Influence of Terpolymer Based on Amide, Carboxylic, and Sulfonic Groups on the Barium Sulfate Inhibition

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The influence of terpolymer based on amide, carboxylic and sulfonic groups on the barium sulphate inhibition


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**ABSTRACT:** In oilfield production systems, inhibitors are widely used to prevent mineral scale formation and the most common and efficient way to apply inhibitors downhole is by using squeeze treatments. Polymers are an important class of compounds used as scale inhibitor, however many specific conditions still require high performance additives. In this work, some ionic copolymers based on acrylamide, maleic acid and vinyl sulphonic acid were synthesized, characterized by FT-IR, elemental analysis and size exclusion chromatography, and tested regarding to barium sulphate prevention. Static inhibition efficiency (IE) was carried out at 95 °C and pH 5.5 for two seawater/formation water volume ratios, i.e. 10/90 and 60/40. The minimum inhibitor concentration (MIC) for each polymer was also determined. Polymers containing –COOH, –CONH2 and –SO3H groups exhibited higher efficiency regarding barium sulphate inhibition than those containing only –COOH and –CONH2, for both saturation ratio. This behavior could be associated to a synergistic effect of carboxylic groups (–COOH), that can interact with barium ions, and acrylamide (–CONH2), which CO can interact with barium ions and NH2 with sulphate ions. It seems that vinylsulfonic group contributed to chain flexibility more than to ion interaction.
**Keywords:** barium sulphate, scale inhibitor, copolymers, acrylamide, maleic acid, vinylsulfonic acid, saturation ratio

1. **INTRODUCTION**

Waterflooding in oil reservoirs is a well-established technique to improve oil recovery after primary drainage. However, this process can cause some problems, such as; scale deposits.\(^1\) Once the scale is formed it may adhere to different producing well equipment, valves, pumps, topside facilities and it can have a negative impact on flow assurance.\(^2\)–\(^4\) The most common types of oilfield scales are the sulphates (BaSO\(_4\), CaSO\(_4\) and SrSO\(_4\)) and carbonates (CaCO\(_3\)). Of these, barium sulphate is particularly troublesome due to extremely low solubility, tightly adherent deposition, and difficulty in its removal.\(^5\)–\(^9\)

Calcium carbonate scale is formed during the production of water with high calcium and bicarbonate contents and it forms due to the CO\(_2\) evolution caused by a decrease in pressure. Barium sulphate formation happens when barium-rich formation water comes in contact with sulphate-rich injection water.\(^3\),\(^6\),\(^10\),\(^11\) Deposition of inorganic barite and other sulphate salts may appear wherever mixing of such incompatible brines takes place.

The main factor for inorganic scale formation is the saturation ratio (SR), which must be greater than 1 to form barite crystals, where SR is given by the following equation 1.

\[
SR = \frac{[Ba^{2+}]_0[SO_4^{2-}]}{K_{sp}}
\]  

(1)

Where \([Ba^{2+}]_0\) = initial barium ion concentration (mol/L); \([SO_4^{2-}]\) = initial sulphate ion concentration (mol/L); and \(K_{sp}\) = barium sulphate solubility product, at temperature T, specific pH and ionic strength level. The SR depends on a number of experimental conditions, including the SW/FW mixing ratio, temperature (T), pH, and ionic strength.\(^3\),\(^12\),\(^13\)
According to Mackay,\textsuperscript{14} in a typical barite scaling example, the maximum amount of precipitation of barium sulphate occurs at a 10/90 SW/FW mix. However, the maximum thermodynamic scaling tendency (SR), which is essentially the driving force to reach equilibrium precipitation, is at 60/40 SW/FW mix. Therefore, in order to inhibit the formation of barium sulphate, then a lower concentration of scale inhibitor will be required for the 10/90 SW/FW mix, since this system has a lower scaling tendency whereas a much higher quantity of SI would be required to inhibit the 60/40 SW/FW mix since this case has the highest scaling tendency for this system.\textsuperscript{14-16}

