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Effects of Temperature on Silicate Scale Inhibition During ASP Flooding

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Abstract: Alkaline/Surfactant/Polymer (ASP) flooding is a widely acceptable enhanced oil recovery technique. Despite its popularity as a potentially cost-effective chemical flooding method, it is not devoid of some problems, a major of which is the excessive formation of silicate scales. Silicate scale is a very serious problem in the oil and gas industry, which can form in perforation holes, casing surface, tubing and surface facilities. As the ASP flood progresses into the production well, produced liquid from different layers intermingle, there is decrease in pressure and temperature and there is rapid decrease in the pH of the mixed waters. These among other factors result to precipitation of silicates and its deposition on tubing, surface pipeline, pumps and surface production facilities, resulting into excessive production loss, increasing the average workover periods which influence the production and cause low commercial effectiveness. This study studied the effects of temperature on the performance of some scale inhibitors to mitigate silicate scales. Scale Inhibitors tested here are: RC1, RC7 and PASP. The study is part of an ongoing research on green scale inhibitors for mitigating silicate scales during ASP Flooding. Future publications will cover some proposed PGLU based green scale inhibitors.

Key words: Alkaline/Surfactant/Polymer (ASP) flooding, silicate scales, temperature, scale inhibitors

INTRODUCTION

In oil and gas operation, oil recovery has been conventionally divided into three phases: Primary, secondary and tertiary. Over the years, they defined the production from the reservoir in a step wise manner. After the primary and secondary phases become uneconomical, the third phase of oil recovery comes into play. Tertiary techniques use miscible gases, chemicals and/or thermal energy to displace additional (Green and Willhite, 1998). Alkaline/Surfactant/Polymer (ASP) is one of such methods which have been identified as a cost-effective Chemical Enhanced Oil Recovery (CEOR) process yielding incremental rates between 21.4-23.24% OOIP in excess of secondary recovery in oil fields it has been used (Shutang and Qiang, 2010). Since the previous Chemical Enhanced Oil Recovery Techniques (CEORs) possess essential downsides such as adsorptive surfactant loss in a plain surfactant flood or extended duration of a dilute alkaline flood, the ASP offers to overcome such problems (Arensdorf et al., 2010). The simple yet fundamental fact that a combined chemical phase behavior of the injected surfactant and the in situ generated natural surfactant is identified within an ASP Flood makes it more rewarding in comparison to alternative CEORs (Liu, 2008).
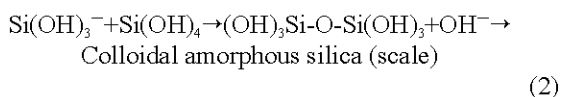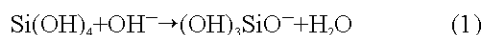
SILICATE SCALES

Inspite of the successes recorded by ASP Flooding as a cost effective CEOR, it is associated with severe problems, one of which is silicate scale deposition. Silica (SiO_2) is available in numerous crystalline and amorphous forms. Crystalline silica possesses a very low solubility in water, on the order of 6 mg L^{-1} SiO_2. On the other hand, amorphous silica has a much greater solubility in the range of 100-140 mg L^{-1} SiO_2. The possibility of silica scaling raises once the dissolved silica levels in an aqueous system exceeds the amorphous silica solubility limit (in the range of 120-140 mg L^{-1} at normal temperature). Once dissolved in water, silica forms silicic acid [$H_4Si(OH)_4$] (Amjad and Zuhl, 2009) . However, at silica concentration above 140 mg L^{-1}, silicic acid undergoes base-catalyzed polymerization leading to the formation and deposition of colloidal polysilicic on system surfaces. Silica scaling can occur by one of the three possible routes:

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- Condensation of monomeric silicic acid on solid substrate containing "-OH" group
- Polymerized silicic acid or colloidal deposition and
- Biogenic amorphous silica by living organisms (Kostas *et al.*, 2007)

The prospect for silica scaling arises in the event the dissolved silica level in the system exceeds the solubility limit (~100 mg L^{-1} at ambient temperature) for amorphous silica. Colloidal silica formed during silica polymerization can break down a system or deposit on surfaces. On top of that, polyvalent metal ions present in feed water streams can complex silica and catalyze the precipitation. The mechanism of silica polymerization is very complex and is thought to occur via the base catalyzed reactions in Eq. 1 and 2 as suggested by Amjad and Zuhl (2009).

$$Si(OH)_4+OH^-\rightarrow(OH)_3SiO^-+H_2O \qquad (1)$$

$$Si(OH)_3^-+Si(OH)_4\rightarrow(OH)_3Si\text{-}O\text{-}Si(OH)_3+OH^-\rightarrow$$
$$\text{Colloidal amorphous silica (scale)}$$
$$(2)$$

