PRECIPITATION CAUSED BY LIQUID CO_2 IN CARBONATE FORMATION TREATMENTS, A POTENTIAL PROBLEM RESOLVED

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INTRODUCTION

Injection of liquid carbon dioxide with treating fluids has been used for many years to improve results and to eliminate some of the problems associated with the stimulation of oil and gas wells. One purpose is to promote faster cleanup without the need of swabbing. When the pressure is released at the wellhead after the treatment, the carbon dioxide vaporizes and forces the treating fluids from the formation. Presence of this gaseous carbon dioxide in these fluids reduces the weight of the fluid column so that normal reservoir drive can then help unload the fluids from the well. Rapid recovery of the stimulation fluids is normal.

Under certain conditions, dissolved carbon dioxide and calcium salts can react to form a calcium carbonate precipitate. This paper discusses the conditions of temperature, pressure, and pH under which calcium carbonate does not precipitate.

EQUILIBRIUM CALCULATIONS

The most useful tools in helping to answer questions like "How much of a substance will dissolve?" and "Will precipitation occur?" are chemical equilibrium calculations.

Chemical equilibrium is the study of those factors that influence the extent to which a reaction takes place. The quantity of products formed in relation to the quantity of reactants used is one such factor. The equilibrium constant relates the concentration of the reactants to the products. Equilibrium constants are useful in determining how much of a certain reactant or product will be present at equilibrium. For slightly soluble substances that form precipitates, such as $CaCO_3$, the equilibrium constant is simplified and called the solubility product constant (K_{sp}).

The following set of equations was used to study the $CaCO_3$-CO_2 equilibrium system to determine the amount of CO_2 necessary to cause precipitation of calcium carbonate in spent acid solutions. The particular condition of interest was the equilibrium of $CaCO_3$-CO_2 at 400° F under 12,000 psi. Due to lack of equilibrium data in the literature for these conditions, the following equilibrium equations and constants were used to obtain an approximate solubility of CO_2 in spent acid.[1,2]

(1) $CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$ $K_{sp} = 2.4 \times 10^{-6}$ at 392°F and 911.4 psi CO_2 pressure

(2) $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $K_1 = 1.7 \times 10^{-4}$ at 77°F and 14.7 psi

(3) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $K_2 = 5.6 \times 10^{-11}$ at 77°F and 14.7 psi

(4) $CO_2 + H_2O \rightleftharpoons H_2CO_3$ $K_3 = 2.6 \times 10^{-3}$ at 77°F and 14.7 psi

Substituting Equations (2), (3), and (4) into (1) yields

$$(5)\ K_{sp} = \frac{[Ca^{2+}]\,[CO_2]\,K_1K_2K_3}{[H^+]^2}$$

Rearranging (5) and solving for Co_2 gives

$$(6)\ [CO_2] = \frac{[H^{+2}]^2\,K_{sp}}{[Ca^{2+}]\,K_1K_2K_3}$$

With the calcium ion concentration $[Ca^{2+}]$ known, the equilibrium carbon dioxide concentration $[CO_2]$

was calculated for various pH values. Figure 1 shows the results of these calculations. The carbon dioxide concentration represents the amount of CO_2 that could be present in solution without causing $CaCO_3$ to precipitate. Once this concentration is exceeded, however, precipitation of $CaCO_3$ will occur. Solutions of 20-percent and 40-percent $CaCl_2$ were considered since these would be equivalent to the concentrations of calcium chloride obtained upon spending of 15-percent and 28-percent HCl, respectively, on calcite. As the pH increases, the solubility of CO_2 in both 20-percent and 40-percent calcium chloride solutions decreases. Also, at any specific value of pH, as the calcium chloride concentration increases the solubility of CO_2 decreases. Therefore, based on the above equilibrium calculations, the lower the pH the greater the solubility of CO_2 in calcium chloride solutions.

RESULTS OF MODEL STUDIES

Model studies were conducted to experimentally verify the effects of pH, temperature, and pressure on the solubility of CO_2 in calcium chloride solutions. Three separate series of tests were conducted.

