

Effect of Produced Sand Particles and Fines on Scale Inhibitor: A Review

Uche C. Anyanwu¹ and Gbenga F. Oluyemi¹

¹School of Engineering, Robert Gordon University, Aberdeen, AB10 7GJ, Scotland, UK.

Abstract

Scale inhibitors are deployed as preventive and rejuvenation operation in oil and gas industry when production operations are under threat or menace of scale blockage. The application of scale inhibitors is carried out through a method known as squeezing. In general, the squeeze process is governed by inhibitor-rock interaction which is described by adsorption/desorption isotherm. Most reservoirs produce loose sand grains or fine sand which float and flow within the pore spaces along with the squeezed scale inhibitors. Hypothetical reports have shown that not all scale inhibitors pumped into the formation adsorb onto the formation rock. A number of factors (irreversible adsorption, pH changes, competing ions, concentration and temperature) have been considered to affect the adsorption and return profile of these scale inhibitors. This review work examines the performances of most common scale inhibitors used in the oil and gas production activities, theoretical application in reservoirs and how loose fine sand grains affect the adsorption and desorption characteristics of squeezed scale inhibitors. Additionally, presented were overviews of previous reports on fine sand production and migration of fine sands through formation pores in reservoirs.

Key Words: Adsorption; Scale Inhibitors; Fine sands; Colloids; Reservoir.

1.1 Introduction

The squeezing of scale inhibitor into formations to treat scale problems in order to sustain production at the right level has been a dominant practice in the oil and gas sector. Many researches have been carried out in this field (Jordan et al., 2016; Farooqui and Sorbie 2016; Stamatakis et al., 2006, Andrei and Malandrino 2003; Oluyemi 2013; Veloso et al., 2014). Squeezing of inhibitor into the formation takes into account geophysical complexities such as mineralogical composition of the rock and geochemical processes. Many experimental, mathematical and numerical simulation modelling works (Liu et al., 2010; Selvaraju and Pushpavanam 2009; Garmeh et al., 2009) have been carried out to evaluate behaviour, performance and interaction of the squeezed chemicals within porous media in relation to their efficiency in addressing the scale formation. While a squeeze treatment is designed to provide a steady release of inhibitor, which has been retained in the formation (Kahrwad et al., 2009), the precise retention mechanism and performance of the inhibitors in sand producing reservoir is a subject of concern that requires concerted research.

The success of a squeeze treatment is determined by the length of time in which inhibitor is released back into the produced fluid at minimum inhibitor concentrations (MIC) and; this time is dictated by the retention/release mechanism of inhibitor in the reservoir (Tantayakom et al., 2005; Yan et al., 2015). In

adsorption squeeze treatments, the amount of inhibitor adsorbed and the lifetimes are dependent on the properties and surface chemistry of the reservoir system (Andrei and Malandrino, 2003).

In scale inhibitor (SI) squeeze treatment, it is known that adsorption/desorption or precipitation/dissolution (Phase separation) mechanisms govern the interaction between the scale inhibitor and formation rock (Ibrahim et al., 2012). Adsorption refers to the mechanism where SI is physically or chemically adsorbed onto the mineral surface of the porous medium. It is normally described by an adsorption isotherm $r(c)$ and may be a function of several variables such as; concentration of inhibitor $[c]$, calcium concentration $[Ca^{2+}]$, pH and temperature (Sorbie and Gdanski, 2005). Adsorption of scale inhibitor is thought to occur through electrostatic and Vander Waals interaction between the inhibitor and formation minerals (Jordan et al., 1995). In carbonate formation where unconventional squeeze treatment method is used, majority of the acid phosphonate inhibitor is precipitated near the formation face. The formation of Ca-phosphonate resulting from the reaction of acid with carbonate in the formation proceeds very rapidly and this has a shortcoming in a carbonate formation (Brown et al., 2011). The un-precipitated inhibitors occurring during these unsuccessful treatments are quickly swept from the formation because they are not retained (Tantayakom et al., 2005). The result of this being shorter treatment lifetimes and inefficient use of inhibitor, demand

for subsequent treatments, lost production time and significant cost.

With respect to many reports that the use of scale inhibitor squeeze chemicals is a common and efficient method of dealing with scaling problems in oilwells, the criteria for potential scale inhibitor squeeze treatment necessitates retention of a greater percentage of the squeezed inhibitor on the adsorbent either through adsorption or precipitation and steady rate release above minimum inhibitor concentration (MIC) for a long period of time (Ghosh et al., 2012). Retention of a greater percentage of the squeezed inhibitor for a long period of time will require a reliable squeeze plan to be performed. This will necessitate the control of the fluid flow in the porous media through accurate estimation of the chemical behaviour. Further report maintained that cross-sectional area of chemicals decreases when they are adsorbed onto the rock surface resulting in permeability decrease (Agbabozorgi and Rostami 2016). Their study however did not account for chemical interactions with loose particle. Contrastingly, in an experimental work with 20/40 mesh size commercial grade silica sand in a dynamic flow mode, report has shown that chemical adsorption through porous medium is not only governed by its retention but also by inaccessible pore volume (Idahosa et al., 2016). However, their report did not account for the influence of fine particles on the retention of polymers in porous media.

