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Abstract

The present paper reports experimental measurements on precipitation of inorganic salts in aqueous solutions. The Focused Beam Reflectance Measurement (FBRM) was utilized as detection technique. The equipment measures the chord length of dense particles in the range of 0.5 μm to 2,000 μm . The chord length can be transformed into particle sizes, once the shape of the particles is known. The presence of solids of calcium carbonate and calcium sulfate were investigated in aqueous solution and their precipitation was studied based on *NACE Standard TM0374-2007*. Calcium carbonate and calcium sulfate precipitates were generated by mixing two incompatible brines. Concentrations of each compound in the brine were measured in a batch configuration. The concentrations of the brines were previously calculated by chemical simulation software (Oli Studio Stream Analyzer). The software determined if and when the concentration of the two incompatible brines would result in formation of scale, depending on the temperature and the ratio of the two streams. FBRM was able to detect alterations in the number of particles along time in both cases. Furthermore, the chord length distribution (CLD) was also obtained. CLD was converted to particle size distribution (PSD) by calculating the cross probability of size versus chord length. It was possible to differentiate between the calcium carbonate particles and the calcium sulfate particles, due to the differences in the shape of the particles and their respective sizes. These measurements were also confirmed by means of an optical microscope. Results were definitive in confirming the presence of each salt precipitates and the evolution in time of the solids formation.

1. Introduction

The productivity of oil and gas reservoirs may be impaired by the commingled flow of saline water, not only by the additional pressure drop caused by water, but also due to the solidification of some of the ions present in the water, upon changes in pressure and temperature. To date, most designs rely on the thermodynamic equilibrium, ignoring the kinetic aspects of solid formation. With the hope of developing more rigorous models to help decision making during the design phase (risk quantification, inhibitor injection requirements, location of injection point) experimental data are required at high pressure coherent with production conditions. Such data will help design with less conservatism the downhole umbilicals required for inhibition of solid formation.

The present work treats of experimental measurements on precipitation of inorganic salts (calcium carbonate and calcium sulfate) in aqueous solutions. **These compounds were chosen because they pose risks for oil production in high-calcium brines, typical in Brazilian pre-salt fields.** The objective is to check the capability of detection of the precipitates by the Focused Beam Reflectance Measurement (FBRM) technique as well as its adequacy to count the number of solids and its sizes. Such capability, if proved, will be helpful to extend the analysis to organic particles, namely asphaltenes, including the kinetics aspects of solidification. For the time being, experimental batch tests were carried out to evaluate precipitation of inorganic salts in aqueous solutions, while measuring and monitoring counts and dimension of solid particles with the mentioned technique.

¹ Student, Mechanical Engineer - UNICAMP

² Ph.D., Researcher – CEPETRO/UNICAMP

³ Ph.D., Researcher – CEPETRO/UNICAMP

⁴ Professor – CEPETRO/UNICAMP

⁵ Ph.D., Professor – CEPETRO/UNICAMP

⁶ Ph.D., Researcher – REPSOL SINOPEC BRASIL

The salt concentrations in the aqueous solutions were previously calculated by chemical simulation software (Oli Studio Stream Analyzer) to render the formation of precipitates, in function of the pressure, temperature and the ratio of the two streams. The technique of FBRM was employed to detect and measure the target solid particles at the experiments. The equipment operates by scanning a focused laser beam across a fluid sample. The time duration of the backscattered light reflected in the particles detected is measured and multiplied by the velocity of the rotating laser beam. The chord length distribution (CLD) was converted to particle size distribution (PSD) by calculating a probability matrix. The probability matrix refers to the probability of occurrence of a particle with a determined chord length. A specific algorithm was developed to perform the conversion. The methodology assumes particles to have a circular shape, so it applies properly to calcium carbonate precipitates. The assumption of a circular geometry translates to spherical forms when transforming chords into characteristic lengths. Such assumption, as shown by the present work, affects the size detection of particles such as those formed by calcium sulfate.

