

Effectiveness of Calcium Sulfate Scale Inhibitors in Spent Hydrochloric Acid/Seawater System

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Abstract

Previous results have reported the precipitation of calcium sulfate during matrix acid treatments when seawater was used to prepare HCl-based acid. Precipitations of calcium sulfate causes severe damage on the permeability of carbonate reservoirs and negatively impacts the performance of acid treatments. Typically, scale inhibitors are applied in the field to prevent the formation of calcium sulfate scale, and the object of this study is to evaluate the effectiveness of different types of scale inhibitors to inhibit the formation of calcium sulfate scale during the acid stimulation process. Scale inhibition efficiency was determined in batch tests under different temperatures (77 to 210°F) and different degrees of spent acid conditions. Sulfate ions were analyzed in the samples of the batch tests to detect the precipitations of calcium sulfate. Results showed that application of scale inhibitors can successfully mitigate calcium sulfate scale formation up to 210°F. At higher temperatures, the rate of calcium sulfate precipitation increased and the effectiveness of all types of scale inhibitors decreased greatly. Most of the scale inhibitors were not effective in acidic conditions and some of the scale inhibitors even precipitated out of the solution in the presence of high concentration of calcium ions. Methylene phosphonic acid scale inhibitor was the most effective one under various experimental conditions. The findings in this study provided information for better calcium sulfate scale control under acid stimulation conditions.

Keywords: Calcium sulfate; Scale inhibitor; Acid Treatment; Formation Damage; Seawater

Introduction

The potential of calcium sulfate precipitation is greatly increased when seawater is used for matrix acidizing treatments [1-3]. In those processes, calcium concentration is greatly increased, due to the reaction of the hydrochloric acid with calcite in the carbonate reservoir rocks. High concentrations of calcium ions will combine with high levels of sulfate ions in seawater, and significantly increase the scaling tendency of calcium sulfate. Moreover, the solubility of calcium sulfate drops greatly once the acid is spent [4-6]. Those two factors account for the precipitation of calcium sulfate once it exceeds the critical scaling tendency of calcium sulfate [7-9]. Calcium sulfate will deposit in the stimulated flow channels [10], possibly causing blockage of pore throats and severely impairing the formation permeability [11]. Hence, decrease well injectivity or productivity [12,13]. Even worse, the nucleation and precipitation process of calcium sulfate during acidizing treatments may affect the acid reaction with carbonate rocks, and cause a limited acid stimulation effect [3].

Typically, the application of scale inhibitors has been an economical method used to mitigate calcium sulfate [14-16]. The use of scale inhibitors may act either as chelating agents to form a soluble complex [17-19], or as threshold inhibitors, which block the development of the supercritical nuclei [20,21], or as retarders of the growth of the calcium sulfate crystals [22-24]. By simply adding an acid-soluble and effective scale inhibitor into the acid system, mineral scale formation can be prevented during the process of acid stimulation [25-27]. In addition, combining scale inhibition and acid stimulation into a single package inherently reduces well intervention costs and well downtime, and therefore achieves significant economic benefits [28]. In this study, the effectiveness of various scale inhibitors to prevent the formation of calcium sulfate was evaluated in acid stimulation process, and the specific challenges of calcium sulfate scale control were discussed.

Experimental Studies

Fluids preparation

A synthetic seawater solution was prepared according to the composition of seawater in the Arabian Gulf at Kuwait [29], Table 1. The synthetic seawater with a density of 1.028 g/cm³ at 77°F was

Arabian Gulf at Kuwait	Ion Concentration, mg/l
Chloride (Cl ⁻)	23,000
Sodium (Na ⁺)	15,850
Sulfate (SO ₄ ²⁻)	4,000
Magnesium (Mg ²⁺)	1,765
Calcium (Ca ²⁺)	500
Bicarbonate (HCO ₃ ⁻)	142
Total dissolved solids (TDS), mg/l	45,157
pH	7.8
Density, g/cm ³	1.028

*Measured at 77°F

Table 1: Composition of synthetic seawater.