Over the years it has been broadly acknowledged that scale prevention is better than waiting until the problem occurs and then taking remedial action. Usually, removal can incur considerable expense due to both the cost implications from mechanical clean-up but also the down time in production. Therefore, many different technologies have been developed over the years to reduce the risk of scale formation and to remove it if formed within downhole and topside oil/gas facilities.\textsuperscript{17-19}

In oilfield production systems, the most frequently used method of prevention of mineral scale formation is the use of chemical scale inhibitors. The most common and efficient way to apply inhibitors downhole is by using squeeze treatments.\textsuperscript{2,6-8,14,18,20-22}

According to Sorbie and Laing, inhibitors are able to prevent mineral scale formation through two different mechanisms, i.e., nucleation inhibition where crystals of scale form but are then re-dissolved by the endothermic action of inhibitor molecules, and crystal growth inhibition where the inhibitor adsorbs or interacts with the active crystal growth sites hence retarding or stopping the crystal growth process. It is well known that phosphonates operate mainly as crystal growth inhibitors and polymeric species work principally as nucleation inhibitors, although all scale inhibitors can carry out both mechanisms to some extent.\textsuperscript{12,15,23-25}
Polymers can be produced from organic raw, coming from petrochemical industry, and they are extensively used in oil production for many purposes including scale inhibition.4,24,26-29 Many polymeric scale inhibitors have been developed over the years to be applied in oilfields. More recently, green chemicals have also been tested, such as proteins and pectins.9,30 The performance of the polymeric inhibitors is dependent on the functional groups present in the molecules, the molar mass and their charge density.5,24,30,31 In addition, their effectiveness may also be influenced by external factors such as temperature, pH, ionic strength, flow rates, shear forces, nucleation sites, and residence times.12,13,15,16,21,22,32

Typically, an effective scale inhibitor contains at least one of the following functional groups: carboxyl, -COOH; sulphonic, -HSO₃; ester, -COOR; phosphonic acid, -PO₃H₂, etc.5,24,33,34 The development of copolymers has been increasing progressively, since it is possible to incorporate 2 or more of those functional groups on the same polymeric chain and thus possibly improve inhibitor performance.4,24,33-39 For instance, homopolymers based on vinyl sulfonic acid,40 acrylamide24,41,42 or maleic acid,24,41,42 and also copolymers made of acrylic acid/acrylamide24 and maleic acid/acrylamide43 have already been studied. Considering this fact, the aim of this work was to synthesize new copolymers containing in the same molecule three distinguish monomers (with carboxylic groups, amidic groups and sulfonic group), in order to apply them to prevent barium sulphate formation and understand the influence of the inhibitor structure and molar mass on inhibition performance.

2. EXPERIMENTAL WORK

2.1. Materials
Acrylamide for synthesis >99%, maleic acid > 99% HPLC grade, vinylsulfonic acid sodium salt solution 25 % wt technical grade, ammonium persulfate >98%, ethanol, acetone, methanol, calcium chloride 6-hydrate were supplied by Sigma Aldrich. Sodium chloride, potassium chloride, barium chloride 2-hydrate, strontium chloride 6-hydrate, sodium sulphate, sodium acetate 3-hydrate and acetic acid were supplied by VWR. Magnesium chloride 6-hydrate supplied by Merck and polyvinylsulfonic (PVS) scale inhibitor supplied by Clariant. Sodium nitrate solution (NaNO₃) and sodium azide solution (NaN₃) were supplied by Vetec. Bellasol S40 commercial inhibitor scale was donated by BWA. All reagents were used as received.