2. Material and methodology

2.1. OLI Simulator software and batch tests

OLI chemical simulator was used to preview precipitation of calcium carbonate and calcium sulfate. The following parameters were evaluated: pressure, temperature, and ratio of the combined inlet stream. Different conditions were examined out for precipitation of each inorganic salt, in order to obtain the precipitation conditions. The brines were prepared in accordance to *NACE Standard TM0374-2007*. The strategy to obtain precipitates of the inorganic salt was to mix two streams of brines, named brine 1 and brine 2. The precipitation of two inorganic salts was investigated: calcium carbonate and calcium sulfate. Tests with different operational conditions were tried in the OLI simulator. For the precipitation of calcium carbonate, one stream of brine contained NaCl (33.00 g/L), CaCl₂·2H₂O (12.15 g/L) and MgCl₂·6H₂O (3.68 g/L), while the other stream contained NaCl (33.00 g/L) and NaHCO₃ (7.36 g/L). Simulator investigated amount of precipitate in function of brine 2 proportion in the mixture, from 0% to 100%, for three pressure levels (1, 150 and 300 atm) and three temperatures (25, 65 and 100 °C). For calcium sulfate precipitation, one stream had NaCl (7.50 g/L) and CaCl₂·2H₂O (11.10 g/L), while the other was composed of NaCl (7.50 g/L) and Na₂SO₄ (10.66 g/L). Analogous simulations, as in the case of carbonate, were performed.

The low amount of precipitate predicted for 25 °C and 1 atm implicates on rendering no accessible FBRM executes accuracy measurements and detection in the batch tests at laboratory conditions, also, the experiment required a long time to initiate precipitation. So, in order to improve detection of the particles and aiming increase the quantity of precipitate, it was performed new simulations through OLI software at 25°C and 1 atm, 150 atm and 300 atm, optimizing the concentrations of brines to be used on batch tests. The new values for brine concentration are presented at Tables 1 and 2 for calcium carbonate and calcium sulfate.

Table 1. Concentration of components of the two brines for CaCO₃ formation at 25°C.

	Component	Concentration [g/L]
brine 1	NaCl	33.00
	CaCl ₂ ·2H ₂ O	22.15
	MgCl ₂ ·6H ₂ O	3.68
brine 2	NaCl	33.00
	NaHCO ₃	15.36

Table 2. Concentration of components of the two brines for CaSO₄ formation at 25°C.

	Component	Concentration [g/L]
brine 1	NaCl	7.50
	CaCl ₂ ·2H ₂ O	19.10
brine 2	NaCl	7.50
	Na ₂ SO ₄	13.66

Batch tests were performed to detect appearance and growth of the solids of the inorganic salts (calcium carbonate and calcium sulfate). During batch tests, brine was inside a plastic cup, with a propeller rotating at a speed of 400 rpm, as recommended by the manufacturer. Slowly, other incompatible brine, brine 2, was added to the cup, until the precipitation started. Because of equipment setup, batch investigation was carried out only at 25°C and 1 atm. The concentrations of the brines used were taken from the results provided by the OLI simulator. In accordance to the

composition listed in Tables 1 and 2, the brines were prepared from deionized water and analytical grade salts. Figure 1 illustrates the batch test setup used.

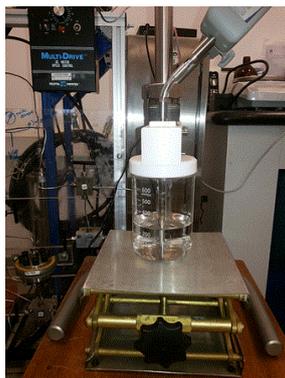


Figure 1. Batch setup.

2.2. FBRM

The Particle Track with Focused Beam Reflectance Measurement equipment relies on a probe-based instrument that is inserted directly into processes to track changing particle size and count in real time. Particles, particle structures and droplets may be monitored continuously, as experimental conditions vary. The equipment uses a laser beam, with wavelength of 780 nm, at a power level of less than 10 mW. The beam goes through a set of optics and is focused fluid next to a sapphire window. The optics rotate at a fixed speed (2 m/s) resulting in the beam spot rapidly scanning across particles as they flow past the window. As the focused beam scans across the fluid, particles backscatter the laser light to the detector. The pulses of backscattered light are detected, counted, and the duration of each pulse is multiplied by the scan speed to calculate the distance across each particle. Such distance is defined as the chord length, a fundamental measurement of the particle related to the particle size. Particles are counted and measured in time, allowing the chord length distribution to be reported in real time. The system used in the present work is a Particle Track™ G600 configuration manufactured by Mettler-Toledo. It uses the iC FBRM control software (HARDWARE MANUAL, 2013). The model system enables analysis of particle dimensions from 0.5 to 2,000 μm , with operating temperature range from -10 °C to 120 °C and pressure up to 30 MPa (300 atm).