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Abbreviated Name	Active Ingredient	Approximate Activity, %
A	Phosphinopolycarboxylic acid	29
B	Sulfonated polymer	31
C	Polyacrylic acid	19
D	P tagged sulfonated polymer	45
E	Diethylenetriamine penta(methylene phosphonic acid)	18
F	Bis-hexamethylene triamine-penta(methylene phosphonic) acid	12

Table 2: Scale inhibitors used in this study.



Figure 1: Visual cell.

Degree of Spent Acid	Case	Density, mg/l	pH	HCl Concentration, wt%	Sulfate Concentration, mg/l
15 wt% Live HCl	Acid	1.07	0	15.42	2300
	Mixtures	1.04	0	3.86	3510
10 wt% Partially Spent HCl	Acid	1.1	0	9.58	2820
	Mixtures	1.05	0.08	2.65	3600
5 wt% Partially Spent HCl	Acid	1.17	0	5.03	3350
	Mixtures	1.06	0.4	1.37	3810
1 wt% Partially Spent HCl	Acid	1.18	0.5	1.11	3600
	Mixtures	1.07	1.1	0.28	3850
0 wt% Completely Spent HCl	Acid	1.2	7.7	0	3920
	Mixtures	1.19	7.8	0	3940

Table 3: Properties of spent acids and mixtures of acid with seawater.

used to prepare HCl acid. All the salts used to prepare the seawater were obtained from Mallinckrodt Chemical Inc. Hydrochloric acid at 15 wt% was prepared using seawater through dilution of 36 wt% HCl, which was obtained from Mallinckrodt Chemical Inc., and 0.45 vol% corrosion inhibitor was added to the acid. The corrosion inhibitor was received from a local service company. To prepare spent-acid solutions, the required amount of calcium chloride was added to prepare spent-acid solutions of 10,5,1, and 0 wt% HCl from live 15 wt% HCl.

Types of scale inhibitors

Six different types of scale inhibitors were tested for performance comparison. All the scale inhibitors were received from a local service

company and the chemistry of all the scale inhibitors were shown in Table 2.

Visual cell

A Hassler-type visual cell was used to observe the precipitation of calcium sulfate at different temperatures shown in Figure 1. The cell is manufactured by Temco, Inc., and can withstand up to 1000 psi and 300°F.

Experimental procedures

In general, the objective of this study is to investigate the effectiveness of scale inhibitors to prevent the formation of calcium sulfate scale during core flood experimental conditions. In our previous work, 10 cm³ of 15 wt% HCl was injected into a limestone core with around 30 cm³ of pore volume [3]. Therefore, the experimental procedures used to determine the efficiency of scale inhibitors are as follows:

- 15, 10, 5, 1, and 0 wt% HCl acids were first prepared using seawater.
- Then 10 cm³ of acid and 30 cm³ (approximate one pore volume of core sample) of seawater was mixed, and scale inhibitor was added as well, taking sample #1. This is the mixture of seawater and spent acid without adding CaCl₂.
- Then the amount of CaCl₂ produced by acid reaction with calcite was added into solution, taking sample #2. The properties of different degrees of acid and mixtures of acid and seawater are shown in Table 3.
- The solution was put into the visual cell to be heated up to 150, 210, and 250°F and samples #3, #4, and #5 were taken.
- A spectrophotometer (Orbeco SP600) was used to measure SO₄²⁻ concentration, using the turbidity method (precipitation with barium chloride).