2.2. Synthesis of copolymers

Copolymers were synthesized using two and three monomers in different ratios of feeding, 0.2M total in solution. Acrylamide-maleic acid (Figure 1) and acrylamide-maleic acid-vinylsulfonic acid (Figure 2) copolymers reactions were carried out in aqueous medium through free-radical polymerization using ammonium persulfate (0.5 % wt% with respect to the monomer) as initiator in an inert atmosphere and distilled water as solvent.

The polymerization setup was composed of a three-necked flask, reflux condenser, magnetic stirrer, N₂ inlet and outlet, thermometer and a heating oil bath.

The solution was stirred at 320 rpm, 60°C for 24h. Diluted monomer solutions were taken for polymerization and after 24 hours the polymerization was stopped by immersing the round bottom flask in cold water.

The reaction products were precipitated in excess of nonsolvent under vigorous stirring and filtered off. Ethanol was used to precipitate copolymers shown in Figure 1 and acetone/methanol (1:1) was used to precipitate the copolymers shown in Figure 2. The
copolymers were purified by dissolving in distilled water and reprecipitating in the same nonsolvent and then vacuum dried at 60ºC for 48 hours.

**Figure 1.** Acrylamide, Maleic Acid Copolymers structure

**Figure 2.** Structure of polymers based on acrylamide, maleic acid and vinylsulfonic acid

### 2.3. Characterization of copolymers

Infrared spectra were recorded as a potassium bromide pellet with a Varian 3100 Excalibur Series, spectrophotometer. The spectrum was obtained between 4000 to 400 cm⁻¹ frequency region at a resolution of 4 cm⁻¹ at room temperature. CHNS elemental were carried out using around 2 mg of sample. The weight average and number average molecular weights (\(M_w\) and \(M_n\)) of the copolymers were determined using Viscotek Max VE-2001 Multi detector gel permeation chromatograph equipped with a refractive index, viscosimeter and light scattering detectors and calibrated by a single standard type of poly(ethylene oxide) - PEO 19K. The eluent phase was aqueous phase containing 0.1 M NaNO₃ and 0.02 % NaN₃.

### 2.4. Solubility of the copolymers

The solubility of the copolymers was tested in three different kind of waters: distilled water, North Sea sea water (NSSW) and Nelson Forties formation water (NFFW). Table 1 shows the water compositions. Solubility tests were carried out using small test tubes, where about 10 mg of the copolymer samples were weighed and then mixed with 2 mL of solvent. The mixtures were stored at room temperature for 24 hours with occasional shaking. The test tubes were checked periodically to detect any solubility of the copolymers.
Table 1. Compositions of North Sea sea water (NSSW) and Nelson Forties formation water (NFFW)

2.5. Static Inhibition Efficiency (SIE)

The Static Inhibition Efficiency Test (IE) is a very common procedure used to evaluate scale inhibitor (SI) performance in the absence of flow and this test was applied to the copolymers synthesized in this work. IE tests were carried out at 95°C, pH 5.5, at 2 and 22 hours sampling time after brine mixing. North Sea sea water (NSSW) and Nelson Forties formation water (NFFW) were mixed at two different volume ratios: 10/90 and 60/40 (NSSW/NFFW). The copolymer was dissolved in NSSW before mixing the brines. For all samples, the pH was then adjusted to pH 5.5 using a sodium acetate/acetic acid buffer. NFFW and SI/NSSW were placed, respectively, into an oven and a water bath pre-heated to 95°C, and then after 1 hour they were mixed. Disposable Azlon plastic bottles were used for this test.