Mechanism of silicate scale formation: The problems connected with silicate are most likely distinct from those of conventional scales. Its development in the oil field is often an intricate and inadequately understood process (Amjad and Zuhl, 2008). The ASP flood has a high pH of 11 or above. During its progression in the reservoir, quartz silica is dissolved (Arensdorf *et al.*, 2010) and becomes stable in the high pH alkaline flood, since its solubility is pH dependent. But, when the ASP water runs to the production well, it meets neutral pH connate water either nearby the well bore or within the well. Interacting with this neutral connate water neutralizes the high pH alkaline water. This pH decrease results in polymerization of dissolved silica to form colloidal silica nanoparticle (Arensdorf *et al.*, 2011).

The idea that the magnesium silicate system is highly pH dependent is well known. Below pH 7, magnesium silicate precipitation does not take place because silica is present primarily in an unionized form. As the solution pH is increased (notably, above pH 9), magnesium silicate is very likely to form. Additionally, the magnesium silicate system is very complicated due to numerous forms of diverse compositions that could possibly precipitate depending on the water chemistry (Mg, SiO_2, pH, temperature, etc.,) (Amjad and Zuhl, 2009). Previous studies have shown that the reaction yielding this silicic acid dimer is kinetically slow, in contrast to the reaction giving trimer, tetramer and pentamer which are very fast. All these equilibrium reactions show very high sensitivity to pH and tend to be accelerated by the presence of hydroxide forming metals e.g., Fe^{2+}, Mg^{2+} or Al^{3+}(Miner and Kerr, 2012).

The existence of magnesium may well reconnect the colloidal silicate particles and form an amorphous magnesium silicate. Usually, in the routine of ASP injection, water is softened (Amjad and Zuhl, 2009) to produce a buffer (a kind of barrier) within the reservoir, between the existing waters (which towards the end of a field life will become a blend of connate water and water flood water). The presence of any residual magnesium following the softening will precipitate as $Mg(OH)_2$ in the ASP. Mg will then be introduced into the neutral pH connate water. Even without the divalent cations, the colloidal silicate particles may continue to grow and form amorphous silica scale (Arensdorf *et al.*, 2010, 2011).

The composition and amount of a silica deposit as well as the rate at which it forms is dependent on pH, temperature, the ratio and concentration of calcium and magnesium and the concentration of other polyvalent ions in the water. It has already been documented that polymerized colloidal silica in the presence of polyvalent metal ions forms flocculated silica (Amjad and Zuhl, 2008). The principal supply of the OH- in the produced fluid will be the injected alkaline. Nonetheless, the principal source of any carbonate and silicate ions will be the reservoir rock, despite the fact that a Na_2CO_3 or an alkali silicate is injected as the alkali. Hence, the formation can contribute significant additional carbonate and silicate ions in the mineral dissolution (Sonne *et al.*, 2012). Cenovus in their reviews for the IETP project at Suffield UU reported that generally there are two kinds of scales produced during the course of ASP projects, in the beginning, calcium carbonate dependent and later on, amorphous silica dependent. Raising pH owing to injection of alkali performs a key role in the buildup of the two types of scales. The earliest type develops once the pH increases between 8.3 and 9 however, the second type is usually aggravated from magnesium and calcium acting like 'glue' to link colloidal silica. In the same manner, studies on Taber projects reported that scale will become noticeable whenever the pH of the produced water lies between 9 and 11. Outside this range, scales are not necessarily deposited within the well equipment.

Other studies have pointed to the fact that the alkali in solution reacts with both formation fluids and mineralogical components such as kaolinite, montmorrillonite and feldspar, from which silicon and aluminium components and soluted into fluids (Sonne *et al.*, 2012).