Results and Discussion

Precipitation of calcium sulfate without scale inhibitors

In the first set of batch tests, 10 cm³ of 0 wt% completely spent HCl was mixed with 30 cm³ of seawater. The visual cell was heated up to 250°F with a confining pressure of 300 psi. The sulfate concentration profiles were shown in Figure 2. Sample #1 was the mixture of acid and seawater without adding CaCl₂. Calcium sulfate began to precipitate out of solution even at 77°F (sample #2) and sulfate concentration dropped sharply to 1,300 mg/l at 210°F. However, sulfate concentration changed only a little from 210 to 250°F, possibly to due to the less change in

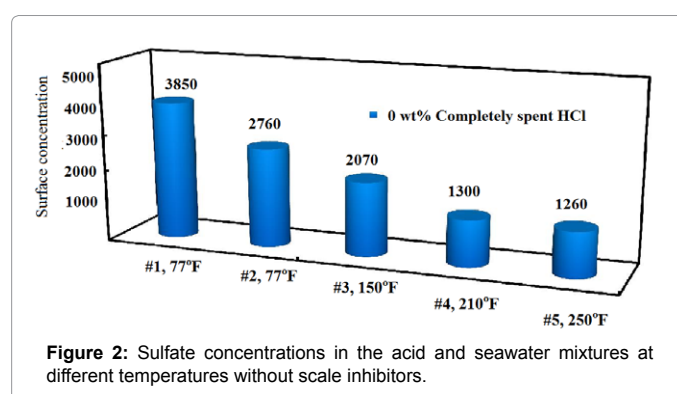


Figure 2: Sulfate concentrations in the acid and seawater mixtures at different temperatures without scale inhibitors.

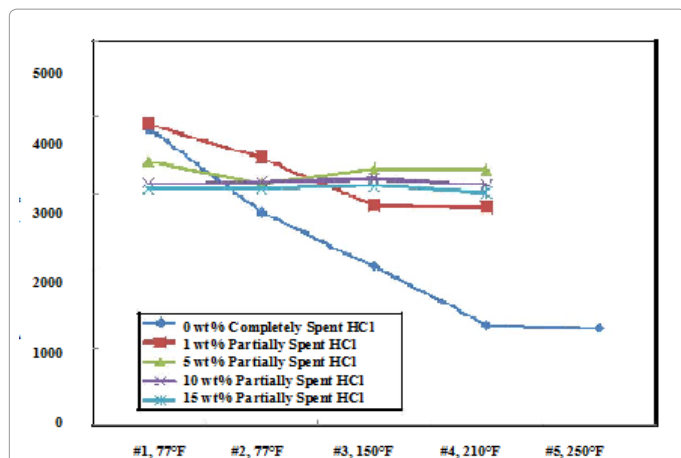


Figure 3: Sulfate concentrations in the acid and seawater mixtures at different temperatures without scale inhibitors.

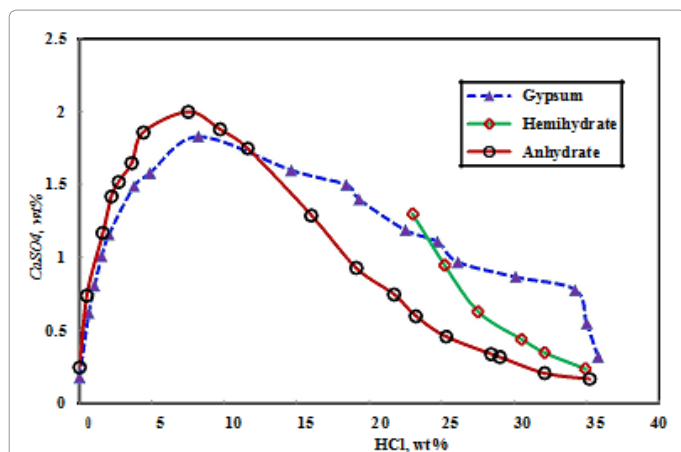


Figure 4: Solubility of calcium sulfate at 77°F (Kruchenko and Beremzhanov 1976).

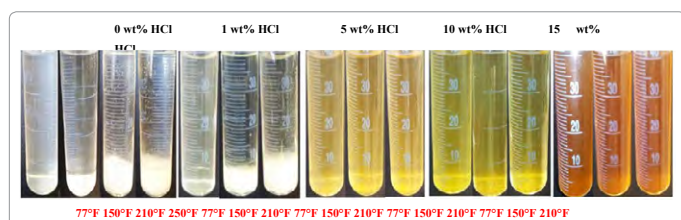


Figure 5: Precipitations were observed in the mixtures of 0 and 1 wt% spent HCl and seawater.

solubility of calcium sulfate from 210 to 250°F. Therefore, the following batch tests were done in the temperatures ranging from 77 to 210°F.

