

Research Article

Silicate Scales Formation During ASP Flooding: A Review

Abubakar Abubakar Umar and Ismail Bin Mohd Saaid

Petroleum Engineering Department, Universiti Teknologi PETRONAS, 31750, Tronoh,
Perak Darul-Ridzuan, Malaysia

Abstract: This study reviewed and assessed some of the inhibition techniques used in the industry with regards to handling oilfield scales in general and silicates scales in particular. Conventional scale inhibitors used are facing restrictions world over, due to their ecotoxicity and non-biodegradability, which has led to the call for green scale inhibition in the oil and industry. Due to the inefficiency of the conventional primary and secondary recovery methods to yield above 20-40% OOIP, the need for Enhanced Oil Recovery (EOR) techniques to recover a higher proportion of the Oil Originally in Place (OOIP) has become vital. Alkaline/Surfactant/Polymer (ASP) is one of such techniques and has proven successful due to its ability to raise displacement and sweep efficiency. Despite its popularity as a potentially cost-effective chemical flooding method, it is not without (its) problems, one of which is the excessive formation of silicate scales. Silicate scale is a very serious problem in the oil and gas industry; which forms in perforation holes, casing surface, tubing and surface facilities. During an ASP flood, as the flood progresses into the production well, liquid produced from different layers intermingle, leading to a rapid decrease in the pH value of the mixed waters. Other factors such as temperature, pressure, divalent cations present also play some roles, but pH variation plays the major role. These among other factors facilitate precipitation of silicates and its deposition on tubing, surface pipeline, pumps and surface production facilities resulting in excessive production loss; increasing the average work over periods, which influences the production and causes low commercial effectiveness. Green scale inhibitors are considered as alternative scale inhibitors due to their value-added benefits to the environment with respect to the methods of treating oilfield scales. It is recommended that the industry should shift to the green technology as an alternative scale inhibition method so as to protect the environment.

Keywords: ASP, green scale inhibitors, OOIP, silicate scale, scale inhibition, scale inhibitors

INTRODUCTION

The current hike in oil prices and energy demand all over the world has necessitated the needs for Enhanced Oil Recovery (EOR) methods. EOR has been classified into five (5) categories, with general intent of either reducing the mobility ratio between injected and in place fluids, eliminating or reducing interfacial tension or act on both phenomena simultaneously (Teknica Petroleum Services Ltd, Alberta 2001). These classes are Mobility-control, chemical, miscible, thermal and other processes such as microbial. Alkaline/Surfactant/Polymer (ASP) is one of such method which has been identified as a Cost-Effective Chemical Enhanced Oil Recovery (CEOR) process yielding incremental recovery rates above 20% in some oil fields like Daqing oilfield in China, which is the most successful case of ASP flooding in the world (Shutang and Qiang, 2010). While the earlier Chemical Enhanced Oil Recovery Techniques (CEORs) have suffered integral drawbacks like adsorptive surfactant loss in a plain surfactant flood or long duration of a

dilute alkaline flood, the ASP promises to alleviate such problems (Stoll *et al.*, 2011). The possession of a combined chemical phase behavior of the injected surfactant and the in-situ generated natural surfactant is a key advantage of the Asp flood over other CEORs. Thus, ASP flooding to recover oil has become more common in recent years.

Significant developments have made ASP flooding a viable option for field enhanced oil recovery and more attractive than polymer or micellar/ polymer flooding (Shunhua, 2008; Bataweel and Nasr-El-Din, 2011). In recent years, apart from Daqing oil field in China, there have been many field pilot tests using ASP flooding in USA, India and Venezuela showing a dramatic recovery of 21.4- 23.24% OOIP over secondary recovery (water flooding) (ElRaies *et al.*, 2010).

Despite the recorded successes, yet it is not without challenging problems troubling the production engineers. The formation of strong emulsions and excessive formation of silicate scale especially with the current higher concentration of alkali has become

Corresponding Author: Abubakar Abubakar Umar, Petroleum Engineering Department, Universiti Teknologi PETRONAS, 31750, Tronoh, Perak Darul-Ridzuan, Malaysia, Tel.: +601116309566

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Table 1: Main components analysis of scale samples in different ASP flooding stages (Jiecheng *et al.*, 2011)

Stage	Feature	Organic (%)	CaCO ₃ (%)	MgO (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)
Initial Stage	Fast scaling speed and large quantity of carbonate	15.90	55.30	0.84	0.25	0.51	20.09
Mid Stage	Increasing silica scale and stable speed	10.57	16.93	0.27	0.15	2.96	66.96
Late Stage	Stable speed	9.90	14.90	0.62	0.14	1.10	70.80

noticeable (Wang *et al.*, 2004; Karazincir *et al.*, 2011; Jia *et al.*, 2002; Stoll *et al.*, 2011; Arensdorf *et al.*, 2010; Arensdorf *et al.*, 2011). Chemical flooding is associated with several operational issues. Problems like Low injectivity or complete plugging of injection wells, polymer degradation, pump failures, incomplete polymer dissolution, corrosion and scaling have been encountered (Bataweel and Nasr-El-Din, 2011). This study reviewed and assessed some of the inhibition techniques used in the industry with regards to handling oilfield scales in general and silicates scales in particular, with focus on green scale inhibitors as alternative chemicals for scale treatment.