3. Results and discussion

3.1. OLI simulation

The formation of CaCO_3 was considered as suggested by NACE Standard. Figure 2 shows results for three different temperatures: 25°C, 65°C and 100°C. Figure presents the quantity of precipitated solids in function of quantity of brine 2 (V2) in the aqueous solution for a pressure range (1 atm up to 300 atm) at three temperature levels. When brine 2 was not present in the aqueous solution, that is to say, only brine 1 formed the aqueous solution, the abscissa axis indicates zero precipitates. On the other end, when the aqueous solution is constituted only by second brine, the abscissa axis indicates 1 and it does not carry precipitates either. In between these two conditions precipitation occurs at different levels. Maximum precipitation is observed in the 60% to 80% proportion range of brine 2 in the mixture. The simulation results also show that by increasing the pressure, the amount of precipitates consistently decreased. And that, by increasing the temperature, the amount of precipitates increased. Figure 2 shows the plot of relative mass of precipitated solids in function of the proportion of brine 2 in the aqueous solution.

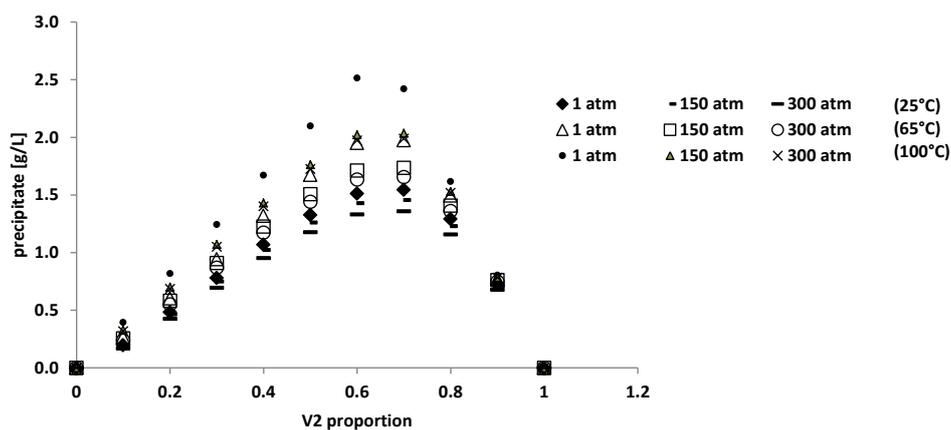


Figure 2. Precipitated calcium carbonate.

The same analysis was performed to study calcium sulfate precipitation and the results are presented in Figure 3. The maximum precipitation was observed when both brines were mixing at same proportion. Similarly, when comparing at different temperatures, the higher the temperature evaluated, the more calcium sulfate is precipitated. In all cases, the lower is the pressure, the greater is the presence of precipitates.

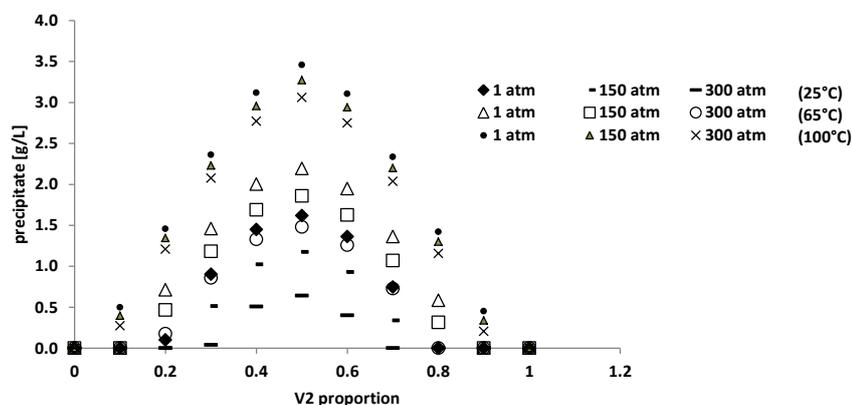


Figure 3. Precipitated calcium sulfate.