Silicate scale inhibition processes and functions of scale inhibitors: Scale is believed to deposit forming a set of stages as shown in Fig. 1. Majorly, the stages of scale formation are precipitation, sedimentation and crystal growth. It is these basic stages of scale formation that is utilized by different chemical scale inhibitors in preventing scale formation, as shown in Fig. 2. Thus, scale inhibitor
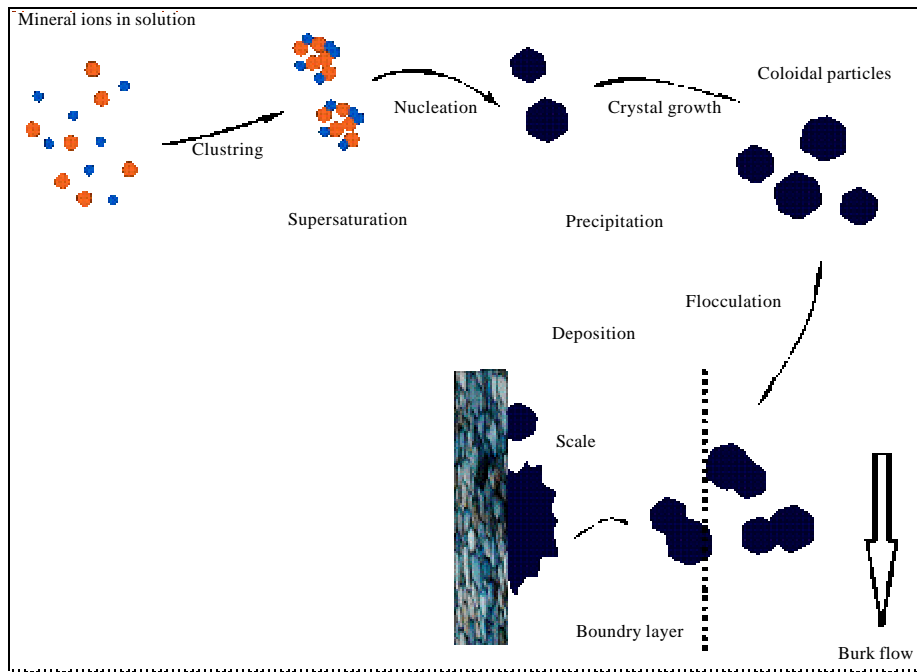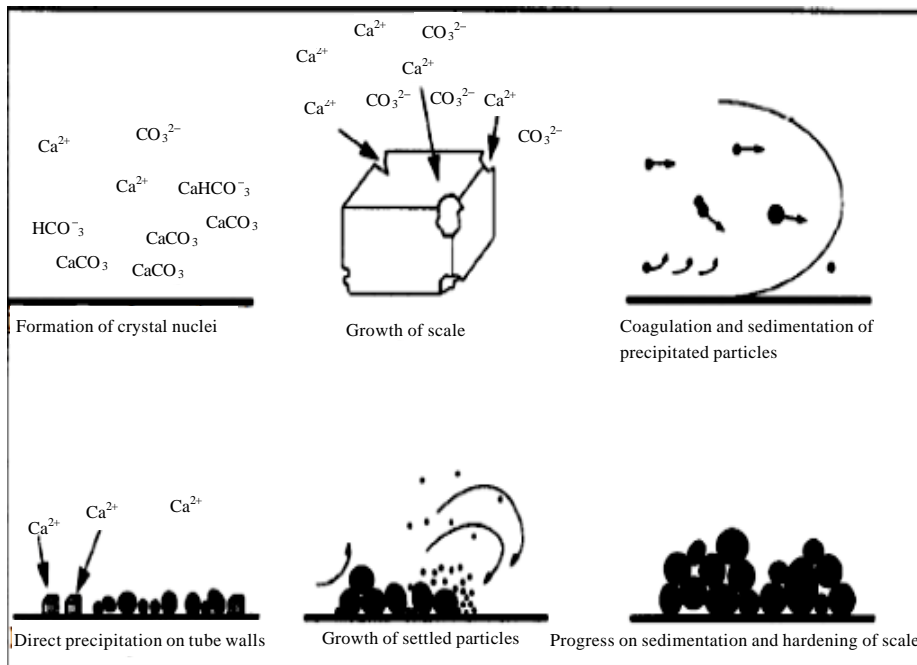
Fig. 1: Steps of scale deposition

Fig. 2: Pathways of scale prevention

action is classified as a threshold inhibition, crystal modification and dispersancy. The functions of the inhibitors is seen as for the case of precipitation, precipitation inhibition, threshold effect and chelating

effect. For sedimentation, the function of the inhibitor is seen as to its dispersing effect while it is seen as crystal distortion effect for the crystal growth stage (Siegmeier *et al.*, 1998). Precipitation of silicate may be impossible to be prevented, because silica solubility is strongly on pH and any distortion of the pH will result to silica precipitation. Crystallization originating from a particular solution are generally divided into two-step process. The first process is the spontaneous nucleation (birth) of a new crystal. The subsequent process is the morphologic development (growth) of the crystals into bigger and extra complex components. Spontaneous nucleation should happen prior to the crystals morphologic progression commences. The circumstances that happen to be conductive to nucleation tend to be a function of thermodynamic stability of molecular elements within the system.