Inductively Coupled Plasma Spectroscopy (ICP) was used to determine the barium concentration in the brine systems. Samples gathered at 2 and 22 hours after brine mixing were sampled; 1 mL of supernatant was taken and diluted in 9 mL of quenching solution, which was made using 1000 ppm of commercial scale inhibitor - poly(vinyl sulfonate) (PVS) - and 3000 ppm of potassium (KCl) in distilled water with the pH adjusted to 8 - 8.5. This quenching solution KCl/PVS is used to prevent further precipitation and act as an ionisation suppressant for the atomic absorption determination of barium. The inhibition efficiency was then calculated by Equation 2.

\[
\%\text{Efficiency}(t) = \frac{(M_B - M_I) \times 100}{M_B} = \frac{(C_O - C_B) - (C_O - C_I) \times 100}{(C_O - C_B)} = \frac{(C_I - C_B) \times 100}{(C_O - C_B)}
\]

where: \(M_B\) is the mass of barium precipitated in supersaturated blank solution; \(M_I\) is the
mass of barium precipitated in test solution; $C_0$ is the concentration of barium originally in solution (i.e. at $t = 0$); $C_I$ is the concentration of barium at sampling; $C_S$ is the concentration of barium in the blank solution (without inhibitor) at the same conditions and sampling time as $C_I$; and $t$ is the sampling time.

All tested were carried out, at least, in duplicate and the result expressed as the average of these two results. The error was $< 5\%$.

3. RESULTS AND DISCUSSION

3.1. Copolymer characterization

The copolymers were characterized by Elemental Analysis, FT-IR Spectrometry and Size Exclusion Chromatography. Table 2 shows the composition and molar masses of the copolymers, and Figures 3 and 4 exhibit FT-IR spectra of the copolymers containing two and three kind of mers, respectively.

Table 2. Characterization data of copolymers

Figure 3. FT-IR spectra of 35AM:65MA and 63AM:37MA.

Figure 4. FT-IR spectra of 41AM:22MA:37VS, 44AM:30MA:26VS and 57AM:30MA:13VS.

The composition data presented in Table 2 shows that the calculated composition is significant different from that in the feed. For the copolymer containing acrylamide and maleic acid, the results are in agreement with literature, since the reactivities ratios are $(r_1 = 2,2$ and $r_2 = 0)$ respectively. Vinylsulfonic acid is in the copolymers in lower content than that in the feed, this factor is also related with the higher reactivity ratio of
acrylamide monomer when compared with vinylsulfonic acid one \((r_1 = 0.15\) and \(r_2 = 3.5,\) respectively). From here, the copolymers will be named as shown in the code column in Table 2. The molar masses of the copolymers containing three kind of mers were lower than that containing only two kinds, which is desirable for the application being studied in this work. Altough the molar masses of the copolymers containing two kinds of monomers are not in the optimal range for scale inhibition \((1,000 – 30,000 \text{ g/mol})\), this does not nullify the study, since the primary aim of this work was to verify the performance of a terpolymer containing three different functional groups in the same molecule, as mentioned before, and the terpolymers (with different compositions) present molar masses relatively similar.

The FT-IR spectra confirm the structure of the copolymers. The spectras for \(35\text{AM:65MA}\) and \(63\text{AM:37MA}\) (Figure 3) shows a broad peak at round \(3400 \text{ cm}^{-1}\) due to –NH stretching from amide group and –OH stretching from carboxylic groups. The aliphatic chain \((-\text{CH}_2\) of the copolymer stretching vibration shows a peak at \(2923 \text{ cm}^{-1}\). The C=O stretching vibration at \(1720-1650 \text{ cm}^{-1}\) is due to the carboxylic groups (COOH) and the amide groups (CO-NH\(_2\)) absorption. The peak around \(1450 \text{ cm}^{-1}\) is relating to (C-N) stretching. The spectra for \(41\text{AM:22MA:37VS}\), \(44\text{AM:30MA:26VS}\) and \(57\text{AM:30MA:13VS}\) (Figure 4) shows all peaks related to acrylamide and maleic acid with an additional one at \(1190 \text{ cm}^{-1}\) referring to S=O asymmetric stretching, to which is not possible to find in Figure 3, related to vinylsulfonic acid.