The calcium carbonate and calcium sulfate presented low amount of precipitate, in laboratory batch tests at 25°C and 1 atm. The OLI software, it was again used to check with higher brine concentrations of the specific reagents salts. In order to increase the quantity of precipitate, it was performed simulations through OLI software at 25°C and 1 atm to optimize the concentrations of brines to be used on batch tests. The new values for brine concentration were showed at Tables 1 and 2 for calcium carbonate and calcium sulfate, respectively, and OLI results are showed in Figures 4 and 5, at 25 °C.

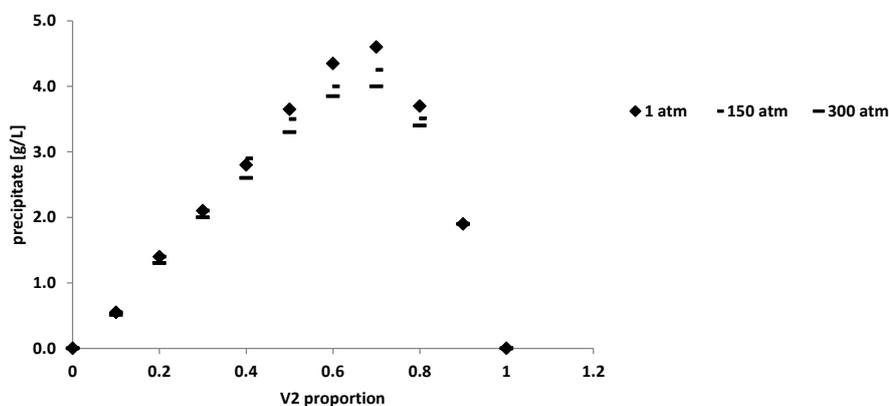


Figure 4. Calcium carbonate precipitates at higher brine concentrations.

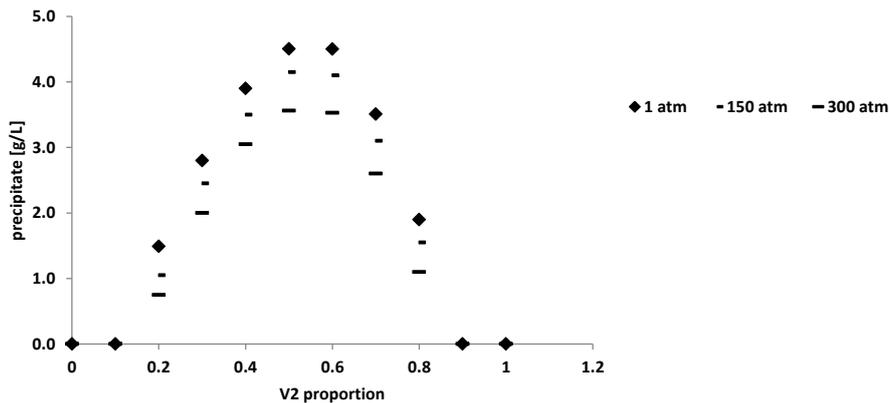


Figure 5. Calcium sulfate precipitates at higher brine concentrations.

3.2. FBRM Results

Composition brines presented at Table 1 were used to carry out the batch tests for calcium carbonate formation. First, 400 ml of brine 1 (composed by $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NaCl) was introduced in the recipient cup. After that, 16 ml of brine 2 composed by NaHCO_3 and NaCl were sequentially added at intervals of ten minutes until reaching 192 ml in total. The detector was kept on monitoring for seven hours. Figure 6 presents the evolution of counting for CaCO_3 separated in 3 chord length ranges, of less than 10 μm , between 10 and 50 μm and from 50 to 150 μm . Due to the precipitation, counts of particles with chord lengths less than 10 μm and from 10 to 50 μm increased.