SCALE COMPOSITION AND DESCRIPTION

Scale definition: The definition of the concept of scale is as difficult as the field menace itself. Many definitions of the oil field menace in literatures did not satisfactorily represent the problem. Scale can satisfactorily be defined as a secondary deposit of mainly inorganic chemical compounds caused by the presence or flow of fluids in a system at least partially manmade (Vetter, 1976). This definition is still considered incomplete because it does not differentiate between a real scale and pseudo-scales. It is true of many instances where some scale inhibitors (e.g. phosphonates and polymers) used in treating the scales itself would react with Ca²⁺ and/or Mg²⁺ present in the oil field brine to form a pseudo-scale which does not only look like a real scale, but causes the same problem like the real scale (as in a production well located in the Williston Basin of North Dakota) (Vetter, 1976; Krumrine *et al.*, 1985).

The problems of scales are usually associated with the deposition of inorganic minerals such as calcium carbonates (CaCO₃) and sulfates of calcium, strontium and barium. Depending on the nature of the scale and the composition of the fluid, scale deposition can be found within the reservoir, near the wellbore perforation which causes formation damage, or can be found in surface or subsurface production facilities with different level and severity of operational problems (Shar *et al.*, 2010).

The composition of scaling samples is basically made up of organic, inorganic and crystal water (Jiecheng *et al.*, 2011). A scale may occur as a single-mineral phases, but more commonly it is a combination of different elements, which can occur when a solution becomes saturated, mostly due to changes in temperature during injection operations, changes in pH values or if two different chemicals that will precipitate are brought together. From a thermodynamic point of view, there is a stable region, a metastable region and an unstable region, separated by the binodale curve and the spinodale curve, respectively (Fink, 2003).

Table 2: Residue composition of ASP flooding production well scale (Jia *et al.*, 2002)

No	Residue Composition, %				
	SiO ₂	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃
1.	72.73	9.04	0.57	0.98	0.25
2.	77.90	16.00	1.08	0.00	2.59
3.	72.58	2.80	2.20	0.39	22.01
4.	70.68	13.40	1.10	2.43	4.45

Table 3: SEM/EDAX Elements compositions of scale samples (Shar *et al.*, 2010)

Elements detected	Wt. (%)
Calcium	53.07
Strontium	41.26
Barium	5.68

Table 1 below shows the scaling characteristics of oil wells in different stages. In the initial scaling stage, carbonate precipitation is the dominant scale, accounting for over 50%, while silicon scale accounts for around 20%. Calcite scale contents keep reducing in percentage in the medium stage, correspondingly that of silicon increases. The late stage shows how silicon scale dominates the scale composition with over 70% while calcite scale reduces to its minimum. It is obvious therefore, that the initial stage of an ASP flood does not encounter excessive silicate scales as compared to later stages, or after the maturity of the ASP flooded area.

The best and most reliable analytical technique for determining the composition of any scale deposit is X-Ray diffraction and energy dispersive spectroscopy (XRD/EDS). When these two tools are used together, one can conveniently and quickly determine the percent mineral composition of a scale sample (Charles, 1998). The scales from oil wells are not single compositions. They consist of silicon scale, carbonate scale and organic impurities. Silicon exists as silicate or SiO₂, while Ca²⁺ and Mg²⁺ exist as carbonates (Jinling *et al.*, 2009).

As shown in Table 2, an analysis of four scale samples has revealed the percentage composition of each scale sample. As seen, the contents of SiO₂ in the inorganic residues (after being subjected to 700 °C in a furnace) are all above 70%, indicating that the three samples are all silicate scales.

Table 3 shows the SEM/EDAX analysis carried out on a scale sample, showing the dominant elements in the scale sample as calcium and strontium.

Types of scales: The classification of scale is of course related closely to its definition. As stated above, Vetter (1976) defined scale as a secondary deposit of mainly inorganic chemical compounds caused by the presence or flow of fluids in a system at least partially manmade. Going by this definition, all deposits of calcium sulfate

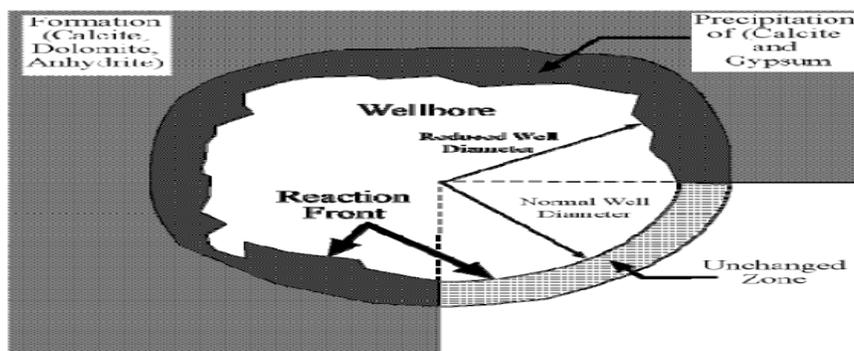


Fig. 1: Schematic precipitation of calcium carbonate and calcium sulfate in wellbore section (Frenier and Wilson, 2000)

(CaSO_4), calcium carbonate (CaCO_3), barium sulfate (BaSO_4), strontium sulfate (SrSO_4) and the carbonates, oxides and hydroxides of iron as scales. In oilfield operations, the most commonly encountered scales are the sulfates, such as calcium sulfates, barium sulfate, strontium sulfate and the carbonates, such as calcium carbonate.