The first series of tests were performed to determine the effect of CO_2 on the pH of the calcium chloride solutions. These tests consisted of bubbling carbon dioxide through 20-percent and 40-percent calcium chloride solutions for approximately 30 minutes at 77°F and 14.7 psi. As the CO_2 was bubbled through the calcium chloride solutions, the pH was measured with a calibrated pH meter. A

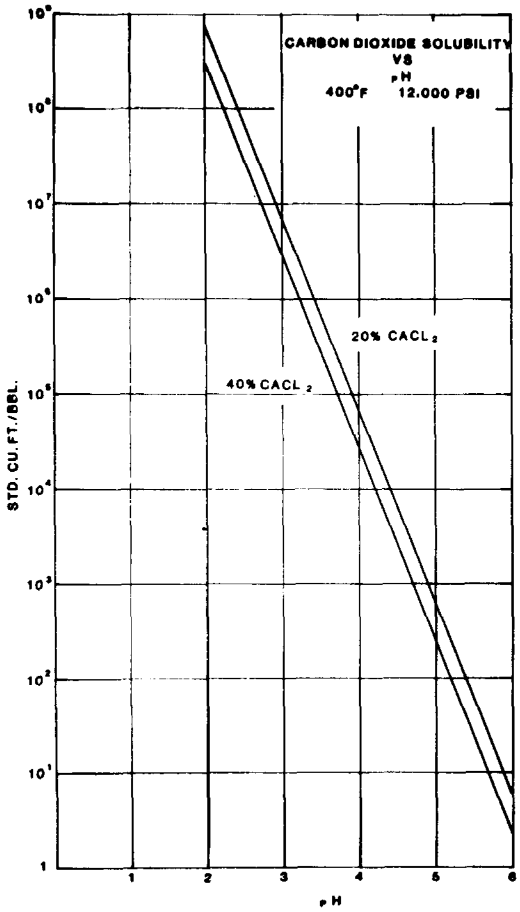

FIG. 1—CARBON DIOXIDE vs pH AT 400°F AND 12,000 psi

TABLE I—pH OF SPENT ACID

Type of Solution	Temperature (°F)	CO_2 Pressure (psi)	pH Initial	pH Final	Visual Observation
20% $CaCl_2$*	77	14.7	9.2	4.45	No observable ppt.
40% $CaCl_2$*[1]	77	14.7	7.6	2.75	No observable ppt.
15% HCl + 10% CH_3COOH**	400	800	0	3.5	No observable ppt.
28% HCl**	400	800	0	4.0	No observable ppt.

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* CO_2 bubbled through solution, pH measured with pH meter.

** pH measured using methyl orange indicator.

[1] A 40% calcium chloride solution is equivalent to 28% HCl completely spent on calcite.

lowering of the pH was observed to take place. While most of the CO_2 was not soluble in the calcium chloride solutions at atmospheric pressure, the amount that did dissolve formed carbonic acid and therefore resulted in lowering the pH. No precipitate was observed. These results are shown in Table 1.

The second series of tests were conducted to study the effect of temperature, pressure, and pH on 28-percent HCl and on a mixture of 15-percent hydrochloric acid plus 10-percent acetic acid reacting on calcite in a CO_2 atmosphere. After reaction, the 15-percent hydrochloric acid plus 10-percent acetic acid mixture should have a lower pH value than the 28-percent hydrochloric acid due to the slower spending rate and buffering effect of the acetic acid. Calcite crystals and 28-percent HCl were place in a visual pressure cell. Another pressure cell was filled with calcite crystals and a mixture of 15-percent hydrochloric acid plus 10-percent acetic acid. The cells were then pressured with carbon dioxide and heated to 400°F. Methyl orange indicator was added to the two solutions while bubbling CO_2 into the cells. Addition of indicator was repeated over a 48 hour period approximately every 6 hours. The results of these two tests are given in Table 1. In each case no precipitate was observed. This was due to the low pH values and the limited amount of CO_2 present in the test cell. Theoretical calculations shown in Figure 1 indicate that at a pH of 4, 2.56×10^4 SCF of CO_2 could be soluble in spent 28-percent HCl. An even larger amount of CO_2 would be soluble in the spent mixture of 15-percent hydrochloric acid plus 10-percent acetic acid mixture at a pH of 3.5. Because of pressure limitations of the test cells, these high concentrations of CO_2 could not be obtained. Therefore no precipitate was formed. It is not known what effect temperature has on the color change of the methyl orange indicator. This may account for the anomaly in the pH data shown in Table 1 where a lower pH value was measured in the 40-percent $CaCl_2$ solution that had CO_2 bubbled through it at 77°F and 14.7 psi as opposed to the spent 28-percent HCl acid solution in a pressure cell at 400°F and 800 psi.

