

# A New Strategy for Minimizing Precipitations during ASP Flooding in Carbonate Reservoirs

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**Abstract**—A large quantity of world's oil reserves exists in carbonate reservoirs. Carbonate reservoirs are very sensitive to chemical enhanced oil recovery process because of containing large amount of calcite, dolomite and calcium sulfate minerals. These minerals cause major obstacles during alkali-surfactant-polymer (ASP) flooding. Alkali reacts with these minerals and form undesired precipitations which plug effective porous openings, reduce permeability and cause scale occurrence at the wellbore. In this paper, a new chemical combination consists of acrylic acid and alkali was used to minimize precipitation problem during ASP flooding. A series of fluid-fluid compatibility tests were performed using acrylic acid and different concentrations of alkaline. Two types of alkalis namely; sodium carbonate and sodium metaborate were screened. As a result, the combination of acrylic acid and sodium carbonate was not effective in preventing calcium and magnesium precipitations. However, acrylic acid and sodium metaborate showed promising results for keeping all solutions without any precipitations. The ratio of acrylic acid to sodium metaborate of 0.7:1.0 was found to be optimum for achieving a compatible solution for 30 days at 80°C.

**Keywords**—Fluid-fluid compatibility test, Carbonate reservoirs, Precipitations and ASP flooding.

## I. INTRODUCTION

ASP flooding is a combination of principal technologies from a number of traditional EOR chemical methods. These methods include alkaline, surfactant and polymer flooding. The purpose of ASP flooding is to increase oil production by reducing the waterflood residual oil saturation. ASP flooding combines interfacial tension-reducing chemicals (alkali and surfactant) with a mobility control chemical (polymer). Alkali and surfactant both minimize capillary forces that trap waterflood residual oil, while the polymer improves reservoir contact and flood efficiency [1][2]. Therefore, ASP displacement mechanism is consequently the combination of these individual processes [3].

When ASP is flooded into these reservoirs, it produces many complexities. The complexities include precipitation, surfactant and polymer retention and permeability reduction. These complications are due to varying salinities and hardness concentration in carbonate reservoirs. Nevertheless, owing high divalent minerals content in carbonate reservoir rocks are huge obstacles to ASP flooding in carbonate reservoirs. These cations being insoluble in formation brine or injected brine

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precipitate in the presence of Alkali ( $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ ) as shown in the equation (1) and (2).

These precipitates as well as naturally existing minerals (calcite and dolomite) cause formation pore plugging, permeability damage, and ultimately scale occurrence in the wellbore [4][5][6][7].

Traditionally, Sodium tripolyphosphate (SPTT) has been combined with ASP slug to mitigate precipitation [8]. Softened brine or fresh water has also been injected before and after ASP slug injection to sequester hardness effect [9][10]. Because softened water preparation is an expensive process. So, Ethylene-diamine-tetra-ecetate (EDTA) has sometimes been replaced for softened water to acquire the same purpose in cost effective way [4]. However, these techniques are not effective strategies for dealing with this high salinity and high divalent ion containing carbonate reservoirs.

Acrylic acid ( $\text{C}_3\text{H}_4\text{O}_2$ ) has been used to avoid precipitation in carbonate reservoirs. When acrylic acid is mixed with brine or alkali, it reacts with sodium ions to generate in-situ sodium acrylate ( $\text{C}_3\text{H}_3\text{NaO}_2$ ) which is a precipitation inhibitor [11][12]. Sodium Metaborate ( $\text{NaB}(\text{OH})_4$ ) as an alkaline has high tolerant capacity for high salinity and high hardness. It can sequester multivalent cations with no precipitation up to 6000 ppm of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  [13][14][15]. In this research, a combination of acrylic acid and sodium metaborate were used to control this problem at high hardness concentration in carbonate formations.

In this study, acrylic acid and alkali interaction tests have been performed to control formation of precipitates at high hardness concentration. Sodium acrylate and alkalis interaction tests have also been conducted to achieve the same objectives.

## II. EXPERIMENTAL METHODOLOGY

### A. Materials

Two alkalis were used in this study: sodium carbonate and sodium metaborate. These were supplied by Sigma Aldrich and Borax respectively. Acrylic acid and sodium acrylate were supplied by Sigma Aldrich. Synthetic hard brine with a total salinity of 59,940 ppm was used to prepare all solutions and main compositions of the hard brine are given in Table I.

### B. Fluid-Fluid Compatibility Tests

The first step for this test is to prepare different samples of sodium carbonate and sodium metaborate using the synthetic brine. Purpose of this test was to evaluate the compatibility of the two alkalis with the brine. Next, base line samples of sodium acrylate and acrylic acid were also prepared using the synthetic brine. The purpose of these tests was to ensure that sodium acrylate and acrylic acid are itself compatible with the

brine. In the third step, sodium acrylate to alkali and acrylic acid to alkali interaction tests were performed. All the compatibility tests were conducted at 80°C for a period of time and observation are made by visual evaluation with the formation of solids which are indications of incompatible fluids.

TABLE I  
COMPOSITION OF SYNTHETIC HARD BRINE

Component	Concentration
Sodium, ppm	20,445
Calcium, ppm	2523
Magnesium, ppm	239
Chloride, ppm	36,733
Total Concentration, ppm	59,940

### III. RESULTS AND DISCUSSIONS

#### A. Alkali-brine Interaction

The two alkalis employed in this study were incompatible with the synthetic hard brine. Sodium carbonate was immediately consumed by  $Ca^{++}$  and  $Mg^{++}$  ions to form their insoluble salts as precipitations. Although sodium metaborate has shown some resistance against water hardness, precipitations were formed after fifteen days at 80°C. This is attributed to the interaction between the  $Ca^{++}$  and  $Mg^{++}$  with the carbonate group. Fig. 1 shows the results of sodium metaborate with different concentrations ranging from 0.2 wt% to 1.0 wt%. Therefore, in order to use alkali with the synthesized brine, the sodium acrylate was used to keep solutions without precipitations.