Figure 3 showed the sulfate concentration profiles under different degrees of acid spent conditions. The sulfate concentrations maintained almost constant in the mixtures of 5, 10, and 15 wt% acids with seawater. In those cases, the calcium ions produced by the reaction of HCl with calcite was not high enough to combine with sulfate ions and precipitate calcium sulfate out of solution. Besides, the solubility of calcium sulfate was more than that in completely spent acid, shown in Figure 4. The more reaction of acid with calcite was, the more calcium ions produced and the less solubility of calcium sulfate was in spent acid. Then calcium sulfate had much scaling tendency to precipitate.

Figure 5 clearly showed the precipitation of calcium sulfate at different temperatures in the mixtures of 0 and 1 wt% spent acids and seawater. The precipitations were collected at each temperature and were analyzed using Scanning Electron Microscope (SEM). Calcium sulfate was identified and the SEM images were shown in Figure 6. Further batch tests were conducted to test the effectiveness of different scale inhibitors in the mixtures of 0 and 1 wt% spent acids and seawater.

Performance of scale inhibitor in 0 wt% completely spent acid

The effectiveness of different scale inhibitors shown in Table 2 in completely spent acid was tested at different temperatures. Figure 7 showed the sulfate concentration profiles in the presence of 50 ppm different scale inhibitors. 50 ppm scale inhibitor was selected based on the previous results He et al. [3]. Contrary to the sharp decrease of sulfate concentration with the increment of temperature without adding scale inhibitors, the sulfate levels in the presence of different scale inhibitors kept almost constant at different temperatures, indicating no calcium sulfate precipitation in the solutions. This was also confirmed by the clear solutions at different temperatures shown in Figure 8. Those results showed that all the scale inhibitors performed very well in the mixtures of 0 wt% completely spent acids and seawater. The pH value of the mixtures were generally around 7.8 and the calcium ions concentration was the most among all the mixtures of different degree of spent acids and seawater. The main concern for this part is to investigate the effect of pH value on the effectiveness of scale inhibitors. That is, whether the scale inhibitors would function well in acidic conditions.

Performance of scale inhibitor in 1 wt% completely spent acid

Precipitation of calcium sulfate occurred in the mixtures of 1 wt%

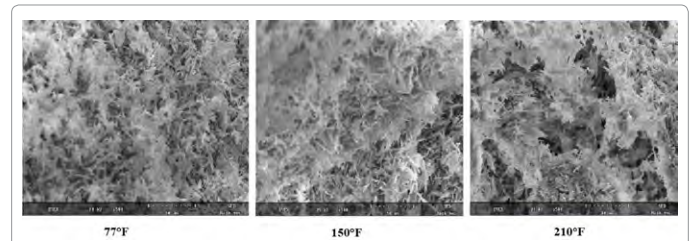


Figure 6: SEM images of calcium sulfate in the mixtures of completely spent acid and seawater without scale inhibitors.

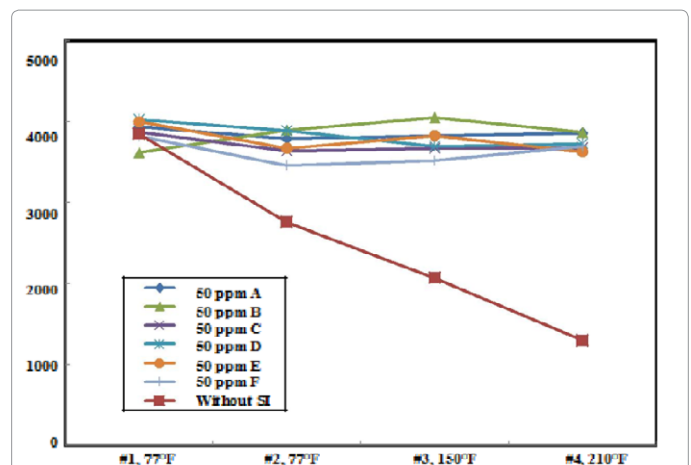


Figure 7: Sulfate concentrations in the mixtures of 0 wt% completely spent acid and seawater with 50 ppm different scale inhibitors.