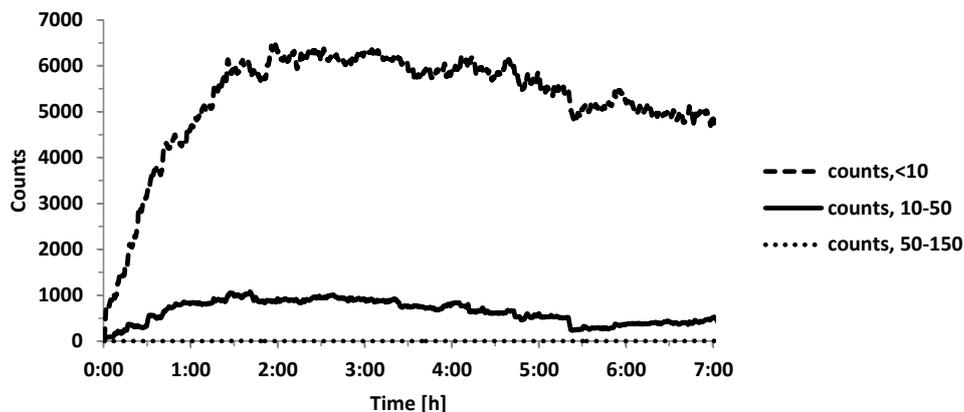


Figure 6. Counts of CaCO_3 precipitates.

After three hours from the beginning of the test, the chord length distribution of the particles inside the recipient followed the pattern showed in Figure 7. The majority of particles were with chord lengths less than 10 μm . Few amounts, less than 1.5 μm and between 10 and 40 μm , could also be detected.

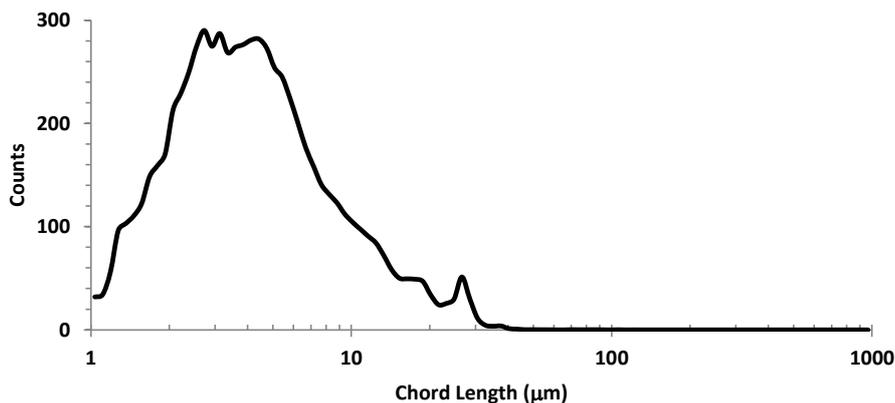


Figure 7. Chord length distribution for CaCO₃, after three hours of test.

The aqueous solution was leaved to stand still for 48 hours and after that the measurement was again carried out to verify if formation CaCO₃ solids had stopped. Figure 8 displays the countings. The smaller particles, with chord lengths less than 10 µm, presented counting below 200, while the range between 10 and 50 µm were around 280 counts. Now, the majority of particles, with 450 counts, were with chord lengths from 50 to 150 µm. This pattern was clearly different from that viewed just after the mixing of two brines.

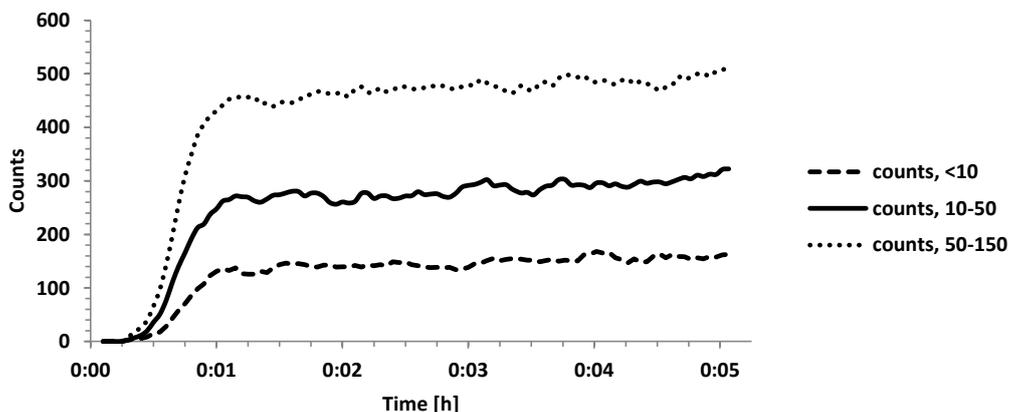


Figure 8. Counts for CaCO₃ solids, after still for 48 hours.