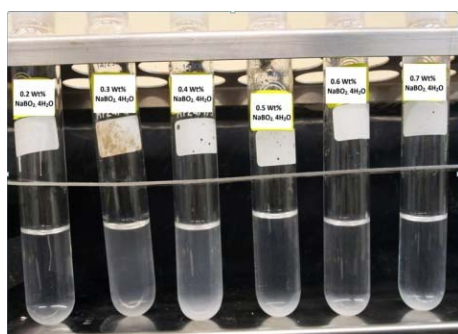


Fig. 1 Occurrences of precipitation by sodium metaborate after 15 days at 80°C

#### B. Sodium Acrylate-brine Interaction

The main purpose of the test is to assess the possibility of using sodium acrylate as a precipitation inhibitor with the use of hard brine. Therefore, different sodium acrylate concentrations were prepared in the absence of alkali using synthetic brine. As a result, all samples were incompatible with the hard brine and precipitates were generated in all samples. Thus sodium acrylate was not used in this study for further experiments. Fig. 2 shows incompatibility of sodium acrylate with hard brine.

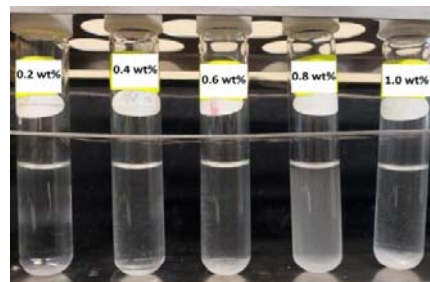


Fig. 2 Incompatibility of sodium acrylate with hard brine after 15 days at 80°C

#### C. Alkali-acrylic acid-brine Interaction

Based on the previous compatibility tests, sodium carbonate and sodium metaborate were not compatible with the synthetic brine. It is essential that  $Ca^{++}$  and  $Mg^{++}$  ions must be removed from the brine. In this test, alkali and acrylic acid were used together with the brine to form in-situ inhibitor. Hence, different acrylic acid to alkali weight ratios were used to evaluate the performance of the in-situ precipitation inhibitor at 80°C. Table II summarizes the results for different acid to alkali weight ratio using sodium carbonate and sodium metaborate.

TABLE II  
SUMMARY OF THE ACID-ALKALI COMPATIBILITY TEST AFTER 30 DAYS AT 80°C

Days	Sodium Carbonate 1wt%					
	Acrylic Acid, wt%					
	0.2	0.3	0.4	0.5	0.6	0.7
	pH					
	9.87	9.06	8.61	8.00	7.12	6.49
0	c	c	c	c	c	-
1	ppt	ppt	ppt	ppt	ppt	ppt
Days	Sodium Metaborate, 1 wt%					
	Acrylic Acid, wt%					
	0.2	0.3	0.4	0.5	0.6	0.7
	pH					
	9.59	8.94	8.40	7.61	6.81	6.09
0	-	-	-	-	-	-
1	-	-	-	-	-	-
5	-	-	-	-	-	-
10	ppt	ppt	ppt	ppt	-	-
15	ppt	ppt	ppt	ppt	-	-
20	ppt	ppt	ppt	ppt	-	-
30	ppt	ppt	ppt	ppt	ppt	-

ppt denotes precipitation, - denotes clear solution, c denotes cloudy

As presented in Table II, the formed in-situ inhibitor was ineffective in the case of sodium carbonate. The optimum acid to alkali weight ratio was beyond the highest ratio used in this study. Even with the highest acid to alkali ratio of 0.7:1, precipitations were formed after one day of mixing. The acid was fully consumed by the alkali and the generated inhibitor was inadequate to prevent the  $Ca^{++}$  and  $Mg^{++}$  precipitations.

In the case of sodium metaborate, the in-situ inhibitor was very effective in preventing  $Ca^{++}$  and  $Mg^{++}$  precipitations over 30 days at 80°C. It was also observed that the efficiency of the inhibitor increased as the acid to alkali weight ratio was

increased in the case of sodium metaborate. For instance, with a small acid to alkali weight ratio, the produced inhibitor (sodium acrylate) was insufficient to prevent the precipitations. All the acid was neutralized by the added alkali and sodium ions present in the brine. However, when a high acid to alkali weight ratio was used, only the required amount of acid was neutralized by the added alkali. The sodium acrylate concentration was increased as a result of the reaction of the alkali and sodium ions with the acrylic acid. The inhibitor adsorbs on the active growth sites of the  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  surfaces to prevent them from precipitating. As a result, the acid to alkali ratio of 0.7:1 was found to be the optimum ratio in the case of sodium metaborate to prevent any precipitations.

#### IV. CONCLUSION

On the basis of results obtained from aqueous compatibility test, the following conclusions are drawn.

- Sodium carbonate is incompatible with hard brine, sodium acrylate and acrylic acid.
- Sodium metaborate shows effective performance with hard brine and no precipitates formed at 30°C temperature. However, precipitations were generated when the samples were at 80°C.
- Direct usage of sodium acrylate did not prevent the divalent ions from precipitating. Even, it was incompatible with hard brine and also showed cloudiness and precipitates with the alkalis.
- The generated in situ inhibitor was very effective to minimize precipitation. The acid to sodium metaborate ratio of 0.7:1 was found to be the optimum ratio for keeping solutions without any precipitation.

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