- **Calcium Carbonate Scales:** This is the most frequently encountered scale in oilfields. Due to the fact that calcium carbonate scales have the greatest stability in oilfields circumstances, it has become the commonest encountered scale in oilfield production operations. As many other mineral scales, calcite deposition depends on several factors such as temperature, pH, ionic strength, pressure and dissolved salts (Ajienka and Eseosa, 2011).
- **Calcium Sulfate Scales:** The precipitation of this material is somehow complicated, mainly because it exists in more than one crystal modification. For example, there is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4) and hemi-hydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$). Depending on the conditions under which the calcium sulfate precipitates, any one of these three modifications can start the precipitation (Vetter, 1976). Among various mineral scales in the oil industry, calcium sulfate is one scale that results to major problem of flow assurance and formation damage issues. CaSO_4 is somewhat dependent on temperature, but is typically precipitated because of a decrease in pressure or an increase in the relative concentrations of calcium or sulfate. Its solubility is fairly pH dependent, hence can readily precipitate in an acid environment (AmerBadr, 2007).
- **Barium Sulfate Scales:** This is the most insoluble scale that can be precipitated from oilfield waters, forming a very hard scale which is very difficult to remove. Basically, its solubility is increases with increasing temperature, increasing pressure and increasing salt content of the brine. Generally, temperature change has the largest effect on the

precipitation of BaSO_4 in most wells. Though, salt concentration also has a reasonable effect, it hardly takes the lead since only few cases exist where the brine content changes appreciably within a well (Vetter, 1976).

Figure 1 below shows a schematic of precipitation in a wellbore section, of calcium carbonate and calcium sulfate.

In the wellbore section, scale can form in the completed interval of a production well as one brine enters the completion, while other brine is following up the tubing from a lower section, or as fluid pressure decreases. Similarly, it can form around the injection well, as injection brine enters the reservoir, contacting formation brine (Amerbadr, 2007).

According to Kan and Tomson (2010), common oilfield scales are classified as “pH independent” and “pH sensitive”. The scaling tendencies of sulfates (calcium sulfate, barite and celestite) and halite scales are not a strong function of brine pH values. The carbonates (calcite, dolomite and siderite) however and sulfides scales are acid soluble and their tendencies are strongly influenced by the brine pH. For pH sensitive scales, the scale prediction is more complicated since issues that control the brine pH also affect their scaling tendencies. According to Vetter (1976), barium sulfate is the easiest to predict, while calcium sulfate is much harder to predict than barium sulfate.

SILICATE SCALES DURING ASP FLOODING

Alkaline/surfactant/polymer flooding:

Origin and definition: The current high oil prices combined with the challenges of discovering and developing offshore and remote oil fields have made improving recoveries from existing mature oil fields attractive (Dang *et al.*, 2011). Outside the ‘oil family’ some people are mindful that an oil reservoir habitually will yield only a fraction of the oil held underground (Watkins and Chant, 1985) what is technically known as “Original Oil in Place” (OOIP). It is not surprising that such a deduction be made by non-experts since oil

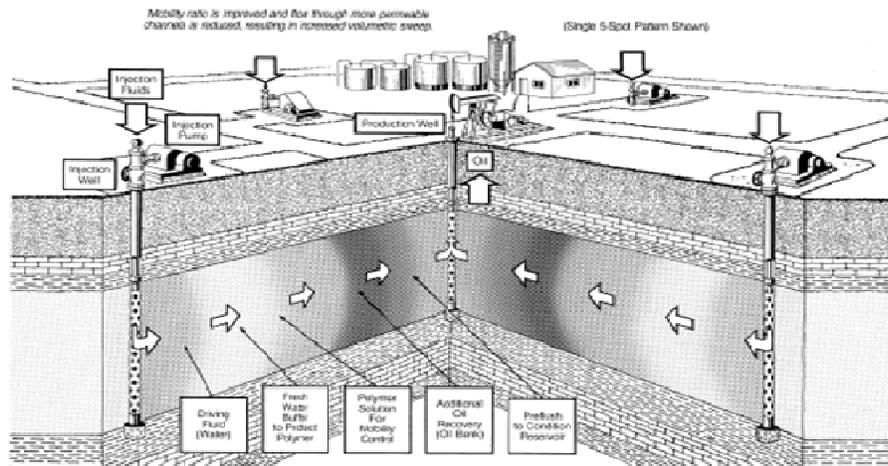


Fig. 2: Schematic of chemical flooding EOR (Crabtree *et al.*, 1998)

obtained from reservoirs via conventional primary and secondary are expected to produce about 20-40% OOIP (Shunhua, 2008; Green and Willhite, 1998) leaving some oil “stranded” in the reservoir. However, time and effort has been devoted to projects designed to improve the recovery of hydrocarbons after the primary and secondary methods are uneconomic, known as Enhanced Oil Recovery. The Society of Petroleum Engineers, (SPE), defined EOR as “One or more of a variety of processes that seek to improve the recovery of hydrocarbon from a reservoir after the primary production phase” (SPE Glossary, 2009). This definition is interesting because it does not necessarily imply that the oil has to be “stranded” in the reservoir before EOR can be applied. It only gives an option to a continuous production economically after primary and secondary methods exhaust their ability to yield economic hydrocarbon production.

The target of enhanced oil recovery is to improve sweep efficiency by reducing the mobility ratio between injected and in-place fluids, eliminate or reduce the capillary and Interfacial Tension (IFT) and consequently improve the displacement efficiency or act on both occurrences simultaneously (Shiyi *et al.*, 1998; Zhang and Huang, 2003).

EOR processes involve the injection of a fluid or fluids of some type into a reservoir. The injected fluids and injection processes supplement the natural energy present in the reservoir to displace oil to a producing well. In addition, the injected fluids interact with the reservoir rock/oil system to create conditions favorable for oil recovery. These interactions might, for example, result in lower IFT's, oil shelling, oil viscosity reduction, wet ability modification or favorable phase behavior. The interactions are attributable to physical and chemical mechanisms and to the injection or production of thermal energy (Zhang and Huang, 2003). As a promising technique to recover more oil, EOR has been classified into 5 categories, with general

intent of either reducing the mobility ratio between injected and in place fluids, eliminating or reducing interfacial tension or act on both phenomena simultaneously (Teknica Petroleum Services Ltd, Alberta 2001). These classes are Mobility-control, Chemical, Miscible, Thermal and Other processes such as Microbial (Zhang and Huang, 2003).

