

Barium Sulphate Scaling Prevention

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ABSTRACT

Mineral salt precipitation is a flow assurance issue during oil and gas production which often results in significant decline in productivity and expensive work-over operations if its formation is not managed effectively. Formation water produced alongside oil and gas contain significant amount of mineral salts which causes a high risk of precipitation inside the reservoir due to changes in temperature and pressure. A proper understanding of the formation containing these salts is necessary to minimize the severity of their effects especially in the plugging of tubes, valves, pumps and other production flow systems which can potentially lead to well abandonment. Studies pertaining to the challenge of oilfield scaling by Barium Sulphate have been made. Incompatibility between the formation water and seawater was observed to be the major cause of precipitation of Barium Sulphate. Barium Sulphate scale is relatively more difficult to treat, therefore preventing its formation through the use of scale-control chemicals (inhibitors) is the most effective means of containing scale formation. Application of Scale Control chemicals into the vicinity of the wellbore formation either by squeeze treatment or continual injection has been observed to manage the precipitation challenge very effectively. The goal of this study is to investigate the efficiency of polymers as a scale inhibitor in a typical petroleum production system and quantify their sensitivity to concentration, composition, saturation as well as the water/solution chemistry. The results obtained from the experiment shows that a low molecular weight of about 2200 provides excellent inhibitory performance in the Inhibitor Efficiency test conducted for less than 22 hours. Optimal inhibition efficiency was noticed at a concentration of 5 ppm and an increase in acidity of the solution leads to increase in the inhibition efficiency of the Inhibitor.

Key words: *Scale Precipitation, Barium Sulphate, Formation and Sea Water, Inhibitors, Oil and Gas Production, Flow Lines, Production Facilities and Inhibitor Efficiency.*

1. INTRODUCTION

In the offshore environment, injection of sea water into oil reservoirs via production wells to sustain the reservoir pressure and also for secondary enhance oil recovery is a common operation, though some levels of risks due to mineral scales deposition on production conduit and flow lines could lead to a flow assurance problem plaguing the oil and gas industry. It becomes a major operational issues associated with surface and subsurface oil and gas production equipment when the scales are deposited in both the production and injection wells. A supersaturated condition is essentially the main cause of scale formation and it occurs when a solution containing dissolved materials are present at a much higher concentrations than their equilibrium concentration. However, the amount and location of the scale formation can be influenced by several other factors but supersaturation is the most prominent. Therefore, the knowledge of scale formation problems are needed to ensure safe, uninterrupted and simultaneous transport of gas, oil and water mixtures through wells/pipelines from the reservoir to an offshore or land-based processing facility.

Oilfield scale consists mainly of inorganic salts, with calcium carbonates, barium and strontium sulphates as the commonest components. Scale can form from brine (formation water) as it undergoes changes in pressure and temperature, or where two incompatible fluids are intermingled. This is due to the chemistry of the produced water and thus requires an

inhibitor during injection into oil reservoirs. In major field operations, the application of scale inhibitors has been one of the most economically efficient methods to mitigate Barium and Calcium Sulphate (Yuan 2004; Fan et al. 2010; Hoang et al. 2009). Application of the scale inhibitors may act either as:

- ✚ Threshold Inhibitors which prevents the development of the supercritical nuclei (He et al. 1994; Tomson et al. 2003), or as
- ✚ Chelating Agents to form soluble complex (Moore et al. 1972; Jamialahmadi and Mueller 1991; Al-Khaldi et al. 2011), or as
- ✚ Retarders of the growth of the sulphate crystals (Amjad and Hooley 1986; Amjad 1988).

A sulphonated polymer-based scale inhibitor was selected for this research work because of its higher barium and calcium tolerant compared with phosphate scale inhibitors (Jordan et al. 1995) as well as possessing a superior inhibitor retention efficiency. Besides, the sulphate groups are strongly ionized, which are expected to promote stronger electrostatic interactions between polymer and the surface of calcium

containing crystals and better inhibit scale formation (Lioliou et al. 2006).