### 3.2. Static Inhibition Efficiency (SIE)

In order to evaluate the molecules as scale inhibitor, it is necessary to follow some requirements and the solubility in water is the most important of them. Therefore, the copolymers solubilities were tested in distilled water (DW), North Sea sea water (NSSW)
and Nelson Forties formation water (NFFW). All copolymers could be dissolved in all kinds of waters tested.

As mentioned in the experimental section, the tests of static inhibition efficiency were carried out using two different NSSW/NFFW ratios: 60/40 and 10/90, corresponding to maximum and minimum of barium sulphate saturation, respectively. The polymer concentration ranges at each water system is shown in Table 3.

Table 3. Concentration of polymer used in each water mixing ratio

3.2.1. Static inhibition efficiency for polymers using NSSW/NFFW (60/40)

The static inhibition efficiency (IE %) of barium sulphate for all polymers was evaluated at “reservoir-like” conditions, i.e. T = 95°C, pH 5.5 and at sampling times of 2 and 22 hours after mixing NSSW/NFFW. “Minimum Inhibitor Concentration” (MIC) is a standard term expression used when the inhibitor presents an IE ≥ 90% at both 2 and 22 hours. However, according Shaw in some cases an IE ≥ 90% only at 2 hours can also be related to MIC.12,15,13,21

In this work, the main objective was to determine the MIC values for each polymer, understanding the effect of the polymer structure and the molar mass on BaSO₄ IE by testing them over the two distinct brine mixing ratios of NSSW/NFFW. The MIC for the BaSO₄ IE will of course depend on the barite saturation ratio (SR); it will be higher for the 60/40 ratio since the SR is higher for this case. The static inhibition efficiency using NSSW/NFFW (60/40) was addressed first and since it has the highest saturation ratio (SR), it was tested over a wide range of SI concentrations (5 - 500 ppm).

Inhibition efficiency results for all polymers studied at this brine mixing ratio (60/40 NSSW/NFFW) are shown in Figures 5 and 6. For all polymers, an increase in the efficiency with increasing polymer concentration is observed. It is already expected since
the inhibitor acts by interaction with ions; therefore, the higher polymer concentration, the higher ion concentration is hindered. The results in Figure 5 show that 35AM:65MA presents a higher IE than 63AM:37MA, with 35AM:65MA achieving IE 76% at 500 ppm active compared with 52% for 63AM:37MA at the same concentration. This behaviour could be associated with lower molar mass of 63AM:37MA (510,540 g/mol) compared to 35AM:65MA (271,050 g/mol). As reported extensively, the molar mass plays an importante role in polymeric scale inhibitior efficiency, since longer polymeric chains may present conformation as loops and tails in solution, hampering the scale inhibitor adsorption onto barite crystal nuclei.\textsuperscript{22,24,33-35,42} Moreover, 35AM:65MA presents a higher maleic acid/acrylamide ratio than 63AM:37MA, with a better performance for the former being expected.\textsuperscript{4,24,33,34}

**Figure 5.** BaSO\textsubscript{4} static inhibition efficiency (SIE) at 60/40 NSSW/NFFW for: (a) 35AM:65MA and (b) 63AM:37MA

Figure 6 shows static inhibition efficiency of the polymers 41AM:22MA:37VS, 44AM:30MA:26VS and 57AM:30MA:13VS. For these polymers containing a third monomer (vinylsulfonic acid) the IE increased significantly. According to Amjad, a sulffonic group when attached to the molecule amidic group provides greater structure flexibility resulting in stronger interaction with crystals and hence stronger inhibition.\textsuperscript{33-35} The best performance of these polymers could be attributed not only to polymer structure but also to molar mass, which are lower than that obtained for the polymer presented in Figure 5.