Mechanism of ASP flooding: Chemical combination flooding is especially applicable for tapping crude oil with certain of acid value (Arensdorf *et al.*, 2010). Various literature exist regarding the study of chemical flooding which include alkaline flooding, surfactant flooding, polymer flooding and Alkaline Surfactant Polymer Flooding (Shunhua, 2008; Krumrine *et al.*, 1985; Dang *et al.*, 2011; Watkins and Chant, 1985; Green and Willhite, 1998; Zhang and Huang, 2003). ASP flooding, a new type of chemical flooding termed “Enhanced Alkali Flooding” is a combination process which promises to mitigate the flaws suffered by previous chemical flooding processes such as long duration of dilute alkaline flooding and significant adsorptive surfactant loss in a plain surfactant flood (Vetter, 1976).

During an ASP flood, in conjunction with the added surfactants, the surfactants generated in situ by the chemical reactions between the injected alkali and the natural organic acids in the crude can result in ultra-low interfacial tension (IFT). The ultra-low IFT at the oil-brine interface emulsify and mobilize the residual oil in a reservoir (Green and Willhite, 1998). The purpose of the surfactant is to lower the IFT between the residual oil and the injected fluids, while the alkali exists to further lower the IFT by reacting with acidic components of the oil to form additional surfactant within the formation.

Figure 2 and 3 below show schematic of a chemical enhanced oil recovery and scaled pipes and valves respectively.



Fig. 3: Scale deposits in pipes and valves (Duccini *et al.*, 1997)

The polymer used in ASP is designed for better sweep of the reservoir due to its ability to increase the viscosity of the fluids (Krumrine *et al.*, 1985).

Advantages of ASP over other CEORs: While the earlier Chemical Enhanced Oil Recovery (CEOR) techniques have suffered central drawbacks like adsorptive surfactant loss in a plain surfactant flood or long duration of a dilute alkaline flood, the ASP promises to alleviate such problems (Stoll *et al.*, 2011).

The possession of a combined chemical phase behavior of the injected surfactant and the in-situ generated natural surfactant is a key advantage of the ASP flood over other CEORs. Thus, the use of ASP flooding to recover oil has become more common in recent years. Significant developments have made ASP flooding a viable option for field enhanced oil recovery and more attractive than polymer or micellar/polymer flooding. Chemical flooding is associated with several operational issues. Problems like Low infectivity or complete plugging of injection wells, polymer degradation, pump failures, incomplete polymer dissolution, corrosion and scaling have been encountered (Stoll *et al.*, 2011; Shunhua, 2008; Green and Willhite, 1998; Shiyi *et al.*, 1998; EOR Brochure, 1986).

Silicate scale formation during ASP flooding: Alkali-Surfactant-Polymer (ASP) flooding technology, as an important technology of tertiary oil extraction, has been found to enhance oil recovery by over 20% and hence has been used in full-scale in the Daqing oilfield, which is the most successful case of ASP flooding in the world (Jiecheng *et al.*, 2011). This combination system has been recognized as a cost-effective chemical flooding process for light and medium oils. Apart from Daqing oil field in China, there have been many field pilot tests using ASP flooding in USA, India and Venezuela showing a dramatic recovery of 21.4-23.24% OOIP over secondary recovery (water flooding) (ElRaies *et al.*, 2010; Jia *et al.*, 2002; Zhang and Huang, 2003; Qi *et al.*, 2000; Shutang and Qiang, 2010). Despite the recorded successes, yet it is not without stern problems. The formation of strong

emulsions and excessive formation of silicate scale especially with the current higher concentration of alkali has become noticeable (Bataweel and Nasr-El-Din, 2011; Wang *et al.*, 2004; Karazincir *et al.*, 2011; Jia *et al.*, 2002; Arensdorf *et al.*, 2010; Arensdorf *et al.*, 2011).

During ASP flooding, the alkali react with the rock minerals and formation water, thereby increasing the concentration of scaling ions (Ca^{2+} , CO_3^{2-} , SiO_2^{3-}) in the system. The production fluid encounters drastic change in temperature and pressure as it moves into or close to the well, thus breaking the scaling ion balances leading to the formation of scales in the wellbore, on the surface of downhole equipment and inner surface of transferring pipes (Cao *et al.*, 2007).

Factors that determine silicate Scale formation in ASP flood:

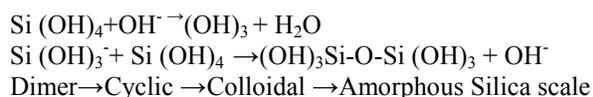
ASP flooding is a tertiary Enhanced Oil Recovery (EOR) method designed to lower Interfacial Tension (IFT), water wet the formation and decrease water mobility to produce residual oil. This result is achieved via a combination of alkali, surfactant and polymer (Demin *et al.*, 2007). Even as ASP improves recovery rate dramatically, the alkali in solution reacts with both formation fluids and mineralogical components such as kaolinite, montmorillonite and feldspar, from which silicon and aluminum components and soluted into fluids. The primary source of the OH^- in the produced fluid will be the injected alkaline. However, the primary source of the carbonate and silicate ions will be the reservoir rock, even though a Na_2CO_3 or an alkali silicate is injected as the alkali. Thus, the formation can contribute significant additional carbonate and silicate ions in the mineral dissolution (Jennifer *et al.*, 2012).