Figure 9 indicates the chord length distribution observed four minutes after re-starting the measurements with the batch cup left still for 48 hours. Comparing to Figure 7, the chord length was shifted to greater values. The high count in the 50-150 range shows a dense concentration of particles around 100 µm. The value is characteristic of the CaCO₃ salt; leading to conclude that the component was completely precipitated.

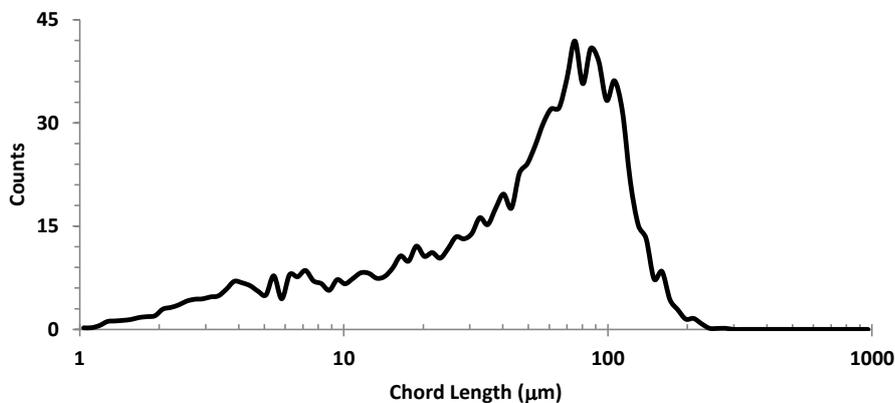


Figure 9. Chord length distribution four minutes after restart

In order to investigate CaSO₄ precipitation, the batch test was carried out by filling the cup with 400 ml of first brine (Na₂SO₄ and NaCl), whose concentrations are presented in Table 2. After that, 16 ml of brine composed by CaCl₂·2H₂O and NaCl were sequentially added at intervals of ten minutes, until a total of 192 ml of the second brine was injected. Monitoring of the solution by the particle detector was maintained for two first hours. Figure 10 presents the counting observed in three ranges of chord lengths (less than 10 μm, range between 10 and 50 μm and range between 50 and 150 μm).

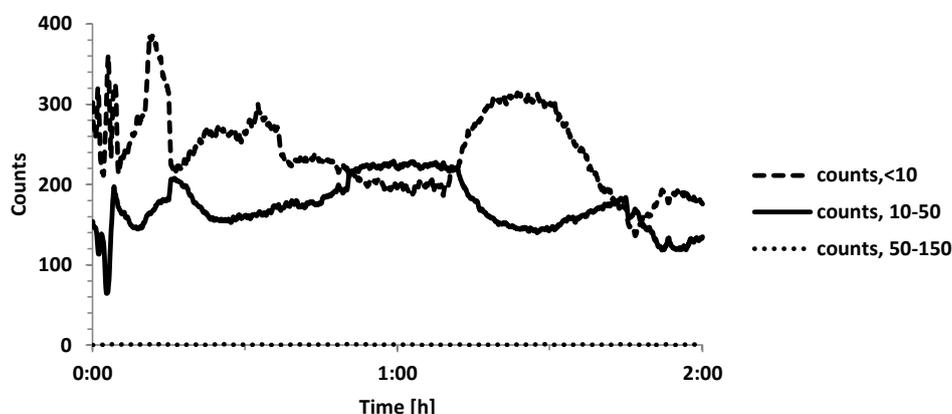


Figure 10. Counts for CaSO₄.

It was observed that stabilization was not reached in these two hours.

The chord length distribution for the precipitated CaSO₄, registered at one hour of test, can be seen in the plot of Figure 11. This pattern, with only with small particles, indicates that the process of precipitation was not finished.