Knowledge of the adsorption-desorption parameters is essential to estimate the

performance and mobility of scale inhibitors in the reservoirs. It has been reported that the design of a squeeze treatment in a system with different layers of sand, necessary information on the adsorption characteristics of the scale inhibitor is essential. Additionally, report on adsorption characteristics of a solute such as atrazine in porous media such as soil is said to be affected by the addition of other solutes such as detergents (Sevaraju and Pushpavanam 2009). The reaction between scale inhibitors and formation minerals determine the inhibitor retention and release during production (Yan et al., 2015). Under multiphase flow conditions the efficiency and persistency of an inhibitor film depend on four main factors. These factors include the type of adsorption of the inhibitor film, the chemical composition of the multiphase flow, the wall shear stress or mass transport coefficient and the sand particle type/concentration (Neville and Wang 2008).

1.2 Fine Sand Production in formations:

Fine sand production in oil and gas wells has been an issue of concern because it has caused operational and economical problems in the oil and gas industry. Main issues with respect to fine sand production are potential risk of well failure, limited productivity, erosion of facilities and increased operational expense. Figure 1 shows production separator that was shut down because of ingress of formation fine sands.



Figure 1: Pictorial view of ingress of fine sand into a production separator that resulted in production shut down (Oyeneyin, 2015)

Fine sand production is currently a subject of extensive study in the oil and gas industry. The study of sand production has focused on prediction of failure of sand and subsequent production, estimation of produced sand volume and rate and measures for controlling or excluding sand in the well (Berntsen, 2012). Studies to evaluate the effect of fine sand on corrosion inhibitor activity using rotating cylinder flow (RCF) and Flow Loop for comparison have shown that inhibitor was capable of adsorbing on sand thereby cancelling out its activity (McMahon et al., 2005).

However, virtually little or no knowledge exists on how fine sand production affects the effectiveness of common types of scale inhibitors used in the sand-producing reservoirs for flow assurance purposes. Figure 2 shows the arrangement of four different reservoir core formation sortings with different amounts of loose clay/fine sand particles within the formation pores. As envisaged in the poorly sorted, low porosity high clay/fine sand

formation core, the effects these loose sand particles will have on the adsorption and desorption characteristics of the squeezed scale inhibitor have not received in-depth studies.

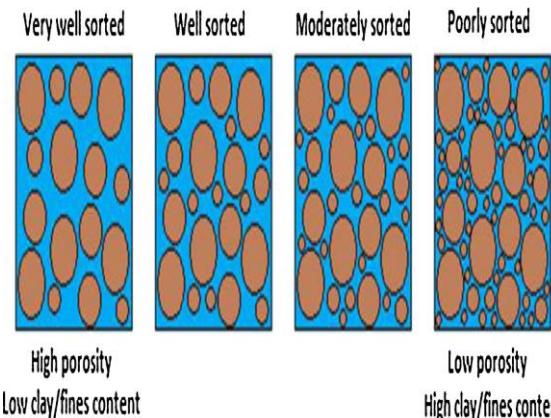


Figure 2: Pore arrangement of four reservoir cores with potential clay/fine sand contents (Molnes et al., 2016).

The effectiveness of chemical inhibitor performance in sand-producing reservoirs can be deduced when there is good understanding of the fluid-sand interactions. Knowledge of this will be helpful in the design and optimisation of scale inhibitor squeeze applications especially in reservoirs or wells with the potential to produce sand.

1.3 Migration of Colloidal Fines:

Several physical and chemical processes accompany the squeezing and adsorption of scale inhibitors onto formations thereby affecting their desired performance. The migrations of colloidal particles, that are present in natural porous media such as rocks and unconsolidated porous media such as packed beds are considered to facilitate or hinder the mobility of other colloids in porous media (Cai et al., 2014) and in some cases are entrenched into the gas oil fraction during distillation (Wang et al., 1999). It has been reported that the existence of mobile colloidal

fines under certain conditions can serve as adsorbents and potentially relevant transport mechanism for materials (Tusher et al., 2002). The detachment of an adsorbed particle results from a balance between external forces exerted on it. These forces are adhesion or physicochemical interaction, drag and lift forces. Furthermore, physicochemical interactions between particles or a particle and grain surface include Van der Waals and electrical double layer forces (Nisrine et al., 2013). This physicochemical interaction could also account for the continued adsorption of the solute on loose sand particles. However, it has been reported that particle release is caused by electrostatic repulsion which is enhanced by low ionic strength and not flow-induced shear forces (Abadzic and Ryan, 2001). Solutes such as polymers, surfactants and resins adsorbed on the particle surface affects the colloidal suspension stability by increasing steric interaction in non porous media with tendencies to alter apparent surface charge on colloidal particles (Wang et al., 1999).