CHEMICAL SCALE INHIBTORS

Scale inhibitor is a kind of chemical substance that prevents or disrupts inorganic scale nucleation, precipitation and sticking to production gateway, completion system or processing facilities which are the three factors triggering scaling issues. Its performance is influenced by the pH, temperature, calcium and magnesium ion levels and the existence of several other chemical substances (e.g., corrosion inhibitor) inside the scaling brine mixtures. Its threshold level for any identified amount of inhibition is called Minimum Inhibitor Concentration (MIC) which is normally 0.5-20 ppm.

In the Oil Industry, scale inhibitors fall under 3 major categories: Inorganic phosphates, organophosphorous and organic polymers. Each one has its specific application as well as environmental hurdles. Another important breakthrough in the area of scale inhibition is blending scale inhibitors. Some hands in hand behavior amongst various scale inhibitors (especially the polyacrylates and phosphonates) have recently been discovered. The reasons for this kind of synergism might be that varied chemical forms work by using totally different mechanisms. One feasible justification could be that the anionic polymer chain disrupts the nucleation process while the smaller phosphonates molecule adsorbs to crystal nuclei, stopping active growth sites and stopping further crystal growth (Kostas *et al.*, 2007).

MATERIALS AND METHODS

Reagent grade chemicals and distilled water were used in accordance with standard operating procedures

Table 1: ASP and synthetic formation water used in silica polymerization test (Arensdorf *et al.*, 2010)

| Salts | ASP ($g\,L^{-1}$) | Synthetic formation water | |
		Connate anion ($g\,L^{-1}$)	Connate cation ($g\,L^{-1}$)
NaCl	2.50	2.4	3.5
KCl	0.08	-	0.16
$Na_2SiO_3.\,5H_2O$	14.20	-	-
$MgCl_2.\,6H_2O$	-	-	2.0
$CaCl_2.2H_2O$	-	-	0.6

used in the industry as well as previous research works, with slight modifications in preparing the brine solutions.

To examine the effect of temperature on inhibitor performance, a number of experiments were carried out, adopting some modified silicate scale polymerization procedures (Arensdorf *et al.*, 2010; Amjad and Zuhl, 2008). Both static and dynamic test methods were conducted. Turbidity measurements were conducted using Turbidimeter Hach 2100Q.

One Liter of 100 ppm silicate scale solution was prepared from sodium silicate, dissolved in a known volume of distilled water. The solution filtered prior to usage. Another separate one liter of synthetic formation water was prepared by carefully measuring different salt compositions as shown in Table 1. In order to reproduce silicate scale, the amount of magnesium salts added is doubled the original amount, to prepare high magnesium content brine. Add desired amount of NaCl and stir thoroughly and filter before it is stored for usage. Adjust pH to 10.7. In this procedure, use a ratio of 1:1 sodium silicate: brine solution at different temperatures without using any inhibitor. Temperatures used for this study are 30, 60 and 90°C. A fan-assisted oven is used to raise the temperature of the solution. The temperatures are raised at a range of $10°C\,h^{-1}$ from room temperature to reservoir temperature. A visual inspection of the bottle is made to observe formation of precipitates after each hour. At high temperatures, put sample bottle in a water bath full of cold water, to lower temperature below 50°C before taking NTU readings.

RESULTS AND DISCUSSION

From the work of Amjad and Zuhl (2008), it has been established that there are a pair of contesting variables triggering temperature effect: (a) Silica supersaturation decreases as temperature increases on account of greater silica solubility and (b) Silica polymerization rate will increase when temperature increases. Figure 3 below shows how silica polymerization increases when the temperature of the solution increases. The turbidity which is used as a measure of precipitation increases with increase in solution temperature from 30-90°C.
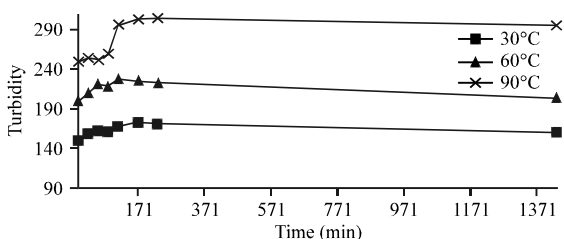
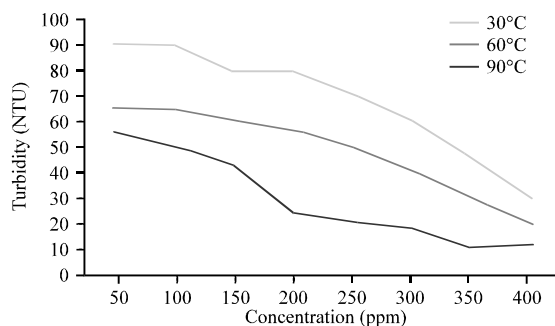Fig. 3: Effect of temperature in silica polymerization
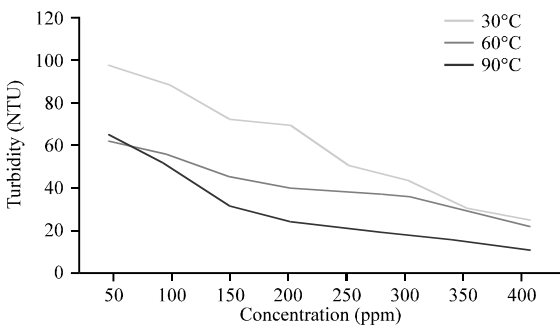