2. PROBLEM STATEMENT

Seawater is injected into the reservoir for the purpose of pressure maintenance and improves secondary recovery in offshore production location. Seawater contains significant concentration of sulphate ion while formation water is rich in divalent cations such as Ca^{++} , Sr^{++} , and Ba^{++} . When these two incompatible waters mix, unstable, supersaturated brine is created which precipitates calcium sulphate, strontium sulphate, and barium sulphate within the reservoir rock. Such scale deposition could have adverse effects on reservoir performance, primarily through damaging reservoir permeability. Due to crystallisation and growth mechanisms, scale deposits can clog and plug parts of production installations from well bore area, to topside equipment such as perforation, casing, valves, pumps, safety equipment and gas lift mandrels leading to high cost of intervention on subsea wells and high cost of replacement or recovery of plugged equipment. Various scale inhibitors are being used in oilfields in dealing with the scaling challenges but there is growing concerns about the eco-friendliness of some of these scale control chemicals making it imperative to explore the so-called “green” inhibitors. Therefore, it is important to study the chemistry of Barium Sulphate scale precipitation so as to effectively prevent its formation. This study presents the problem of Barium Sulphate scale precipitation during water flooding operations and incompatibility issue with formation water.

3. PREVIOUS WORKS

An extensive experimental works have been conducted on the study of scale formation and prevention in oil fields. The kinetic and thermodynamic studies are both reviewed.

Tahmasebi et al (2007) conducted an experimental and theoretical study to determine the permeability reduction due to barium sulphate deposition in porous media. In their study, brine solutions containing barium and sulphate ions were injected in a packed glass beads porous media at elevated temperatures, various flow rate and brine concentrations. A novel empirical equation to predict the permeability reduction and mobility reduction due to barium sulphate scale formation was suggested based on experimental parameters.

Fan et al (2010) quantitatively evaluated the precipitation kinetics of barium sulphate in the presence and absence of scale inhibitors. The nucleation kinetics of barium sulphate in 0 - 3.2M NaCl solutions was determined from 0 to 200 °C at various supersaturation conditions. A semi-quantitative model was developed to predict precipitation kinetics of barium sulphate as a function of temperature, pH, saturation index, and scale inhibitor concentration.

4. PREVENTION OF SCALE FORMATION

Prevention of the formation of supersaturation of brine is effectively handled by preventing scale from precipitating during oil production. In most instances, it accomplished by regulating the operating conditions of the reservoir, one of which is ensuring that the wellbore pressure is sufficient to prevent the liberation of gas and the injection of compatible water with formation water.

However, the most cost effective means of handling scale precipitation is the application of inhibitors. Scale formation are either influenced by temperature and/or pressure changes that are favorable to the precipitation of the mineral salts from formation waters, the mixture of incompatible waters during waterflooding operations or pressure maintenance. Scale prevention is done by performing squeeze treatments in which the scale inhibitors are injected in the producing formation near the wellbore as depicted in Figure 1 (Romero et al., 2007).