A very significant factor that determines whether a scale forms is the pH value of the system. Factors such as temperature, pressure, ionic make-up and other lesser variables also play some roles (Krumrine *et al.*, 1985). In an ASP flood where the alkaline water flood has a high pH, typically, 11 or higher (Arensdorf *et al.*, 2011); the high pH value can vary at different points within the system. The pH determines which solids phases form scale or precipitate to alter productivity. Though, some precipitates such as hydroxide precipitates are formed as a result of high pH value of the ASP flood, the silicate precipitates tend to be very complex chemically due to their dependence on the degree of the silicate ions polymerization, which is a function of pH value and concentrations. Study has shown that if carbonate scale exists, the silicates will also build to form a mixed scale (Krumrine *et al.*, 1985) and calcium carbonate may provide nuclei for the development of silicate scale (Gill, 1998).

Like carbonates and hydroxides, the solubility of silicates varies considerably over the possible pH range and with the type and concentration of multivalent cations present. Most commonly, the precipitates and scales are salts of magnesium and calcium.

A study into ASP scaling has shown that it is a mixture of carbonate and silicate. The major mineralogical compositions are amorphous state silicon dioxide, hexagonal-spherical calcite and conventional calcite. The minor mineralogical compositions are clastic quartz, clastic feldspar, clastic clay particles and pyrite (Cao *et al.*, 2007).

Mechanism of silicate scale formation: Though believed to be a very complex mechanism, silica polymerization is believed to follow the base catalyzed reaction proposed by Amjad and Zuhl (2008).



The issues associated with silicates are potentially different from those of traditional scales. Its formation in the oil field is a complex and poorly understood process (Arensdorf *et al.*, 2011). The ASP flood has a high pH of 11 or above. As it moves through the reservoir, quartz silica is dissolved (Miner and Kerr, 2012) and the dissolved silica becomes stable in the high pH alkaline flood. However, as the ASP flows to the production well, it encounters neutral pH connate water either near the well bore or in the well. Meeting this neutral connate water neutralizes the high pH alkaline water. This pH reduction results in Polymerization of dissolved silica and form colloidal silica nanoparticle (Jia *et al.*, 2002; Arensdorf *et al.*, 2011).

Miner and Kerr (2012) has reported 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+} .

The presence of magnesium can bridge the colloidal silicate particles and form an amorphous magnesium silicate. Usually, in the sequence of ASP injection, water is softened (Amjad and Zuhl, 2008) to provide a buffer in the reservoir between the existing waters (which in late field life will be a mixture of connate water and water flood water). The presence of any residual magnesium after the softening will precipitate as Mg (OH)_2 in the ASP. Mg is then introduced into the neutral pH connate water. In the absence of divalent cations, the colloidal silicate particles may continue to grow and form amorphous 'silica scale (Arensdorf *et al.*, 2010; Arensdorf *et al.*, 2011).

The polymerization of silica is controlled by pH. This could suggest that adjusting the pH may solve the problem of silica scale deposition. Unfortunately, this is not true and silica scale cannot easily be treated by

simply adjusting the pH, in a way CaCO_3 can be eliminated by operating the process at lower pH. Since the ASP flood has a high pH value, operating below a pH of 10.5 results in to the polymerization of silica and formation of colloidal silica (Kostas *et al.*, 2007). Lowering the pH does not eliminate the problem; it rather shifts it from "magnesium silicate" to "silica scale" (Jennifer *et al.*, 2012).

Location of scale formation: Depending on the location of super saturation, or where the conditions of precipitation are satisfied, scale may be deposited in the flow line only; it can deposit in both flow line and tubing and in some cases even in the perforations and in the formation near the wellbore (AmerBadr, 2007). Generally, there are 6 important regions where scaling can occur during and after injection operations. These are:

- In the injector wellbore
- Near the injection well bottom hole
- In the reservoir between the injector and the producer
- At the skin of the producer well
- In the producer well
- At the surface facilities

Apart from these general locations where scale is found, some oilfields have experienced scale depositions on few other locations different from these regions. An oilfield in southern Alberta that was placed under an ASP flood has experienced severe silicate scaling of production wells. The Progressive Cavity Pumps (PCPs) and associated rods scaled severely leading to their replacements. During ASP fluid injection, among the severe problems the production system is exposed to, is silica scaling and the resultant high frequency of pump failure leading to shortening the running life of the lifting system, low production efficiency and increased operating costs. This has severely affected the normal production of oilfield, thus becoming one of the bottlenecks for the industrial application of ASP flooding (Jiecheng *et al.*, 2011). The N-1DX block of Daqing oilfield in China, is one field that has experienced severe scaling problems after being placed under ASP flooding (Wang *et al.*, 2004). Several pump malfunctioning have been recorded with scale thickness of about 1cm in the wellbore. Serious scale has also been found in surface gathering system and delivery system, with scale measuring around 0.3 cm thickness in single well pipes, gathering systems and in heating furnace, thus negatively affecting the well productivity.