Fig. 4: Effects of temperature on inhibitor dosage (PASP)

Fig. 5: Effects of temperature on inhibitor dosage (RC1)
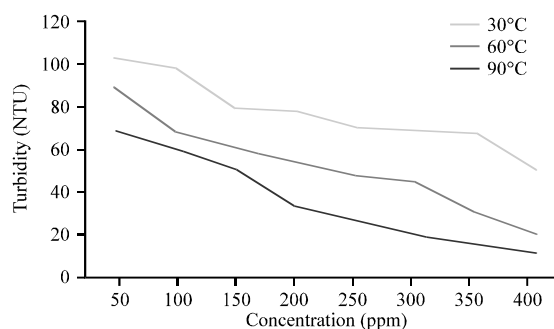

Fig. 6: Effects of temperature on inhibitor dosage (RC7)

Fig. 7: PASP performance at various temperatures

In examining the effect of temperature in silicate scale inhibition, the silica polymerization test is conducted at different temperatures, but in the presence of different inhibitor concentrations, as shown in Fig. 4. The result obtained shows that increasing solution temperature reduces the dosage of chemical inhibitor necessary to inhibit silica polymerization. It can be noted that, at temperature of 30°C a PASP dosage of around 400 ppm is required to mitigate silicate scale, but only around 150 ppm of it is required if the temperature is 90°C. This is due to reduced silica supersaturation at higher temperatures.

In Fig. 5 and 6, the same trend as seen in Fig. 4 is generally repeated. As the inhibitor concentration increases, so also does the inhibition efficiency. However, this action is doubled when there is equally an increase in solution temperature which is attributed to reduced silica supersaturation at higher temperatures.

It is worth noting however, that an interesting trend tends to repeat itself in the case of RC7, as shown in Fig. 6. At temperature of 30°C, a dosage of 300 ppm RC7 is required to achieve a turbidity of 68.5 NTU. This same value is obtained at dosages of 100 and 50 ppm, when solution temperature is 60 and 90°C, respectively. This will give some very useful information, regarding how solution temperature affects inhibitor dosage requirement. Thus, at higher solution temperatures, less inhibitor dosage is required.

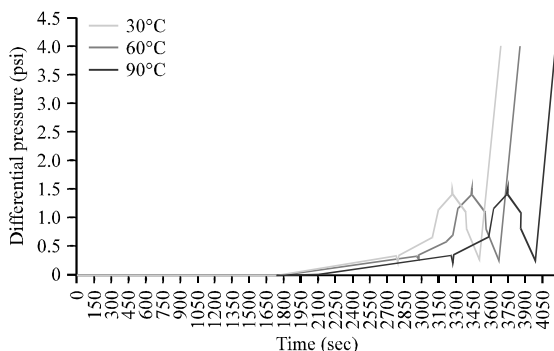Figure 7 shows the result obtained from a dynamic tube block experiment conducted using a PMAC automated tube blocking rig. Here, the performance of PASP was tested under different temperatures, but with a flow rate of 5 mL min^{-1} and a constant inhibitor concentration of 100 ppm.

CONCLUSION

This study which is aimed at assessing the effects of temperature on silicate scale inhibition, has come to terms with previous works done by experts in the area. Silica polymerization tests conducted in the absence of scale inhibitors and at different operating temperatures have

shown that solution temperature significantly affects silica polymerization. The same test procedure conducted in the presence of three chemical inhibitors has shown that increasing the operating temperature significantly reduces the chemical inhibitor dosage required to inhibit silicate scale. Thus, it is adequate to conclude by saying that, temperature of solution is an important factor in mitigating silicate scaling using chemical inhibitors. The higher the solution temperature, the less inhibitor dosage required to treat the scale present.

ACKNOWLEDGMENT

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