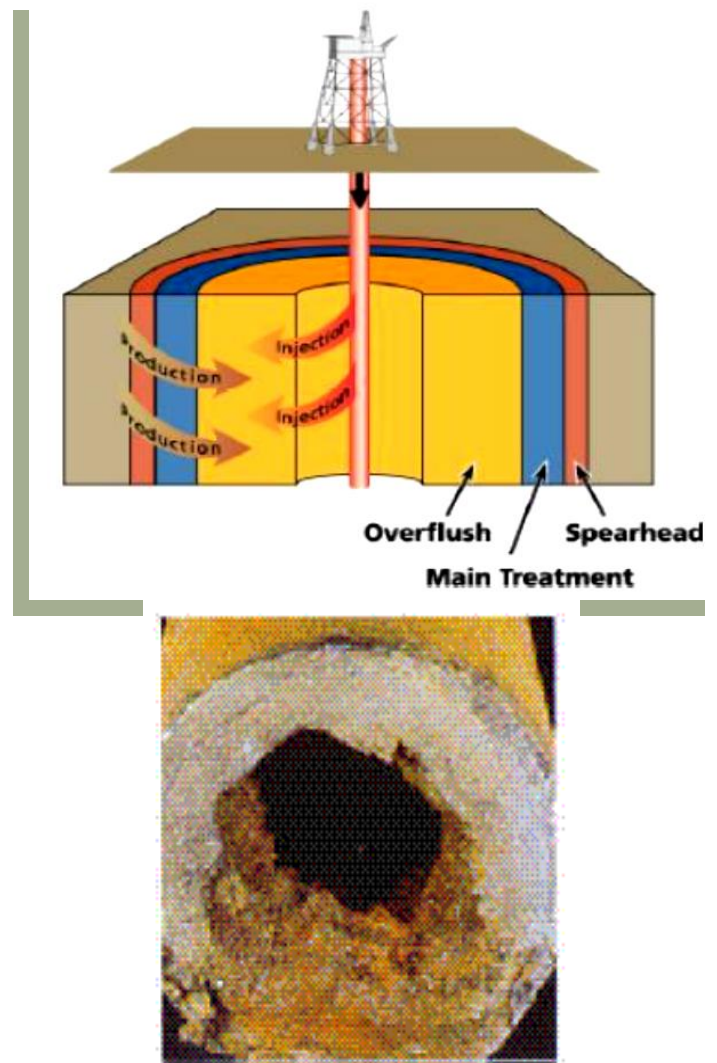


Figure 1: An outline of the scale inhibitor squeeze treatment process

Therefore, the formation of sulphate scales of barium and strontium influenced the buildup of the scaled-up wells, this is mainly as a result of their relative low solubility and limited options available for their removal, therefore preventive measure such as the squeeze inhibitor treatment is mostly considered. There are two most considered modes of interaction for the scale inhibition, viz;

(i) Nucleation Inhibition – Disruption of the thermodynamic stability of the growing nucleons (for homogeneous crystallisation). The mechanism of inhibition then involves endothermic adsorption of inhibitor species, causing dissolution of the barium sulphate embryo crystals.

(ii) Crystal Growth Blocking – Interference/blocking of the growth processes of the growing crystals (for homogeneous crystal growth). The mechanism of inhibition then involves irreversible adsorption of inhibitor species at the active growth sites of the scale crystals, resulting in their blockage.

All scale inhibitors show an ability to work through both nucleation and crystal growth mechanisms. However, most species work predominantly through one of these mechanisms to achieve scale inhibition.

5. COMPARATIVE REVIEW OF WORKS ON PHOSPHONATES AND POLYMERS BASED SCALE INHIBITORS

Scale inhibitors are commonly classified according to the type of compound prominent in them. Scale inhibitors (SIs) which contain no phosphorus and sulphur are commonly described as “green” products. Others which contain some quantity of phosphorus are mostly described as “yellow” products; examples are the Phosphorus “blended” polymers such as Phosphino polycarboxylic acid (PPCA) which are effective in preventing carbonate and sulfate scales. The other group which contains large amount of phosphorus is sometimes referred to as “red” or “black” products, this group is the most environmentally hazardous. The term “red” products are however used to describe the conventional phosphonate Scale Inhibitors.

With regards to the general inhibitor efficiency or barium sulphate, phosphate scale inhibitors are generally considered better inhibitors compared to their polymeric analogues. However with regards to the environmental “friendliness” of the products, the polymer scale inhibitors are preferred (Inches et al., 2006). The preference to phosphate scale inhibitors is mainly due to the presence of phosphonate functionality (usually as an amino phosphonate) which yields the best inhibitor efficiency and scale inhibitor retention (Jackson et al., 1996; Singleton et al., 2000), in spite of this, it has been observed that the higher the phosphorus content in scale inhibitors, the more environmentally unacceptable they become (Jordan et al., 2010, 2011; Todd et al., 2010).

Although some polymer-based scale inhibitors have recently been phosphonate “end-capped” to improve their inhibitor efficiency it, however, lead to a decrease in their biodegradability giving rise to environmental concerns. Example of this type of scale inhibitor is Phosphinomethylated polyamine (a poly-phosphonate) PMPA which has significantly better inhibition efficiency and

retention properties compared to other non-phosphonated polymeric SIs (Przybylinski et al; Singleton et al., 2000). PMPA has been proven to have an extremely high phosphorus content, at a level comparable with conventional phosphonate SIs, and indeed, it is currently thought that PMPA may not in fact be a polymer at all.

6. STRUCTURAL EXPLANATION OF POLYMER BASED SCALE INHIBITORS

According to Van der Leeden and Van Rosmalen (1990), the number of chelate rings that can form per SI molecule and the number of atoms that can form part of the chelate rings is important. Chelate rings containing five or six atoms (including M^{2+}) are the most thermodynamically stable. SI molecules that can form multiple 5- or 6-membered chelate rings are likely to inhibit well. It also reports that hydrophobic functional groups present in polymeric SIs, such as methylene, are detrimental to IE. This finding may also apply to all SIs.

Polymaleic acid, PMA (Figure 2) has been proven to possess greater chelation ability than polyacrylic acid, PAA (Commercially known as K-752), as they can form twice the number of chelate rings per repeating unit. Hence, PMA is likely to outperform PAA in IE tests, particularly over longer residence times. In the PMA structure, a carboxylic acid functional group is attached to every carbon atom in the main chain, whereas in the PAA structure (Figure 3), a carboxylic acid group is attached to every second carbon atom – it is this structural difference which alters their chelation ability. 8-membered chelate rings can only form in the VS-Co polymer structure at locations where 2 acrylic acid units have been polymerised in a row.