Scale forming process: Depending on whether the nucleation pathway is homogeneous or heterogeneous, water, supersaturated with respect to a mineral will give

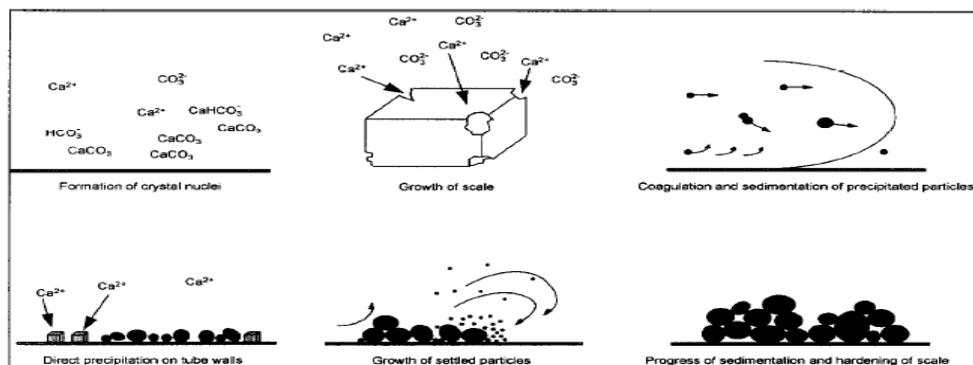


Fig. 4: A model of Scale forming process (Siegmeier *et al.*, 1998)

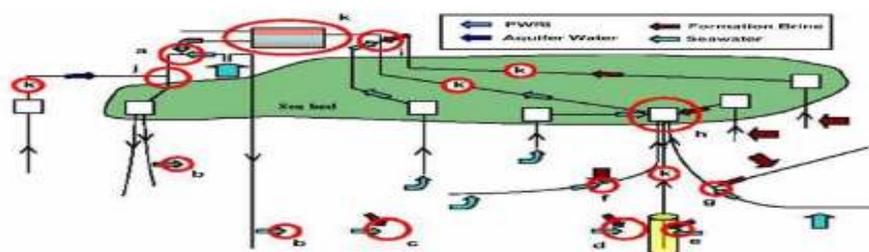


Fig. 5: Locations throughout the flow system where scale deposition may occur (Jordan *et al.*, 2006, 2011)

rise to the agglomerations of scale forming ions due to the random collisions of the moving ions. In other cases, any suspended solid, such as silt or corrosion products may serve as nuclei to cause scale formation (Gill, 1996) or calcium carbonate providing a nuclei for the development of silicates scales (Gill, 1998). Once the nuclei exceed the critical size in a super saturation solution, they begin to grow into visible sized crystals (Gill, 1996). As shown in Fig. 4 below, the scale forming process begin with the nucleation stage and terminates at the sedimentation and hardening stage.

Locations of scale precipitations: In addition to knowing the constituents of a scale, it is also important to know the location (Down hole versus surface) at which the scale is forming. Determining the exact location where scale is forming is not always very possible, but it is suitable to separate between deposits located upon surface or surface equipment and deposits located on the formation face. One can conveniently determine scale depositions on surface or subsurface equipment Such as Subsurface Safety Valves (SSSV), downhole pumps and pumps- by the direct failure of such equipment or by mere observation during work over operations. In terms of analysis, this is obviously the simplest of the situations (Charles, 1998; Farrakhrouz and Asef, 2010)

If it happens that such equipment are replaced or repaired and production rates return to normal, then we assume that there is no damage at the perforation face

itself and that all the damages and the consequent decline in production rate were a result of equipment failure.

Depending on the nature of the scale, scale precipitations will form in any one or more of the following locations in the oilfield as shown in Fig. 5 below: Prior to injection, around the injection well, deep in the formation, when injection brine and formation brine converge towards the production well but beyond the radius of a squeeze treatment, when injection and formation brines converge towards the production well within the radius of squeeze treatment, in the completed interval of the production well, at the junction of a multilateral well with branches producing different brines, at the sub-sea manifold where different wells are producing different brines, at the surface facilities with production streaming flowing different brines and so on.

SCALE CONTROL AND ITS MECHANISM

Normally, scales are formed in a supersaturation condition. That is, when the solubility product of a deposit-forming material is exceeded, it precipitates. A supersaturated solution is a solution that contains a higher concentration of a particular mineral than the solution can hold under the same set of conditions with its solute in equilibrium (Jingluan *et al.*, 2008). Two states of supersaturation exist: Metastable and labile.

Figure 6 represents a normal solubility curve and two different states of supersaturation.

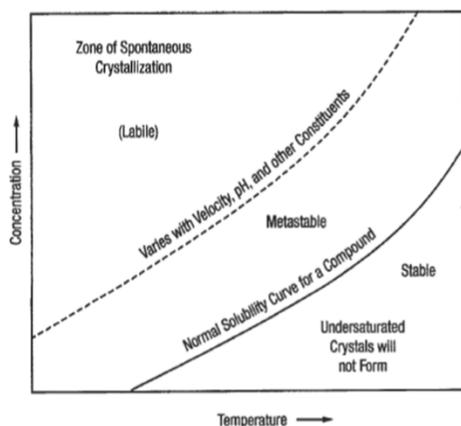


Fig. 6: Variation of solubility and supersaturation with temperature (Jingluan *et al.*, 2008)

Scale control in the oilfield can be achieved by the following mechanisms:

- Preventing germination
- Separating crystal nucleus
- Preventing scale deposition and keeping solids dispersed in water from precipitating on the surface of metals.

The precipitation processes of scales follow a three step pattern:

- Achievement of super saturation
- Nucleation and
- Growth of the nuclei to form particles

Prevention of silica scale: Prevention of silicate scale can be achieved in three ways:

- Silica removal
- Scale inhibition
- Dispersion

This review study will give emphasis on the scale inhibition as the preferred method of preventing silicate scales.