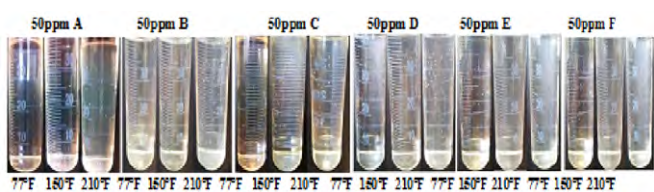


Figure 8: Clear solutions were observed in all the mixtures of 0 wt% completely spent acid and seawater.

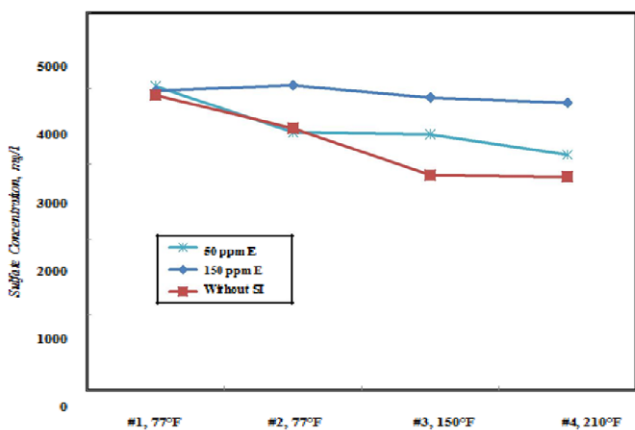


Figure 9: Sulfate concentrations in the mixtures of 1 wt% spent acid and seawater with E.

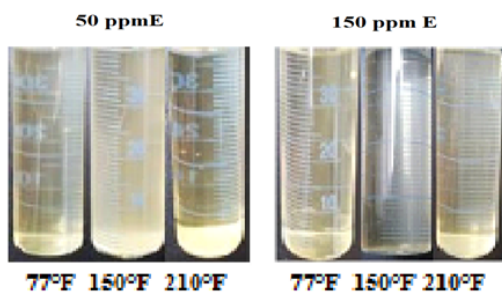


Figure 10: Performance of E as the calcium sulfate inhibitor.

spent acid and seawater, as shown in Figure 5. The pH value of the mixtures is around 1.1. The performance of all the 6 scale inhibitors can be divided into 3 categories in the very acidic conditions. With the addition of 50 ppm E, less reduction in the sulfate concentration level was observed at high temperatures in Figure 9, but there were still some precipitations of calcium sulfate out of solution (Figure 10). When the concentration of E was increased from 50 to 150 ppm, the sulfate level kept almost constant and clear solutions were shown in Figure 10. It was concluded that scale inhibitor E could function well in acidic conditions. However, higher concentrations of E were needed even the calcium ions concentration was less than that of mixtures of completely spent acid and seawater.

Figure 11 indicated that 50 ppm F and 50 ppm C were not effectively to prevent the precipitation of calcium sulfate out of the solutions at high temperatures (150 and 210°F). However, when the concentration of F was increased from 50 to 150 ppm, the sulfate level concentration almost

kept constant while there were still some precipitations out of solutions at high temperatures (Figure 12). F is a methylene phosphonic-based scale inhibitor. It could be probably that F was not compatible with the solution in the presence of high calcium ions concentration and acidic conditions at high temperatures. The performance of C was different from that of F. When the concentration of C was increased from 50 to 150 ppm, the sulfate concentration dropped sharply, even more that without adding scale inhibitors. Cloudy solution was even observed with the addition of 150 ppm C at 77°F. Those findings concluded that some scale inhibitors may function well in neutral conditions, but not certainly function well in acidic conditions. Some scale inhibitors may even be not compatible with the solution at high temperatures while some scale inhibitors may cause more severe damage.