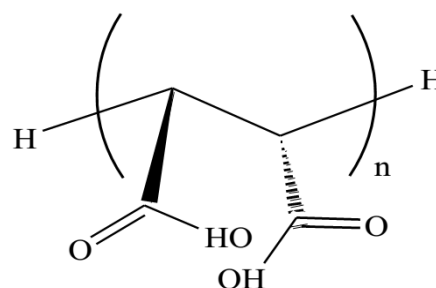


Figure 2 – Chemical molecular structure of Polymaleic acid PMA.

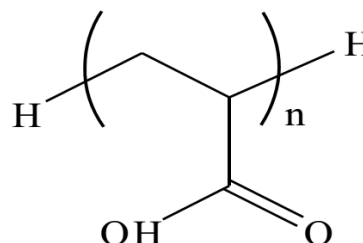


Figure 3 – Chemical molecular structure of Polyacrylic acid PAA

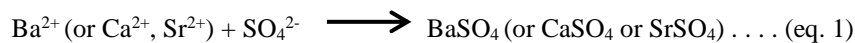
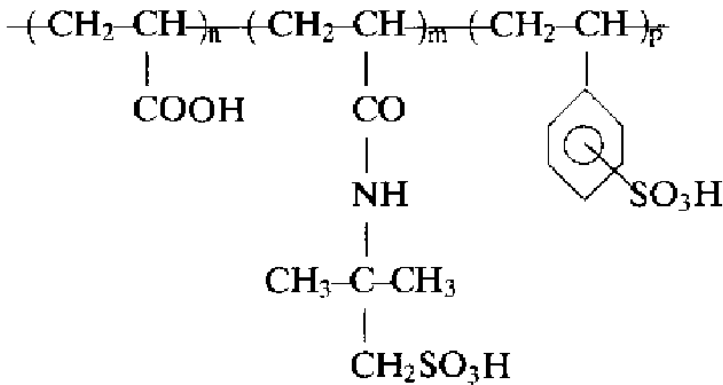
However, the modified PAA-AC when structured with a carbonyl or ester functional group oxygen atom lone-pairs of electrons will result with a reduced membered chelate ring

per unit which provides better chelation ability than PMA. Smyk and Hoot (1988) reported the influence of various polymers on the precipitation of barium sulphate. The results of the study showed that acrylic acid based terpolymers (eg poly (acrylic acid: 2-acrylamido-2-methyl propane sulfonic acid: sulfonated styrene A-SSA commercially known as K-798 Figure 4) perform better than homoacrylic acid polymers and copolymers of acrylic acid and hydroxypropyl acrylate (eg PMA and PAA).

Figure 4 – Chemical molecular Structure of A-SSA

7. THEORETICAL CONSIDERATIONS

The salt precipitation is generally caused by the incompatible mixing of brine waters and the pressure, temperature changes. This precipitation of solids also occurs due to the ionic composition, pH of the solution. Barium Sulphate (and the calcium sulphate) scales are primarily formed by the incompatible mixing of the brines, commonly in the formation water which are rich in cations and anions like barium, calcium, strontium, sodium, chlorides, sulphates, etc.



Thus, the severity of the scaling problem is directly affected by both the rate of scaling and the efficiency of the chemical inhibitors.

7.1 Static Barium Sulphate Inhibition Efficiency

The static barium sulphate inhibition efficiency (IE) (%) is a measure of how effective a scale inhibitor (SI) is at preventing barite formation under a specific set of experimental test conditions, i.e. Temperature, pH, etc., and at a particular time after mixing the two incompatible brines, e.g. usually 2 hours or 22 hours. Hence, 2 and 22 hour IE (%) is often referred to. These sampling times are largely chosen for convenience. In unseeded static IE tests, nucleation occurs ~1/2hr to ~3hrs after mixing the brines. Therefore, an early-time sampling time of 2 hours is reasonable for practical reasons (FAST EPM, 2006). The 22hr sampling time examines the crystal growth inhibition ability of SIs. This exact sampling time is less crucial than the 2 hour sampling time because the reaction rate has slowed significantly by 22 hours. In some studies, sampling has been carried out after 22 hours and prior to 2 hours. Sometimes IE continues to decline after 22 hours, depending on the scale inhibitor and test conditions.