The third series of tests were conducted to verify equilibrium calculations at bottomhole temperature and pressure and to show the effect of a pressure drop. Dry ice (CO_2) was added to a closed test cell. The test cell was then pressured with 20-percent or 40-percent calcium chloride solution to 12,000 psi and placed in an oven heated to 400°F. With the test cell at 12,000 psi and 400°F, the release valve was opened and the pressure allowed to drop to atmospheric. The valve was closed, and the test cell was cooled by quenching in water. The cell was opened, and the solids removed and analyzed by x-ray diffraction. The results of these tests are reported in Table 2. In each case no $CaCO_3$ precipitate was formed. According to equilibrium calculations a pH value greater than 4 would have had to be reached for $CaCO_3$ to precipitate in 20-percent and 40-percent $CaCl_2$ solutions under these test conditions.

TABLE 2—$CaCl_2$-CO_2 COMPATIBILITY TESTS

Temperature = 400°F Pressure = 12,000 psi

Test No.	Percent $CaCl_2$	SCF CO_2	*Results After Opening Test Bomb
1	20	1,200	No solid on the inside of the bomb
2	40	1,200	A very hard crystalline material reformed
3	40	600	A wet deposit was found
4	40	900	A wet deposit was found

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* X-ray diffraction analysis indicates that all of the deposits were $CaCl_2$.

CASE HISTORY

A gas well in Western Oklahoma was treated with 15-percent HCl containing 1200 SCF CO_2/bbl of acid. The 15-percent HCl and the CO_2 were pumped simultaneously at a rate of 20 bpm and 5 bpm, respectively. The well, completed in the Hunton Formation (dolomite), was approximately 25,000 feet deep with a bottomhole pressure of 12,000 psi. The bottomhole temperature was 425°F. Upon flowing back the treating fluid after the treatment, the wellbore became plugged with what appeared to be calcium carbonate. The solids were shaped like small round balls and laboratory analysis revealed they were calcium carbonate. After the calcium carbonate plug was removed from the well, it was discovered to be a dry hole and abandoned.

Based on experience, the pH of the returning fluid would be expected to be reasonably close to what was calculated because the acid should have been completely spent at that temperature. Taking into account the CO_2 produced by the spending of the acid on the formation plus the CO_2 added with the acid, a pH of 4.8 at bottomhole conditions was calculated. Figure 1 shows that at a pH value of 4.8 the maximum amount of CO_2 soluble per barrel of 20-percent $CaCl_2$ is 1500 SCF at 12,000 psi and 400°F. If the pH of the returning fluid exceeds 4.8, calcium carbonate precipitation will occur under these conditions. The calcium carbonate precipitate in this case was probably formed by the returning fluid experiencing a pressure drop. A rapid pressure drop would decrease the solubility of the CO_2 in the spent acid solution. As the CO_2 gas leaves the spent acid solution, the equilibrium of Equation (7) is shifted to the right causing $CaCO_3$ to precipitate.

$$Ca^{2+} + 2HCO_3^- \overset{-\Delta P}{\underset{+\Delta P}{\rightleftarrows}} H_2O + CO_2 + CaCO_3 \qquad (7)$$

Also, the returning fluid could have mixed with formation water, to some degree, thereby increasing the pH of the fluid. A rise in pH would also decrease the solubility of the $CaCO_3$ causing precipitation. All these effects can be additive.

SUMMARY

Calculated and experimental results have shown that under certain conditions of temperature, pressure, and pH, $CaCO_3$ scaling can be avoided. Precipitation of calcium carbonate may be controlled by maintaining a lower pH of the returning fluid. One means of accomplishing this is to use a buffered acid solution such as HCl containing acetic acid. Such solutions can maintain pH between 2.0 - 3.5, depending on temperature.

APPENDIXES

Effect of Temperature and Pressure on the Solubility of Carbon Dioxide in Calcium Chloride Solutions

Temperature Effect

The solubility of carbon dioxide in calcium chloride solution decreases as the temperature increases. This is shown in Figure 2. Mackenzie[3] studied the temperature effect over the range of 115° to 176°F in calcium chloride solutions up to 16-percent by weight at 14.7 psi pressure.