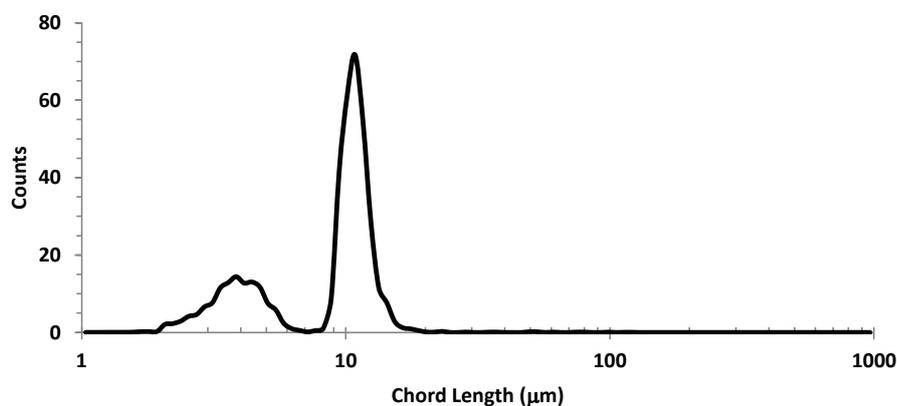


Figure 11. Chord length distribution for CaSO₄ at one hour of test.

The mixed aqueous solution was leaved to stand still in the batch cup for 5 days. On the sixth day the equipment was turned on, and the measurement was again carried out. The particle countings are displayed in Figure 12 for the next 30 minutes.

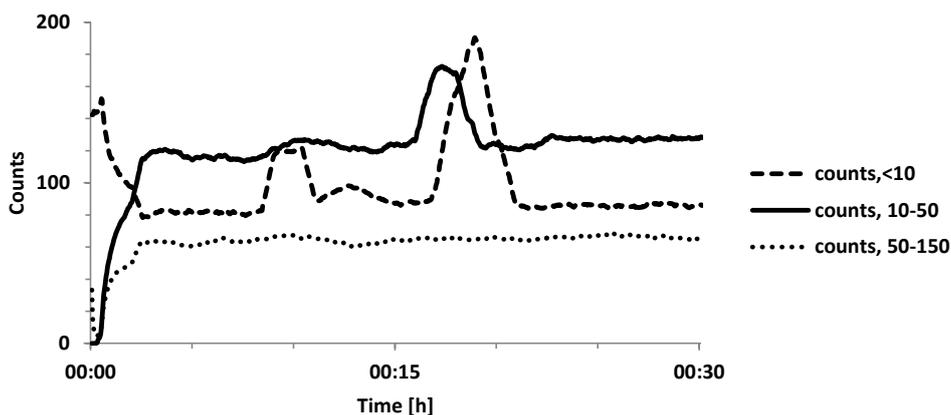


Figura 12. Countings for CaSO₄, after five days of stillness.

Figure 13 shows the chord length distribution, taken at 25 minutes of test. It can be noted that particles had dimensions approximately between 1 and 300 μm of chord length.

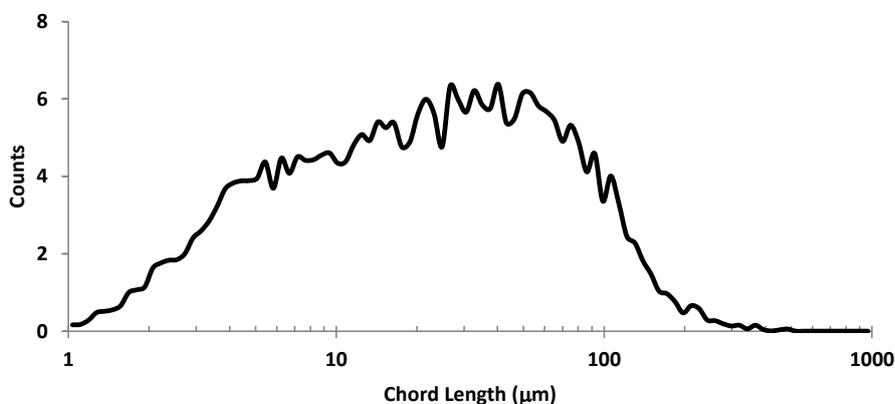


Figure 13. Chord length distribution 25 minutes after re-start.

Calcium carbonate particles were collected and analyzed by optical microscopy. It can be seen in Figure 14 that the particles showed a round shape. The average diameter was verified to be around 80 μm.



Figure 14. Calcium carbonate precipitates, 40x magnification.

