.7	3.3
Sample E, °F	29.3	28.4	10.9	10.8	29.0	28.2	10.2	10.0

Figure 3 shows the analysis of variance results for the PCT measured at 15,000 psi. The total variation observed is 3.72, in which the part-to-part variation accounts for 95.89% (3.57), which means that the majority of the variance comes from the samples, not from the instrument. For the 4.11% of the instrument variation (which is the combination of repeatability and reproducibility), there is no variation from the reproducibility, as the means of the measurements by the two operators are nearly the same. The total Gage R&R variation is within ± 1.2 °F at 15,000 psi.

Gage R&R (Nested) for Meas_15k

```
Source               DF       SS       MS        F      P
Operator              1   0.0623  0.06235   0.0086  0.929
Part No. (Operator)   8  58.3156  7.28944  47.6218  0.000
Repeatability        10   1.5307  0.15307
Total                19  59.9086
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Gage R&R

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                               %Contribution
Source             VarComp     (of VarComp)
Total Gage R&R     0.15307             4.11
  Repeatability    0.15307             4.11
  Reproducibility  0.00000             0.00
Part-To-Part       3.56819            95.89
Total Variation    3.72126           100.00


                                Study Var  %Study Var
Source             StdDev (SD)   (6 × SD)       (%SV)
Total Gage R&R         0.39124     2.3474       20.28
  Repeatability        0.39124     2.3474       20.28
  Reproducibility      0.00000     0.0000        0.00
Part-To-Part           1.88896    11.3338       97.92
Total Variation        1.92906    11.5743      100.00


Number of Distinct Categories = 6
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Figure 3. Gage R&R analysis results for measurements at 15,000 psi

General guidelines for interpreting percent study variation are mentioned below and are used based on criticality of the measurement performed,

- Less than 10% - the measurement system is acceptable
- Between 10-30% - the measurement system is acceptable dependent upon method of measurement and application
- Greater than 30% - the measurement system is unacceptable and should be improved

As the percent study variation from the Total Gage R&R is 20.28%, which is less than 30%, the measurement is acceptable giving the fact that the slight change in sample density can lead to significant change in PCT, especially for near-saturated brines.

Another aspect of this analysis is the number of distinct categories. Typically, the data is considered acceptable if the number of distinct categories is equal to or greater than 5, which means that the instrument can distinguish between different samples. In this case, the number of distinct categories is 6, meaning that the measurement is acceptable.

Figure 4 shows the analysis of variance results for the PCT measured at 100 psi. Similar to the measurement at 15,000 psi, the results show that the % study variation is 15.06% (less than 30%), and the majority of the variation is from the samples and not the measurement system. The actual measurement system variation is within ± 1.1°F at 100 psi. The number of distinct categories is 9 (greater than 5) and is also acceptable.

Gage R&R (Nested) for Meas_100

```
Source               DF       SS       MS        F      P
Operator              1   0.7488   0.7488   0.0631  0.808
Part No. (Operator)   8  94.9419  11.8677  87.1343  0.000
Repeatability        10   1.3620   0.1362
Total                19  97.0527
```

Gage R&R

```
                               %Contribution
Source             VarComp     (of VarComp)
Total Gage R&R     0.13620             2.27
  Repeatability    0.13620             2.27
  Reproducibility  0.00000             0.00
Part-To-Part       5.86577            97.73
Total Variation    6.00197           100.00


                                Study Var  %Study Var
Source             StdDev (SD)   (6 × SD)       (%SV)
Total Gage R&R         0.36905     2.2143       15.06
  Repeatability        0.36905     2.2143       15.06
  Reproducibility      0.00000     0.0000        0.00
Part-To-Part           2.42193    14.5316       98.86
Total Variation        2.44989    14.6993      100.00


Number of Distinct Categories = 9
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Figure 4. Gage R&R analysis results for measurement at 100 psi

Paired t-Test

The paired t-test is used to compare two instruments, when the same set of samples are measured on both the instruments, in this case, the new and the home-made instruments. The paired t-test was conducted by measuring the PCT of the five similar samples and analyzing the results. Again, PCT was measured at 15,000 and 100 psi. A large batch of 11.30 ppg $CaCl_2$ brine was prepared by dissolving 497.42 g of $CaCl_2$ salt (anhydrous) into 875.5 mL of DI water. Table 3 shows the measurement from the two instruments. Note that there are five data points for 15,000 psi and four data points for 100 psi.