When a SI has an IE ≥ 90% at both 2 and 22 hours, this is referred to as the “Minimum Inhibitor Concentration” or MIC. For any scale inhibitor to be suitable for use in the oilfield, it is better to use the working criterion in the laboratory so that the MIC is achieved when IE ≥ 90% at both 2 hour and 22 hour residence times. However, sometimes in a particular application variants on this definition of MIC are used e.g. it may be adequate in some application to define MIC as when IE ≥ 90% at 2 hours only. The MIC of a given SI may be determined in either static IE tests or in dynamic tube blocking tests. For static (jar) tests, IE is mathematically a percentage (%) given by the following expression:

$$\text{I.E.} = 100 \left(\frac{BC(t) - BC_b(t)}{BC_0 - BC_b(t)} \right) \quad \text{(Eq. 2)}$$

where

BC(t) = Barium concentration in the filtrate in the presence of inhibitor at time, t (ppm);

BCO = control sample Barium concentration in filtrate at the beginning of the experiment, t = 0 (ppm); and

BCb(t) = Barium concentration in the filtrate in the absence of inhibitor at time, t (ppm).

8. EXPERIMENTAL SETUP

TYPES OF SCALE INHIBITORS USED

The scale inhibitors being tested in this study include Polymaleic acid (PMA), normal Polyacrylic Acids (PAA) (K-752), Phosphinomethylated polyamine (PMPA), an experimental Low Molecular Weight (LMW) Polyacrylic Acids codenamed ACUMER 1020 polymers, commercially used phosphonate HEDP (1-hydroxyethylidene-1,1-diphosphonic acid).

8.1 Chemicals Reagents Used

Solids (BaCl₂.2H₂O and Na₂SO₄) formulated to the required concentration using distilled water of analytical grade. Seawater and formation water were obtained from a typical Niger Delta source used for the simulation test. The NACE Standard Testing Method for screening scale inhibitors was adapted in this investigation. This procedure was used in conjunction with spectrometry techniques to provide

information with regards to the nature of the deposit and the effect of the respective inhibitors on crystal growth. To ensure that the reactions take place under the same conditions, all concentrations were prepared from stock solutions of barium chloride and sodium sulphate using distilled water and then filtered through 0.22 micron filter paper. Grade A glassware and analytical grade chemicals were used for the experiment. During the precipitation reaction a few drops of hydrochloric acid HCl was added to adjust the pH.

The stock solutions of barium chloride and sodium sulphate used in this study is a commercial material and the polymeric inhibitors used were mostly commercial and some experimental polymers. The polymer concentrations analyzed during these experiments were on dry polymer samples. The experiments were conducted under equal precipitation conditions, i.e., at the same temperature, supersaturation and pH level of the solution. Some of the polymers were tested at different pH values in order to get optimum values. A Brinkmann pH meter equipped with a pair of calomel and glass electrodes was utilized in measuring the pH of the solution. The electrode pair was tested and calibrated with each set of measurements and thereafter tested against NBS standard buffers.

In setting up the supersaturated solutions of barium sulphate for precipitation experiments, we prepared two flasks of 200 ml of distilled water containing two solutions of BaCl_2 and Na_2SO_4 with a concentration of 10^{-4}M maintained at 35°C . The solution of 200 ml of sodium sulphate (Na_2SO_4) concentration of 10^{-4}M was placed in a thermostatic growth cell. Following temperature equilibration, the barium chloride solution (10^{-4}M) was introduced to initiate precipitation reaction at $t = 0$. The conductivity of the solution was then measured. Precipitation formed was monitored by analyzing the aliquots of the filtered solution for barium with the aid of PE6500 ICP/AAS instrument utilizing a 553.6 nm wavelength in the visible region and the nitrous oxide flame. We repeated the same experiments by adding the inhibitor solution to the sodium sulphate solution, before the addition of barium chloride solution to determine its inhibitory effect on the precipitation reaction. The pH values of the barium sulphate in its supersaturated state were regulated using dilute solutions of sodium hydroxide. Precipitation reaction was studied carefully by monitoring three parameters such as pH, conductivity, and temperature measured simultaneously.

9. RESULTS

9.1 Effect of Concentration

Studies of other scaling inhibitors indicated that the precipitation of Barium Sulphate was highly sensitive to the concentration of inhibitors in solution. Therefore the test inhibitors were further analyzed side by side under their observed individual best performing conditions.