The observation assured validity to the transformation of the chord length distribution into the particle diameter distribution, given that the mathematical transform used assumes particles to be spherical, in accordance Hukkanen and Braatz (2003). A routine developed in Matlab provided the conversion, whose results are showed in Figure 15 that presents graphs, one for CLD and other one for PSD. It can be observed that after conversion for PSD, there was a displacement to right in relation to CLD.

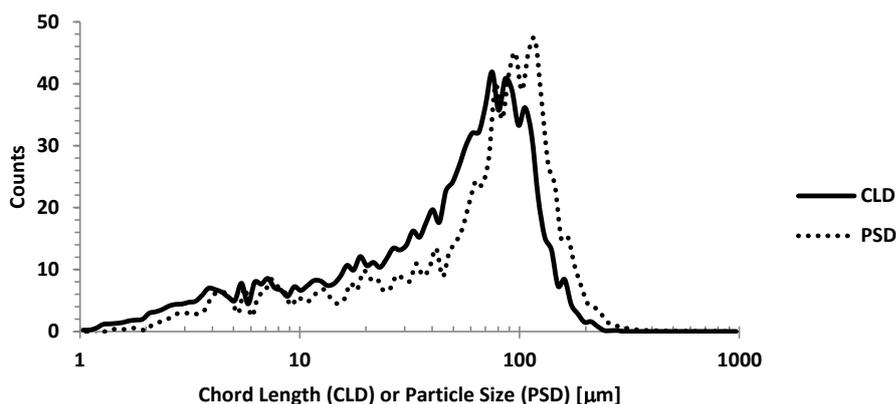


Figure 15. Chord Length Distribution (CLD) converted into Particle Size Distribution (PSD).

Also, the solution with calcium sulfate dihydrate precipitates were collected and analyzed by optical microscopy. It can be seen in the picture of Figure 16 that the particles presented an irregular pattern, of rectangular shapes. Measurements made in the microscope with the calcium sulfate particles showed geometries similar to laminates up to 80 μm in width and 300-800 μm in length.



Figure 16. Calcium sulfate dihydrate precipitates, 40x magnification.

It was not possible to correlate the dimensions observed in the microscope and the results of the FBRM batch tests in calcium sulfate precipitation analysis. As mentioned, the specific algorithm can not be applied to perform the conversion to PSD due to shape particles of calcium sulfate.

4. Conclusions

OLI simulator performed well in the evaluation of the operational conditions to predict precipitation of the inorganic salts. OLI simulation was used as tool to predict different scenarios for the deposition of the mineral scale. The software featured analysis for temperature, pressure, and composition effects for the studied system. As expected with increasing temperature, the amount of precipitate increased. At constant temperature, increasing pressures had the effect of decreasing the quantity of precipitates. The simulator proved helpful in setting up the conditions for the laboratory tests.

Results from the batch tests using the FBRM technology indicated the technique as suitable for particle size and counting in real time of calcium carbonate and calcium sulfate precipitates in aqueous solutions at room conditions and at batch configuration. Results also indicate that right after mixing the two brines, small (less than 10 μm) and medium (10-50 μm) particles could be detected and measured by the laser technique. The counting amount increased in time along the experiment showing the possibility of detecting the kinetics of solid precipitation. It allowed observing that calcium sulfate required longer times to precipitate when compared with calcium carbonate in the batch tests.

FBRM measurements provide chord length that can be converted for diameter of particle for CaCO_3 but not properly for CaSO_4 . It was possible to correlate the dimensions observed in the microscope and the results of the laser measurements. A good agreement was observed between the FBRM measurements and the microscopic observations, both in the number of particles and on the size of the particles.

FBRM technology is a rugged probe instrument and its versatile use has been illustrated in this work. It is possible to insert into large-scale vessels or pipelines to track changing particle size and count in real time at full process concentrations. By monitoring particles continuously, as operating conditions vary, it is possible to determine the cause of poor performance. FBRM is able to quickly identify process upsets at full production scale, which is important to redesign strategies and make improvements on the process.

This technique can also help to mitigate scale problems faced nowadays in petroleum industry, by testing and ranking the impact of chemical inhibitors at high pressure.

Once the formation and kinetics of inorganic salts, like calcium carbonate and calcium sulfate, are studied in function of temperature, pressure and composition, analysis could be extended to other salts of interest for the petroleum industry, such as barium sulfate.

5. Acknowledgements

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6. References

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