Mechanical method; drilling or reaming: Silicate scale is very difficult to remove from oil wells. In the past, mechanical removal has often been the only remedial method (Amjad and Zuhl, 2008). Using mechanical method (drilling or reaming) is quiet easy to understand and has been used to remove all kinds of scale depositions. However, it is not without several disadvantages too and therefore should only be considered as the last option (Vetter, 1976; Sho-Wei *et al.*, 2011). It is very expensive; a drilling rig has to be moved in and, particularly in deep wells, all kinds of complications can be expected during the drilling

process. Another drawback of this method is that It is not a very effective method for re-stimulating a well because it does not remove the scale deposits from the formation (that is, from outside the wellbore), thus ignoring all the formation damage. Also, an impermeable skin may remain inside the wellbore caused by the drilling cuttings squeezed into the perforation holes or production slots in the tubing or liner. A few pounds of cuttings placed in a strategic location can cause the productivity to drop to zero. Therefore, we always prefer chemical procedures over mechanical work overs if the chemical procedure has a chance to achieve its objective (Vetter, 1976).

The chemical method: In oilfields, especially offshore operations, scale formation is one of the major flow assurance issues which can lead to significant reductions in productivity if it is allowed to form uninhibited. Scale prevention using chemical inhibitors, applied either by continuous injection or by squeeze treatment into the near wellbore formation, has been regarded generally as the most cost effective method of solving the scale problem (Inches *et al.*, 2006).

The above limitations of mechanical treatment of scales have given the chemical procedures an upper hand. However, the use of chemicals in the oil industry have attracted environmental regulatory bodies into enacting environmental regulations persuading field operators and in some cases compelling a swift focus to the call of going “green”. In recent years, there have been a lot of advances by researches from the academia and oil industries in a bid to take up the challenge of using “green products” in major oil and gas production operations and produced water disposal treatment, thus answering the call for low toxicity, biodegradable and hydrothermally stable scale inhibitors. The increased awareness and scrutiny of the impact of chemical discharge on the environment is likely to be adopted on a global basis (Wilson *et al.*, 2010).

CONVENTIONAL SCALE INHIBITORS (CSI)

Scale inhibitors are chemicals that delay, reduce or prevent scale formation when added in small amounts to normally scaling water. Most of scale inhibitors presently available function via one of the following inhibition mechanism (Conne, 1983); absorbing onto the crystal surface to prevent further growth of very tiny crystals that precipitate out of the water, or by preventing the scale crystals from adhering to solid surfaces such as pipes and vessels. Chemical scale removal is often the first approach and has been adopted as the lowest cost method of scale treatment, especially when access to the scale is very difficult or scale exist where conventional mechanical removal methods are ineffective or expensive to install (Crabtree *et al.*, 1999). Treatment of scale using chemical

methods is measured by how well the reagents access the scale surface. For instance, scale deposits in tubing exhibit small surface area for a large total deposited mass that the reactivity of chemical systems is usually too slow to make chemical treatment a practical removal method, except by the use of strongest chemical reactants. Large reactant-surface areas, such as porous materials, clay-like particles of extremely thin plates and hair-like projections react quickly, since the acid or reactant volume surrounding the surface is large. The speed and efficiency with which the chemical inhibitors treat the scale is attributed to the surface-area-to-volume ratio, or the equivalent surface-area-to-mass ratio (Crabtree *et al.*, 1999).

Conventional scale inhibitors are hydrophilic, that is, they dissolve in water. In the case of down-hole squeezing, it is desirable that the scale inhibitor is adsorbed on the rock to avoid washing out the chemical before it can act as desired (Fink, 2003). The most common inhibitor chemicals can be compounds and organic polymers. Polyphosphonates classified as inorganic phosphates, organophosphorous Carboxylic Acid (PPCA) and Diethylenetriaminepenta (DETPMP) are two common commercial scale inhibitors used in the oil and gas industry (Bezemer and Bauer, 1969). By inhibition mechanism, PPCA is said to inhibit by nucleation while DETPMP operates by crystal growth inhibition (Chen *et al.*, 2004).

GREEN SCALE INHIBITORS (GSI)

Though the use of green scale inhibitors to inhibit scale in oil and gas wells is relatively an unexplored area (Kumar *et al.*, 2010), there have been several works on this "promising alternative" (Kohler *et al.*, 2004). The inherent and consequent environmental hazards of using these toxic and non-biodegradable scale inhibitors, has hindered the use of phosphonates due to their poor ecotoxicity and many polymers, due to their failure to meet minimum biodegradation requirements (Holt *et al.*, 2009). The use green scale inhibitors has been sporadic and evolutionary (Gupta, 2004) and the trend seems to adopt a rather reactionary response to the present and potential environmental regulations.

Owing to the efficiency and cost effectiveness of the chemical inhibition method in scale management and the strict environmental regulations facing the oil industry, the call for going green with scale inhibitors has become necessary. The chemical scale inhibitors are known to either function by binding to the insoluble scale forming mineral, keeping them in solution or by modifying the crystal structure of the precipitate to prevent the formation of scales. Many of the organic phosphates and phosphonates that are widely in use as scale inhibitors are quite toxic to the environment.

These have been replaced by some organic phosphorus compounds which are less toxic such as

dibutylphosphorodithioic acid and carboxyhydromethylphosphonic acids. All these inhibitors are based on phosphorus chemistry, but environmental regulatory bodies in North Sea (UK, Norway, Denmark and Netherlands) and the US Gulf Coast are encouraging operators to use greener chemicals, hence the popularity of phosphorus free and nontoxic scale inhibitors (Kumar *et al.*, 2010). The phosphorus based inhibitors have been replaced by the acrylate based polymers such as Polyacrylic acid, Polyacrylamide and various Polyacrylates. Emanating from research at the academic level into greener chemicals, recently Poly amino acids, in particular Polyaspartates (PASP) have been proposed, tested and commercialized as scale inhibitors in a variety of industries (Gupta, 2004).