Pressure Effect

Prutton and Savage[4] have studied the solubility of carbon dioxide in 10-, 20-, and 30-percent calcium chloride solutions. These studies were conducted over the pressure range of 220 to 10,334 psi at

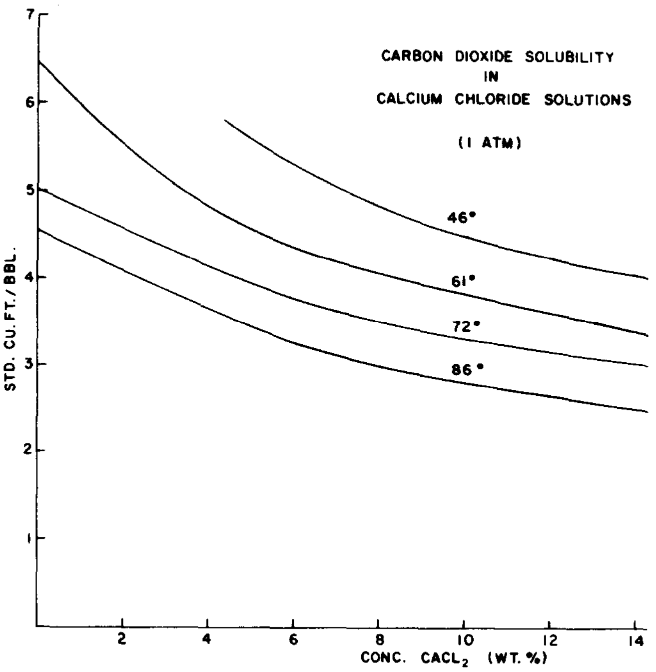

FIG. 2—CARBON DIOXIDE SOLUBILITY IN CALCIUM CHLORIDE SOLUTIONS (1 ATM)

TABLE 3—SOLUBILITY OF CARBON DIOXIDE IN 10.1-PERCENT CALCIUM CHLORIDE SOLUTION

168°F		214°F		250°F	
Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution
235	0.0026	250	0.0021	309	0.0027
235	0.0027	250	0.0022	309	0.0027
911	0.0081	823	0.0081	1117	0.0061
926	0.0083	1764	0.0112	1132	0.0069
2381	0.0133	1764	0.0113	2190	0.0113
2396	0.0133	3131	0.0135	2249	0.0111
4557	0.0154	3131	0.0140	4366	0.0148
4822	0.0158	4204	0.0147	4410	0.0148
6262	0.0170	4204	0.0152	6424	0.0168
6556	0.0168	5101	0.0162	6762	0.0167
8600	0.0184	5174	0.0159	8600	0.0184
9114	0.0192	5586	0.0165	9129	0.0181
		5792	0.0168	10334	0.0193
		7350	0.0174		
		8453	0.0185		
		9085	0.0186		

temperatures of 169°, 214°, and 250°F. Their conclusions were that as the pressure is increased, the solubility of carbon dioxide is also increased. However, as the temperature is increased at constant pressure, the solubility of carbon dioxide is decreased. These results are shown in Tables 3, 4, and 5. It is interesting to note that the change in the solubility of carbon dioxide in water with pressure follows Henry's law up to pressures of about 1,470 psi. Above 1,470 psi, deviations occur. Prutton and Savage[4] observed very large deviations for the solubility of carbon dioxide in the calcium chloride solutions in which there was a definite salting out effect. Sander[5] concluded that the compressibility maximum for carbon dioxide at temperatures from 122° to 212°F lie between 1,470 and 2,940 psi and that above this point the gas phase assumes the property of a liquid, being only slightly compressible. Wiebe and Gaddy[6] confirmed Sander's opinion that the mutual solubility of a liquid in a liquid is affected by pressure to only a slight extent.

TABLE 4—SOLUBILITY OF CARBON DIOXIDE IN 20.2-PERCENT CALCIUM CHLORIDE SOLUTION

169°F		214°F		250°F	
Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution
323	0.0022	338	0.0017	368	0.0017
338	0.0022	338	0.0018	368	0.0019
1073	0.0058	1294	0.0059	926	0.0039
1073	0.0060	1338	0.0058	926	0.0029
2426	0.0088	2087	0.0074	2205	0.0073
2440	0.0086	2087	0.0074	2205	0.0073
4145	0.0097	2484	0.0084	4116	0.0094
4263	0.0098	2499	0.0083	4145	0.0094
6674	0.0107	4263	0.0097	6821	0.0110
6762	0.0108	4292	0.0099	7218	0.0110
8408	0.0117	8320	0.0116	7438	0.0113
8820	0.0118	8438	0.0118	8849	0.0117
		9526	0.0123	9349	0.0115
				9687	0.0115