It can be ascertained from Figure 5 that for all the inhibitors under consideration, a concentration in a relatively low amount 2.0 – 3.0 ppm considerably reduces the precipitation of Barium Sulphate. The first concentration table of our case study, PAA-AC, further indicates that at 2.0 ppm concentration, the precipitation was reduced by 85% and also at 5.0 ppm polymer concentration the precipitation was

completely inhibited for at least 22 hours, further increase in concentration did not produce an expected significantly optimum performance. Normally, Polymer based inhibitors possesses more inhibitory efficiency at low concentrations, this is mainly attributed to their ability to form multiple bonds between the longer macromolecules and the crystal surface thereby allowing stronger adsorption and consequently better inhibition.

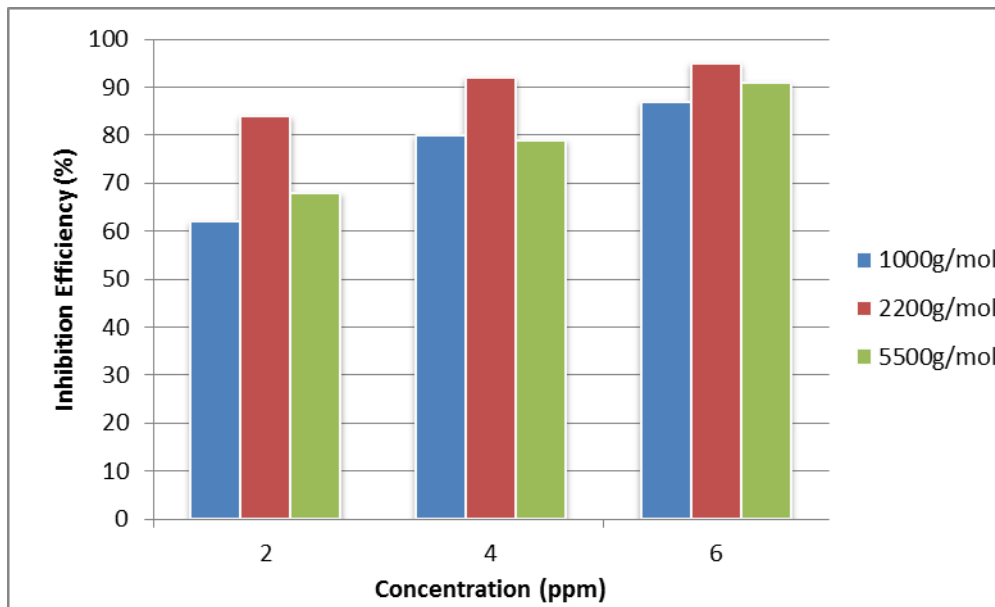


Figure 5 – Effects of Concentration and Molecular weight

9.2 Effects of Supersaturation

The results of the effects of solution supersaturation in the presence of the test inhibitor and four different brine solution of BaSO₄ with its corresponding saturations are presented in

Figure 6. It is observed from the result in Figure 6 that as the supersaturation of the BaSO₄ solution is increased, there is significant decrease in the BaSO₄ inhibition.

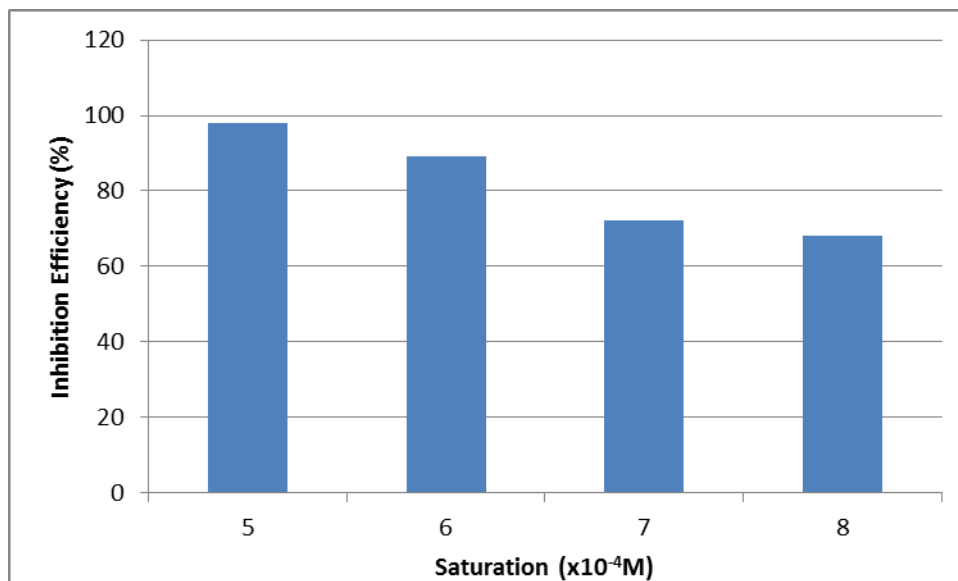


Figure 6 – Effects of Saturation on Inhibition Efficiency

9.3 Effects Of Solution pH

Figure 7 presents the results of the influence of solution pH in the presence of the test inhibitor. Sodium Hydroxide was used to regulate the acidity/alkalinity of the Barium Sulphate solution.