Green chemistry, or pollution prevention at molecular level is said to be the chemistry designed to minimize or eliminate the use or regeneration of hazardous materials associated with manufacture and application of chemicals. It is said that, green chemistry combines critical elements of environmental improvement, economic performance and social responsibility (Taj *et al.*, 2006; Frenier and Wilson, 2000). The number of chemicals allowed to be used as inhibitors has thus been limited, according to mainly three criteria-their level of biodegradability, bioaccumulation and toxicity. According to the Paris Commission (PARCOM), an ideal green inhibitor is non-toxic, readily biodegradable and shows no bioaccumulation (Taj *et al.*, 2006).

Despite the universality of guidelines and regulations put in place in various parts of the worlds, opinions differ even between countries using the same regulations (Hill and Malwitz, 2006). A green inhibitor is not expected to meet or exceed these regulations only; it has to perform its basic function of treating this oilfield menace both downhole and at the surface facilities (Wilson and Hepburn, 1997; Wilson *et al.*, 2010). It is therefore necessary to reach a global harmonized system. If such an agreement cannot be reached, then operators, service companies and chemical manufacturers must voluntarily ensure that the best chemicals and practices are used, at least for the safety of the environment (Wilson *et al.*, 2010; Dobbs and Brown, 1999).

For the purpose of this review study, the Paris Commission (PARCOM) regulations developed for the harmonization of procedures of approval, evaluation and testing of offshore chemicals and drilling fluid in 1990 will be discussed. These guidelines focus on two aspects:

- Standardization of environmental testing.
- A model to use the data in a practical way. We will briefly discuss the environmental testing here.

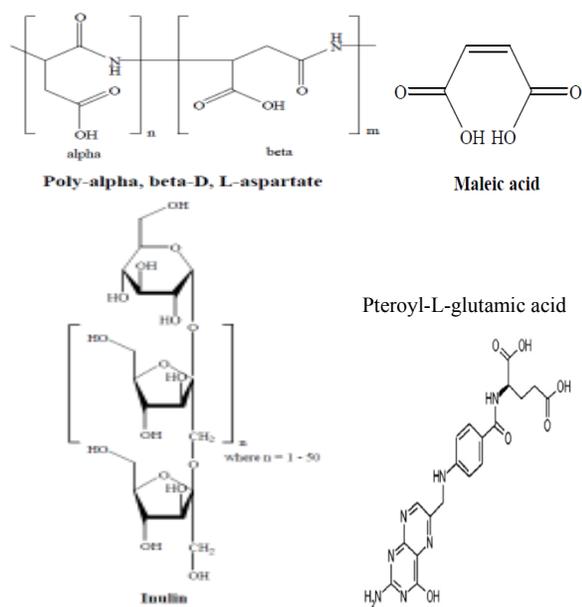


Fig. 7: Shows the molecular structures of some green scale inhibitors (Vetter, 1976; Inches *et al.*, 2006; Dobbs and Brown, 1999)

Environmental testing:

Toxicity: The PARCOM guidelines require that toxicity testing be evaluated on the complete formulation on native environments. Living organisms like algae (primary producer), fish, crustacean (consumers) and seabed worms (decomposers or sedimentary reworkers) are used. Additionally, the toxicity is to be measured as both LC₅₀ and EC₅₀. The EC₅₀ is the effective concentration of chemical required to adversely affect 50% of the population, while the LC₅₀ is the concentration of chemical required to kill 50% of the population. Since EC₅₀ is usually lower than LC₅₀, therefore the more sensitive criterion is the EC₅₀ than the LC₅₀.

Biodegradation: PARCOM requires standardization of environmental testing to evaluate how long the product will persist in the environment. A modification of the OECD 301D is used, which gives 28 days as the biodegradation period.

Bioaccumulation: PARCOM requires standardization of environmental testing for partition coefficient (bioaccumulation). This gives a measure of the distribution of the product between an octanol and water mixture expressed as the logarithm of the octanol/water partition coefficient (log Po/w). A standard High Performance Liquid Chromatography (HPLC) method is used and this test is performed on all the components of the product (Taj *et al.*, 2006).

In summary, the principal criteria a green scale inhibitor in the North Sea should meet to be environmentally acceptable is shown below:

Marine toxicity: EC₅₀ and LC₅₀ > 10Mg/l to North Sea species
Biodegradability: > 60% in 28 days
Bioaccumulation: log (Po/w) [Watkins and Chant, 1985].

CONCLUSION

The possible restrictions as at present and of course the grey areas that require further research is the requirement for efficient biodegradation of the existing green scale inhibitors and their ability to withstand excessively high temperatures downhole. The existing green inhibitors have not found wide acceptance due to their inherent hydrolytic and thermal stability issues. Future green scale inhibitors should give particular attention to their applicability in harsher HPHT environments.

Gill (1996) has suggested that, future inhibitors should be environmentally safe and easily biodegradable or self-destructive at the end of the used cycle, referring to the present time, when the environment is facing the greatest challenge, especially countries with increasing offshore oil fields. Several works conducted on this promising alternative has not only shown a green light to the replacement of the hazardous inhibitors with inhibitors that are more environmentally benign, but has also prompted more research into the area.

Also, the availability of the green sources should be a matter of concern, since the proposed green scale inhibitors are always compounds that are as well required and used in many other industries, including food and pharmaceutical industries.

We suggest that, countries, especially those with increasing growth in offshore operations should as a matter of seriousness, look into the green technology as an alternative to the “red” chemicals that are often used in scale treatments and inhibitions. The development of green scale inhibitors should be considered as a fundamental research and development by the oil industry (Fig. 7).

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