Figure 13 showed the performances of the other 3 scale inhibitors in the mixtures of 1 wt% spent acid and seawater. B behaved like the performance of 150 ppm F. The sulfate concentration levels kept almost constant but there were precipitation out of solutions shown in Figure 14. When the concentration of B was increased from 50 to 150 ppm, more precipitations and more reduction in the sulfate levels were observed at 77°F. In the presence of high calcium ion concentration and acidic conditions, B was not compatible with the solutions even at 77°F. For A and D, they did not function well in the acidic conditions, confirmed by the reduction in sulfate level and precipitations observed in the tubes. It was interesting to note that more reduction in sulfate level occurred even at 77°F when the concentrations of the 3 scale inhibitors were increased from 50 to 150 ppm.

Figure 13 and 14 showed that more damage occurred if the concentration of the scale inhibitor was increased even at 77°F. Further

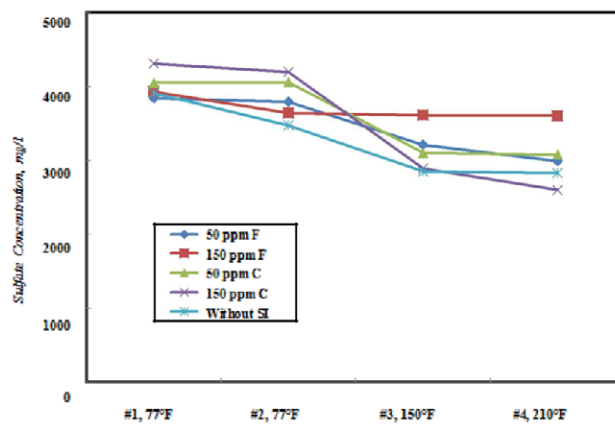


Figure 11: Sulfate concentrations in the mixtures of 1 wt% spent acid and seawater with F and C.

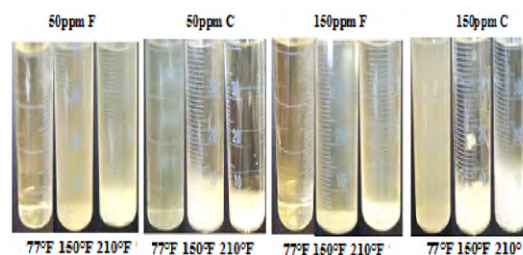


Figure 12: Performance of F and C as the calcium sulfate inhibitors.

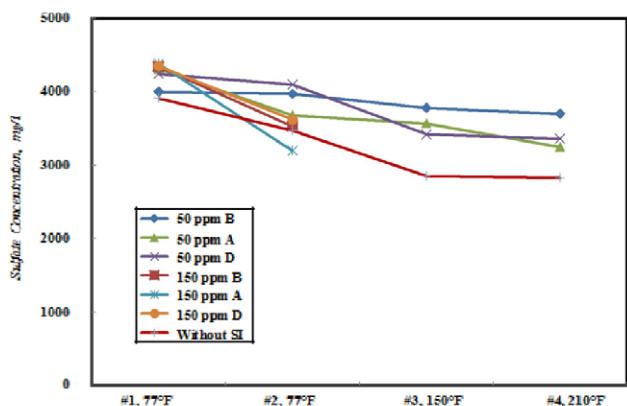


Figure 13: Sulfate concentrations in the mixtures of 1 wt% spent acid and seawater with A, B and D.

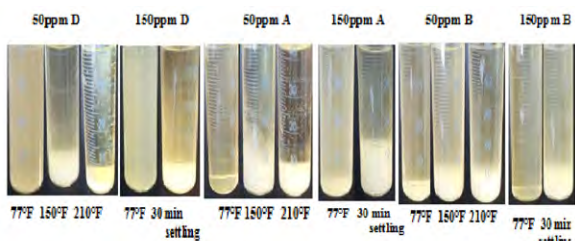


Figure 14: Performance of A, B and D as the calcium sulfate inhibitors.