In this test, it was observed that for every increase in the pH level of the BaSO₄ solution, there was a corresponding increase in the performance of the PAA-AC inhibitor. The

performance of the inhibitor at low pH values shows their ineffectiveness at such conditions. The Scale inhibitor has better inhibitory efficiency at higher pH levels, this is mainly because they are highly dissociated and in the charged state it has more ability to complex with scaling ions such as Ba²⁺, and this makes the inhibition of the growth of barite crystals more efficient.

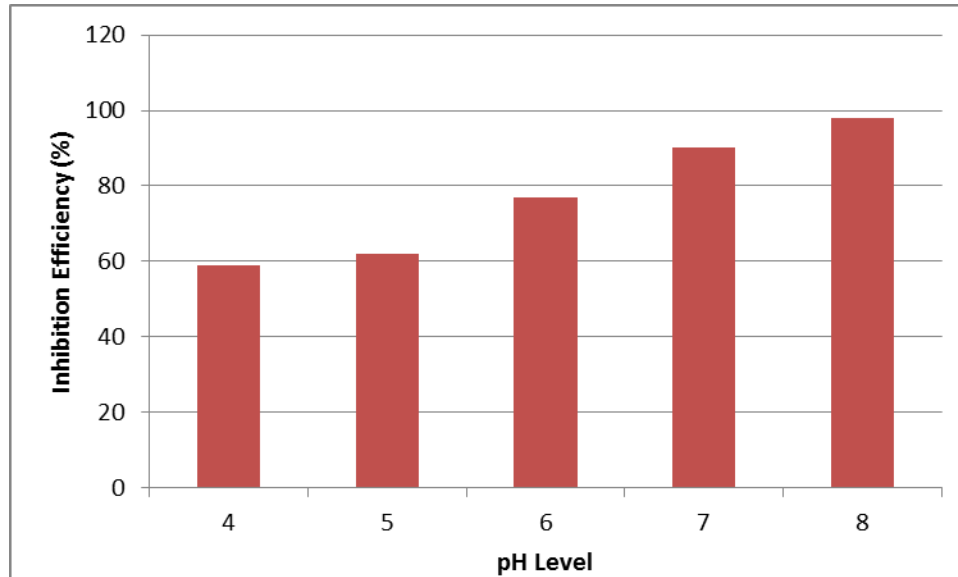


Figure 7 – Effects of solution pH on Inhibition Efficiency

9.4 Effect of Polymer Composition

With results gotten from these experiments, a comparative analysis of the polymer based inhibitors and the phosphonate based inhibitors were also made. The results compare with best results from previous experiments involving BaSO₄ inhibitions in the presence of various Scale inhibitors and were analysed. The order of inhibitor effectiveness as given in Figure 8 can be summaries as:

HEDP > PAA-AC >> PMPA > PMA > PAA > Control (No Inhibitor)

It can be ascertained here that the SI with the best performance imparted the most negative electrophoretic mobility to the Barium Sulphate particles.