Table 3. PCT measurement of one 11.30 ppg $CaCl_2$ brine for paired t-test

Instrument	New		Legacy	
Pressure (psi)	15,000	100	15,000	100
Run 1, °F	21.2	1.2	21.4	6.0
Run 2, °F	21.2	2.3	24.3	3.6
Run 3, °F	21.2	1.9	20.5	2.1
Run 4, °F	21.0	-	20.5	-
Run 5, °F	21.2	1.8	22.0	0.6

Figure 5 shows the probability plot for the measurement difference between the two instruments at 15,000 psi. The chart shows that the paired differences are normally distributed, ensuring the accuracy and validity of the paired t-test.

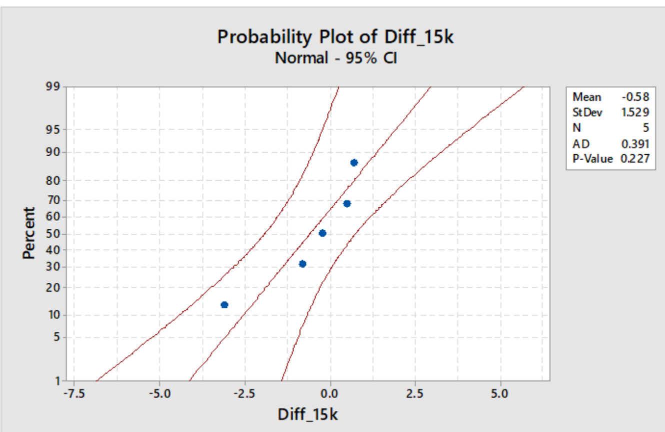

Figure 5. Probability plot for measurements at 15,000 psi

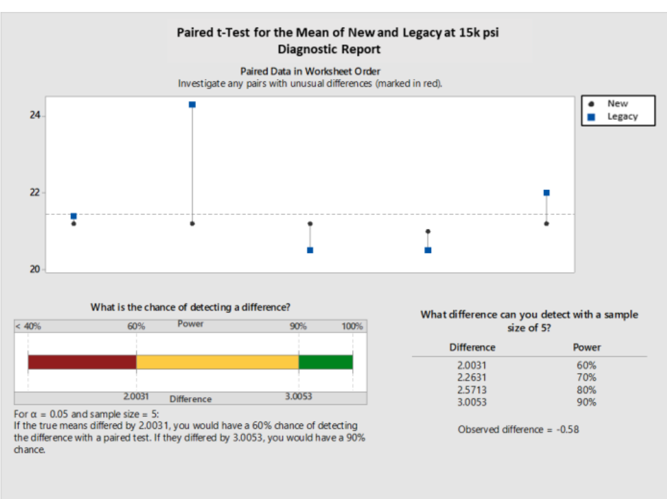

Figure 6. Diagnostic report for the measurements at 15,000 psi

Figure 6 shows the diagnostic report for the difference measured at 15,000 psi, which explains the sample size used for this analysis is adequate or not. Based on the sample size of 5, we have 60% chance of detecting the difference of 2.0 °F and 90% chance of detecting the difference of 3.0 °F between these two instruments.

Figure 7 is the summary report of the analysis for the measurement at 15,000 psi. The report shows that the mean of measurement between the two instruments is not significantly different (21.16 versus 21.74, and p value of 0.444). Because the p value is larger than 0.05, the analysis fails to reject the Null hypothesis that the difference in measurements between the two instruments is zero. The report also shows that, at 95% confidence level, the true mean difference between the two instruments is between -2.48 and 1.32 °F. Finally, the report shows that the variation of the new instrument is much lower than that of the home-made one, as evidenced by the standard derivation of measurements with the two instruments (0.089 versus 1.57). This indicates that the new instrument is more repeatable than the home-made one at 15,000 psi.

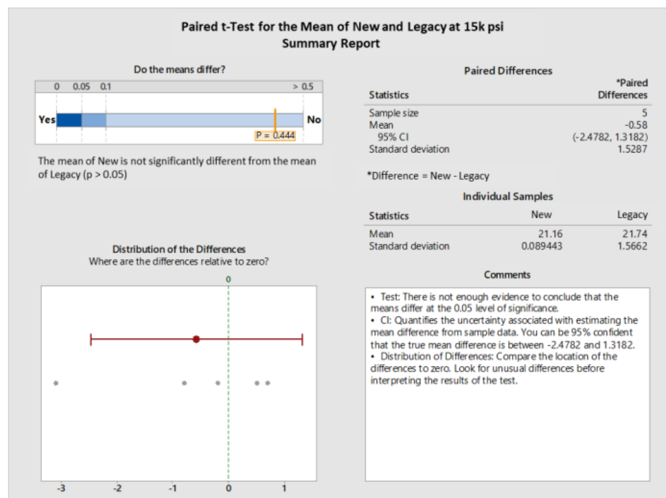

Figure 7. Summary report for the measurements at 15,000 psi

Figures 8-10 show the analysis reports for the measurements at 100 psi. Four data points were measured and used for analysis. Similar to the measurement at 15,000 psi, the paired differences are normally distributed. There is 60% chance of detecting the difference of 4.2 °F and 90% chance of detecting the difference of 6.4 °F between these two instruments.