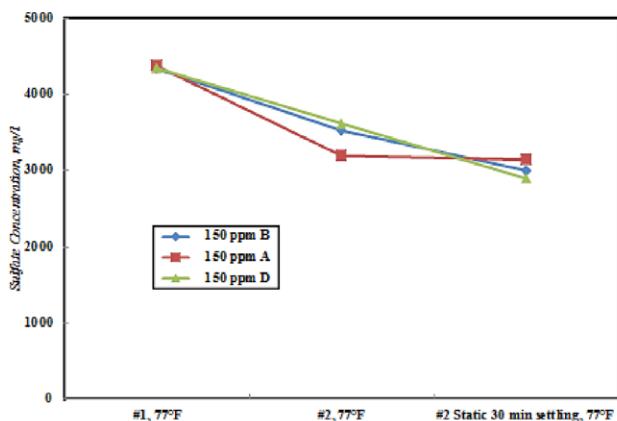


Figure 15: Sulfate concentrations in the mixtures of 1 wt% spent acid and seawater with A, B and D after 30 min static settling.

studies were conducted to investigate settling time effect instead of temperature effect. After statically settling for 30 min, more reduction in sulfate level and more precipitations were observed shown in Figure 15. Those findings concluded that there is one optimum concentration of scale inhibitors used for scale control in acidic conditions. Less scale inhibitor concentration is not enough to prevent formation of scale, but more scale inhibitor usage can cause more damage. All the results of batch tests were summarized in Table 4 and E was the most effective scale inhibitor under different conditions.

Conclusions

Based on the batch tests on the effectiveness of 6 different scale inhibitors, the following conclusions can be drawn:

1. In the acid stimulation process, calcium sulfate began to precipitate out of solution when acid was almost completely spent. 50 ppm of different scale inhibitors can successfully prevent the formation of calcium sulfate in the mixtures of completely spent acid and seawater under various temperature conditions.
2. However, most scale inhibitors did not perform well in acidic conditions. Methylene phosphonic acid scale inhibitor (scale inhibitor E) was the only effective one that can prevent the formation of calcium sulfate under various temperature conditions. The other scale inhibitors either were not sufficiently to prevent the formation of calcium sulfate or were not compatible with the solutions in the presence of high calcium ion concentrations and acidic conditions.
3. The findings in this study confirmed that the selections of appropriate scale inhibitors for field use depends on lots of factors, including temperature, pH value of the solution, and compatibility with solution.

Acknowledgement

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Acid Mixing with Seawater	Type of Scale Inhibitor	Concentration, ppm	#1, 77°F	#2, 77°F	#3, 150°F	#4, 210°F	#5, 250°F
0 wt% Completely Spent HCl	A	50	No	No	No	No	
	B	50	No	No	No	No	
	C	50	No	No	No	No	
	D	50	No	No	No	No	
	E	50	No	No	No	No	
	F	50	No	No	No	No	
	No SI	0	No	Yes	Yes	Yes	Yes
1 wt% Partially Spent HCl	A	50	No	No	Yes	Yes	
		150	No	Yes	Yes*		
	B	50	No	No	Yes	Yes	
		150	No	Yes	Yes*		
	C	50	No	No	Yes	Yes	
		150	No	No	Yes	Yes	
	D	50	No	No	Yes	Yes	
		150	No	Yes	Yes*		
	E	50	No	No	Yes	Yes	
		150	No	No	No	No	
	F	50	No	No	Yes	Yes	
		150	No	No	Yes	Yes	
No SI	0	No	No	Yes	Yes		
5 wt% Partially Spent HCl	No SI	0	No	No	No	No	
10 wt% Partially Spent HCl	No SI	0	No	No	No	No	
15 wt% Live HCl	No SI	0	No	No	No	No	

Table 4: Summary of batch tests.

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