**Figure 6.** BaSO\textsubscript{4} static inhibition efficiency (SIE) at 60/40 NSSW/NFFW for: (a) 41AM:22MA:37VS, (b) 44AM:30MA:26VS and (c) 57AM:30MA:13VS.
As shown in Figure 6c, the minimum inhibitor concentration (MIC), at early-time, for 57AM:30MA:13VS was 500 ppm active, reaching 92% IE. This behavior could be associated to a synergistic effect of carboxylic groups (-COOH), that can interact with barium ions, and acrylamide (-CONH₂), where the CO can interact with barium ions and NH₂ with sulphate ions.²⁴,²⁵,³⁵ It seems that vinylsulfonic group, at the pH used in this test contributed to chain flexibity more than to ion interaction.¹³,²⁴ The molar masses of this family of polymers can be considered similar among them and they are close to the value mentioned in literature for better performances.²⁴,³⁵,⁴¹,⁴² Inhibition efficiencies for 41AM:22MA:37VS and 44AM:30MA:26VS, at 500 ppm, were ~86% and ~78%, respectively. It is important to point out that, after 22 h, polymer 57AM:30MA:13VS also presented the best performance; although it being a slight difference. It suggests that its structure was able to chelate with more Ba²⁺ ions in a longer time than the other polymers tested.

The functional groups in the copolymer chain are instrumental for the interaction with the scale deposit nuclei forming, by absorbing onto barite particles and preventing them from precipitating and settling on the equipment surfaces, pumps, valves, pipelines, etc. In addition, the performance of the scale inhibitor decreases as increasing the polymer molar mass to an over value.²⁴,³⁴,³⁵,⁴² The order of effectiveness at higher saturation ratio (60/40), at 95 °C and pH 5.5, for all copolymers was:


It is important to highlight that among the terpolymers with different content of mers, the best performance (above 90%) was achieved by the structure presenting the highest molar mass ($\bar{M}_n = 37,160$ and $\bar{M}_w = 89,160$). This indicates that the main influence in this case
was the terpolymer composition, although better performance could be achieved by the same composition in a lower molar mass.

A commercial inhibitor scale (Bellasol S40) achieved a performance of 88% at a 20 ppm (which is in agreement with literature\textsuperscript{13}), showing a significantly better result than those obtained with the polymers synthesized in this work, which showed a concentration of about 250 ppm for similar performance. Such a difference suggests that the terpolymer 57AM:30MA:13VS should be obtained in a lower molar mass in order to become suitable for commercial application.

3.2.2. Static inhibition efficiency for polymers using NSSW/NFFW (10/90)

In this section, all inhibition efficiency results are presented for the lower saturation ratio (10/90 NSSW/NFFW) for all polymers. Figure 7 shows the results for 35AM:65MA and 63AM:37MA and Figure 8 exhibits the results for 41AM:22MA:37VS, 44AM:30MA:26VS and 57AM:30MA:13VS. All polymers exhibited better inhibition efficiency in this system because of its much lower saturation ratio than that for the mixing ratio 60/40 NSSW/NFFW. Comparing the two NSSW/NFFW ratios, the same trend is observed, that is, polymers containing relatively higher molar mass (Figure 7) and three kinds of mers (Figure 8) presented higher efficiency than those containing only two different kinds of functional groups. The best performance in this saturation condition can also be observed by the lowest concentration required to achieve high BaSO\textsubscript{4} inhibition efficiency; and also, to compare the two different set of polymers. For saturation ratio of 60/40 NSSW/NFFW it was found a MIC of 500 ppm. On the other hand, for the saturation ratio of 10/90 NSSW/NFFW the highest performances were achieved with about 40 ppm, by the polymers containing only two kind of mers (Figure
7); and only 5 ppm were required to achieve the best performances by polymers containing three kinds of mers (Figure 8).

**Figure 7.** BaSO₄ static inhibition efficiency (SIE) at 10/90 NSSW/NFW for: (a) 35AM:65MA and (b) 63AM:37MA

**Figure 8.** BaSO₄ static inhibition efficiency (SIE) at 10/90 NSSW/NFW for: (a) 41AM:22MA:37VS, (b) 44AM:30MA:26VS and (c) 57AM:30MA:13VS

It is important to point out that the whole set of polymers showed a significant improvement in inhibition efficiency, at 2 and 22 hours, for almost all scale inhibitor concentrations, in this much lower saturation ratio.