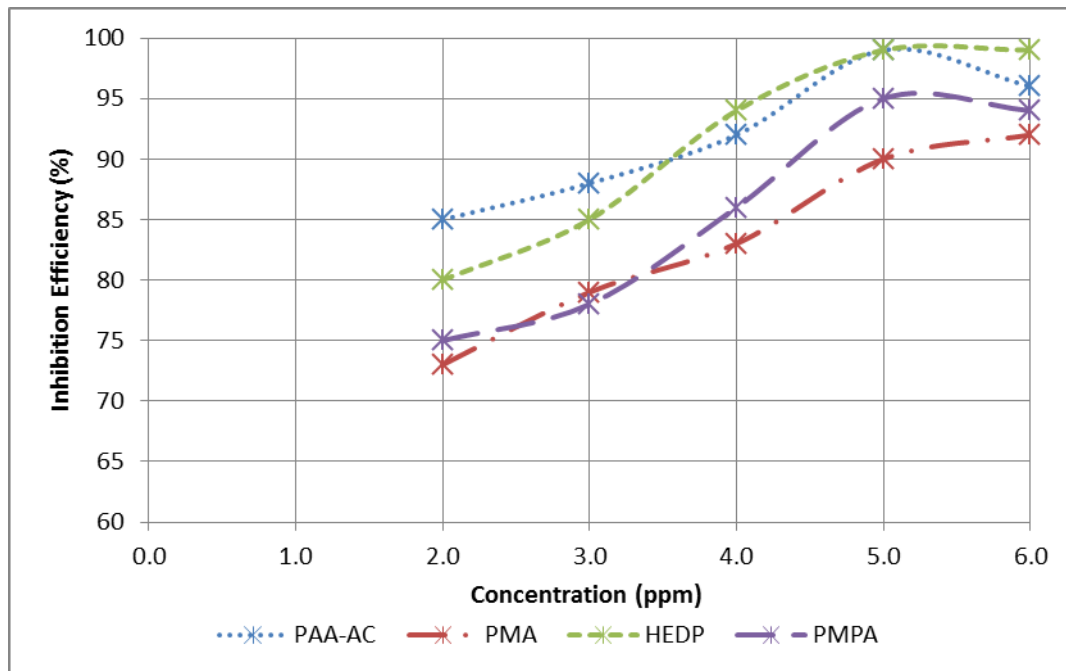


Figure 8 – Effects of Polymer Composition on Inhibition Efficiency

10. PERFORMANCE OF BARIUM SULFATE INHIBITORS

The results discussed above on barium sulphate precipitation with selected polymer and non-polymer based inhibitors composed of varying functional groups and at different concentration can be categorized into the following two types:

1. The anionic-charged low molecular weight PMA, PAAs and phosphorus-containing inhibitors (i.e. PMPA and HEDP) that exhibit significantly high inhibitory performance on BaSO₄ scale precipitation.

2. The neutral or cationic-charged inhibitors, such as benzene poly(carboxylic acids) and poly(acrylamide), which showed low inhibitory effect on BaSO₄ scale precipitation.

The performance of BaSO₄ precipitation inhibitors as observed in this study may be due to one or more of the following reasons:

- The possible change in the ionic strength of the inhibitor.
- High level formation of stable complex with barium and/or sulphate ion by the scale inhibitor which reduces supersaturation of the solution and consequently the effective solubility of the Barium Sulphate salt.

- The possible adsorption of the scale inhibitor on the nuclei of the precipitating crystals which may affect the crystal's thermodynamic stability and consequently inhibit its growth.

Considering the state of the BaSO₄ solution as well as the inhibitors under various experimental conditions employed in the present investigation, an adsorption mechanism seems to offer a more realistic explanation due to the observed fact that the inhibitor concentrations used were so small which means that the formation of barium inhibitor complex and/or a subsequent increase in ionic strength would have effect on the supersaturation state of the BaSO₄ solution. Instability of precipitated crystal in the presence of scale inhibitors in brine system is widely attributed to the adsorption mechanism.

11. CONCLUSION

The experimental results obtained in this study shows that the prevention of Barium Sulphate scaling in the reservoir is mostly effective if the two key factors considered below are handled effectively;

1. Scaling Rate: Prevention of the formation of a saturated brine (i.e. making sure that the injection or mixing of the injected water (seawater) with the formation water does not raise the solution's saturation beyond acceptable level).

2. Low Molecular Weight polymer inhibitors: It has been noted that polymer based inhibitor group performs best under certain conditions. The conditions to be considered include;

- The molecular weight of the inhibitor to be used: It was observed that a low molecular weight of about

2200 provides excellent inhibitory performance in the Inhibitor Efficiency test less than 22 hours.

- b) Concentration of the inhibitor to be used: Optimal Inhibition efficiency was also noticed at a concentration of 5 ppm.
- c) pH value of the solution brine: It was also noted that increase in acidity of the solution leads to increase in the inhibition efficiency of the Inhibitor. In the oil field, it is therefore imperative that the pH value of the polymer based scale inhibitor should be maintained at about 7 or above for best inhibitory performance.
- d) Polymer composition
- e) Cost: PMA tends to fulfill the first four considerations very favorably, however it is considered to be relatively more expensive whereas the low molecular PAA-AC is more cost-effective and also provides comparatively excellent inhibitory performance.

Environmental considerations:

In this study, PMA, normal PAA and the LMW PAA-AC were all considered as a group in their environmental compatibility in contrast to phosphonate based inhibitors. PAA-AC was confirmed to have a complete biodegradability (into simple components) and distinguished from other inhibitors that are considered to have partial degradation (into different related components).

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