TABLE 5—SOLUBILITY OF CARBON DIOXIDE IN 30.2- PERCENT CALCIUM CHLORIDE SOLUTION

169°F		214°F		250°F	
Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution	Pressure (psi)	Mole Fraction of CO_2 in Solution
221	0.0009	1088	0.0031	1220	0.0031
221	0.0009	1117	0.0033	1250	0.0031
1073	0.0036	2220	0.0047	2176	0.0045
1088	0.0037	2264	0.0049	2205	0.0045
2367	0.0052	3440	0.0054	4351	0.0058
2396	0.0051	3499	0.0052	4439	0.0058
4616	0.0060	3837	0.0058	6615	0.0063
4689	0.0061	5704	0.0064	6880	0.0061
6336	0.0067	5718	0.0064	7262	0.0065
6689	0.0066	5909	0.0063	7497	0.0069
7718	0.0070	7718	0.0070	9776	0.0074
8144	0.0070	9261	0.0071		
9188	0.0069				

Table 6 shows that solid calcium carbonate in contact with the calcium chloride and carbon dioxide system resulted in only a small increase of the concentration of carbon dioxide dissolved in 10-percent calcium chloride. Below 100 atmospheres the solubility was generally the same for carbon dioxide in calcium chloride with and without calcium carbonate present. Above 1,470 psi the solubility increased by less than 4-percent.

TABLE 6—SOLUBILITY OF CARBON DIOXIDE IN 10.1-PERCENT CALCIUM CHLORIDE SOLUTION WITH SOLID CALCIUM CARBONATE PRESENT AT 248°F

Pressure (psi)	Mole Fraction of CO_2 in Solution
412	0.0030
412	0.0030
1073	0.0071
1088	0.0082
2279	0.0116
2293	0.0124
4542	0.0153
4675	0.0159
7056	0.0179
7232	0.0184
9452	0.0195
9629	0.0198
12201	0.0220
12848	0.0212

The low solubility of carbon dioxide in calcium chloride and water solutions, even at high pressures, indicates that the reaction of hydrochloric acid on calcium carbonate formations during acid treatments of oil and gas wells results in carbon dioxide being evolved during the reaction.

The Effect of Temperature, Pressure, and Carbon Dioxide Concentration on the Solubility of Calcite

Temperature Effect

Berendsen[7] has shown that the solubility of calcite decreases with increasing temperature. His work was done at 212°, 392°, and 572°F and at 14,500 psi pressure for various carbon dioxide concentrations. The solubility of calcite tends to follow the same pattern as carbon dioxide solubility in water and carbon dioxide solubility in calcium chloride.

Pressure Effect

Miller[8] has studied the solubility of calcite at various temperatures and pressures of carbon dioxide. He found that as the pressure is increased, the solubility of calcite is also increased. His results are shown in Table 7. Berendsen has also studied the effect of pressure on solubility of calcite but over a larger range of temperatures and pressures. His results agree with those of Miller, and he concludes that the effect of pressure is more pronounced at 212°F than at higher temperatures.

TABLE 7—SOLUBILITY OF CALCITE AT VARIOUS TEMPERATURES AND PRESSURES OF CARBON DIOXIDE

Temp. °F	Grams $CaCO_3$ per Liter Partial Pressure CO_2 in					
	14.5	145	290	580	725	1450
32	1.34	2.46	----	----	----	----
50	1.11	2.15	----	----	----	----
68	0.91	1.88	2.33	2.81	----	----
77	0.82	1.75	2.16	2.62	2.85	----
86	0.72	1.63	2.01	2.44	2.62	----
104	0.55	1.39	1.73	2.08	2.22	2.51
122	0.43	1.17	1.46	1.74	1.86	2.15
140	0.36	0.97	1.22	1.44	1.56	1.80
158	0.30	0.79	0.99	1.20	1.30	1.49
176	0.26	0.66	0.83	1.01	1.08	1.24
194	0.23	0.58	0.70	0.85	0.90	1.04
212	0.20	0.52	0.61	0.71	0.77	0.88
221	0.19	0.49	0.53	0.66	0.71	0.81

Carbon Dioxide Concentration Effect

Berendsen has found that small concentrations of carbon dioxide have a strong effect on the solubility of calcite. As carbon dioxide concentration increases, the increase in solubility continues at a decreasing rate to a maximum at concentrations between 0.8 and 1.2 mole/kg CO_2, the precise value of which depends on the particular temperature and pressure conditions. At higher carbon dioxide concentrations, calcite shows a slow decrease in solubility.

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