The key factor for the observed behavior is, indeed, the lower BaSO₄ saturation ratio in this mixing ratio (10/90), since it is easier to inhibit the barite formation. However, another factor should also be taken into account, that is, the Mg²⁺ and Ca²⁺ concentration in solution, which is lower for Mg²⁺ [801.9 ppm] and greater for Ca²⁺ [1842.8 ppm] when compared to 60/40 NSSW/NFW. It is well established that both of these divalent cations are able to facilitate or prejudice the inhibitors performance, as long as SI- Ca²⁺ complex interacts with the growing barite crystal and it is effectively incorporated with the calcium into the lattice. On the other hand, the Mg²⁺ ions interact with scale inhibitor and form SI-Mg²⁺ complex that stop it from inclusion in the barite lattice.¹²,¹⁵,²³,⁵⁰ Therefore, in this case, the system is less “poisoned” by Mg²⁺, thus enabling the scale inhibitor to prevent barium sulphate nucleation and also growth retardation.

**4. CONCLUSIONS**

Polymers performance as scale inhibitor strongly depends upon the water saturation ratio, calcium/magnesium concentration and ionic charge of the functional group present in the
polymer. The molar masses of the polymers tested affected their anti scaling efficiency when they were used at higher saturation ratio, but it was not as significant when lower saturation ratio was used. The -COOH and –CONH2 groups played an important role in terms of prevention of BaSO4 formation. At pH 5.5, vinylsulfonic groups seemed to contribute to chain flexibility more than to ion interaction. Polymers containing –COOH, –CONH2 and –SO3H groups exhibited high efficiency regarding barium sulphate inhibition, for both saturation ratio system. This behavior could be associated to a synergistic effect of carboxylic groups (-COOH), that can interact with barium ions, and acrylamide (-CONH2), which CO can interact with barium ions and NH2 with sulphate ions. At 10/90 NSSW/NFW, all polymers exhibited better inhibition efficiency because of the much lower saturation ratio than that for the 60/40 NSSW/NFW, requiring lower polymer concentration for inhibition. This behaviour could also be associated with a lower concentration of Mg+2 which can “poison” the inhibitor and the Ca2+ which can help the scale inhibitor and interact with the barite lattice.

ACKNOWLEDGEMENTS

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**Table 1.** Compositions of North Sea sea water (NSSW) and Nelson Forties formation water (NFFW). (Reduced [Ca$^{2+}$] from 5038 → 2000 ppm)

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**Table 2.** Characterization data of copolymers

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* By elemental analysis

AM = acrylamide; MA = maleic acid; VS = vinylsulfonic acid
**Table 3.** Concentration of polymer used in each water mixing ratio

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Figure Captions

**Figure 1.** Acrylamide, Maleic Acid Copolymers structure

**Figure 2.** Structure of polymers based on acrylamide, maleic acid and vinylsulfonic acid

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**Figure 5.** BaSO₄ static inhibition efficiency (SIE) at 60/40 NSSW/NFFW for: (a) 35AM:65MA and (b) 63AM:37MA

**Figure 6.** BaSO₄ static inhibition efficiency (SIE) at 60/40 NSSW/NFFW for: (a) 41AM:22MA:37VS, (b) 44AM:30MA:26VS and (c) 57AM:30MA:13VS

**Figure 7.** BaSO₄ static inhibition efficiency (SIE) at 10/90 NSSW/NFFW for: (a) 35AM:65MA and (b) 63AM:37MA

**Figure 8.** BaSO₄ static inhibition efficiency (SIE) at 10/90 NSSW/NFFW for: (a) 41AM:22MA:37VS, (b) 44AM:30MA:26VS and (c) 57AM:30MA:13VS