Again, there is not enough evidence to conclude that the means differ at 95% confidence level (p value of 0.393). The true mean difference between the two instruments is between -5.35 and 2.80 °F at 95% confidence level. Again, the new instrument showed much higher repeatability compared to home-made one at 100 psi.

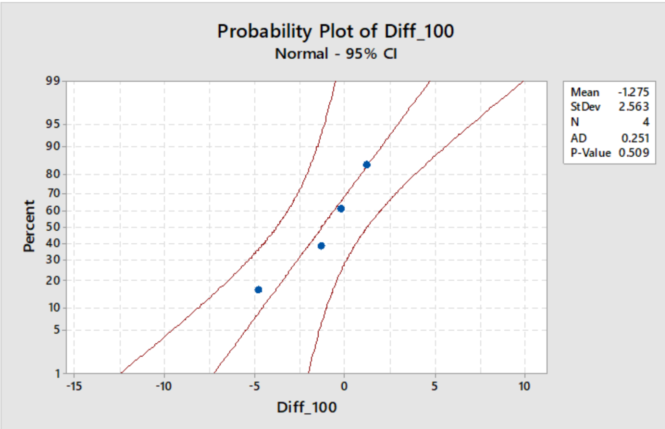

Figure 8. Probability plot for measurement at 100 psi

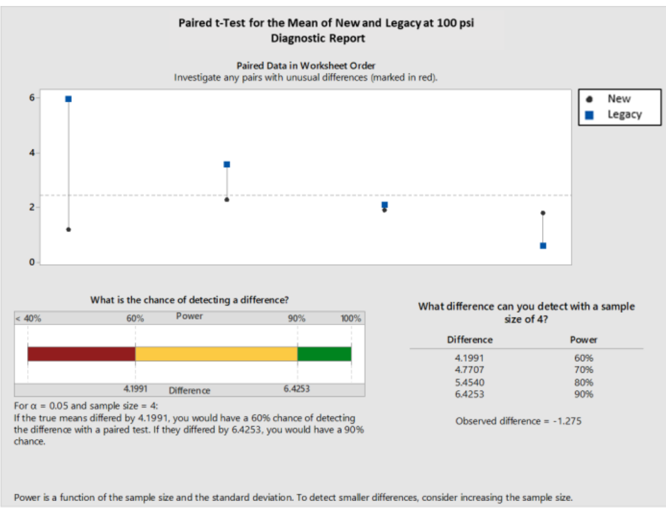

Figure 9. Diagnostic report for the measurements at 100 psi

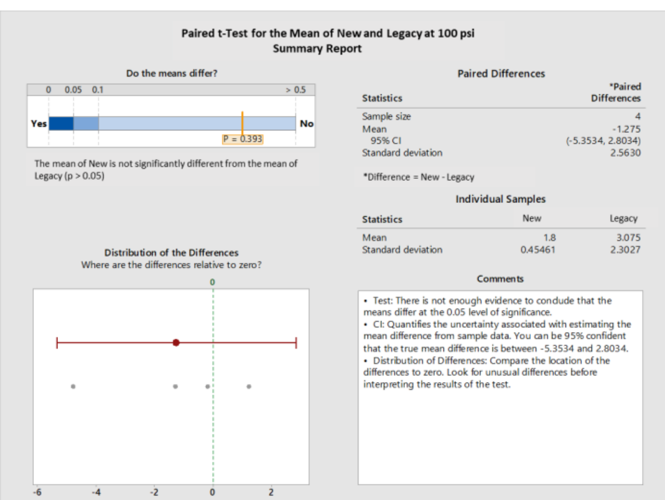

Figure 10. Summary report for the measurements at 100 psi

Conclusion

- Gage R&R was conducted to evaluate the repeatability and reproducibility of the new PCT instrument. A paired t-test was also conducted to compare the new instrument with the home-made one.
- The measurements were run at 15,000 and 100 psi and analyzed at both pressures.
- The gage R&R analysis shows that the measurement system variation (repeatability and reproducibility) is within ± 1.2 °F & ± 1.1 °F at 15,000 and 100 psi, respectively.
- The paired t-test analysis shows that the paired difference is normally distributed, ensuring the validity of the paired t-test.
- The analysis also demonstrates that there is not enough evidence to conclude that the means of the measurements from the two instruments are different at a 95% confidence level.
- The variation for the new instrument is much lower than that of the legacy one, which indicates that the new instrument produces more consistent and repeatable measurements.

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Nomenclature

ppg = *Pounds per gallon*
psi = *Pounds per square inch*

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