Fielder (2000) had carried out scale inhibitor product performance qualification screening using seeded static jar test and continuous stirring whereby suspended solids such as calcite and kaolinite were applied. He suggested that the poor performance of the tested inhibitors may be partially caused by the presence of the suspended solids and or old scale deposits. However, his experimental work on suspended solids did not involve continuous flow or flood test backed up by simulation and moreover, it was not clear whether suspended solids or old

scale deposits were the cause of poor performance of the tested scale inhibitor.

Chakraborty et al. (2014) examined the effects of loose grains silica gel grain size and layers on adsorption chiller. They concluded that the use of various loose grain silica gel designs in the sorption bed allows significant effects on the coefficient of performance and cooling capacity of adsorption chiller. Conversely, they maintained that the coefficient of performance of the chiller was affected by heat capacity, inert mass, heat losses and heat exchanger as a result of loose silica gel grains. Dissolution of grain fabrics from rock-chemical interaction increased the porosity and permeability of the sandstone formation (Wuyep et al., 2019). The dissolved grain fabrics could affect the adsorption and desorption performance of squeezed chemical inhibitor because loose sand grains from the dissolved grain fabric could potentially be adsorbents for scale inhibitors. This rock-chemical interaction is attributed to Wan der Waal forces which bind the chemical to the rock surfaces (Nisrine et al., 2013) by a process known as adsorption.

This review is carried out to examine journal reports on adsorption and desorption behaviour of most commonly used oil and gas scale inhibitors and how production of colloidal fine sands in reservoirs affect the performance of scale inhibitors in sand producing reservoirs.

2.1.1 Scale Inhibitors

Scale inhibitors used in squeeze treatment provide one of the most common and efficient methods for preventing the formation of scales in producer wells. The selection of these scale

inhibitors is geared towards the accomplishment of the following tasks (Ghosh et al., 2012);

- Prevent or delay the formation of scales either sulphate or carbonate scales at very low concentrations otherwise known as minimum inhibitor concentration (MIC) or threshold concentration (C_t).
- Interact with reservoir or formation substrates in order to give high adsorption over a short period of shut in time.
- To a large extent interact with the reservoir or formation materials in order to give long inhibitor desorption or return profile at or above MIC or C_t level.

Additionally, it is not sufficient that scale inhibitors interact appropriately with the formation or adsorbent (Yan et al., 2015), but they must also be compatible with brine composition and comparably stable to thermal degradation. Non-compatibility of scale inhibitors and the brine system might likely result in the precipitation of the inhibitor prior to injection or at the near well bore areas thereby resulting in the formation of makeshift fine scales which might cause the plugging of formation pores. Furthermore, scale inhibitors selected must be such that they are not degraded or dissociated in the course of operation due to the formation temperature and sometimes change in formation temperature.

Scale inhibitors are considered to have very marked effects on the growth rate of crystals deposited in a scaling environment. These

threshold inhibitors function by adsorbing onto the growing crystals and distorting the lattice, which disrupts the crystal growth process (Stamatakis et al., 2006). Interaction between Polyaspartic Acid (PASP) scale inhibitor with calcite crystal surface is mainly because of the strong π-π interaction between the π^4_3 delocalised bonds of -COOH groups in PASP and π^6_4 delocalised bonds on the surface of calcite crystal, and the hydrogen interactions between them and water molecules. Further reported is that polymer inhibitors do not interact directly with calcite crystal in water solution, but indirectly through the chemical bonds and non-bond interactions between PASP and H₂O and calcite (Zeng et al., 2013).

Several classifications and types of scale inhibitors have been reported (Kehland, 2009). Among these classifications, polyphosphonates and polyphosphino polymers have been profusely and widely employed in oil and gas scale control due to their high scale inhibition efficiency, low economical cost and relative environmental compatibility.

Jordan et al. (2016) have reported that phosphonates at elevated temperature, particularly from 70°C perform very well. Additionally, they added that at and above 70°C, the phosphonates exhibit strong retention characteristics and excellent release profiles which make them the choice chemical for scale squeeze treatment, though low temperature does not favour retention of their molecules on the rock rather the phosphonate ester chemicals. In contrast, studies have indicated that

phosphonates generally adsorbed poorly onto sandstone with squeeze lifetimes often unsatisfactory (Andrei and Malandrino, 2003). However, it has been ascertained that the presence of phosphorus in the monomer building block of phosphonates was incorporated to provide good retention properties and relative ease of detection (Fleming et al., 2001; Jordan et al., 1995). Ketrane et al. (2009) in their study have compared the efficiency of five scale inhibitors, three polyphosphates, one polyphosphonate and one polycarboxylic acid and claimed to have observed that phosphonates are better inhibitors than polycarboxylates or polyphosphates. This could be attributed to their characteristic mono or multi-functional groups (-PO₃H₂) that contains short chains and kinetically more stable bonds P-C-P or P-C-N-C-P than P-O-P bonds of condensed phosphates and P-O-C ester linkage which are sensitive to hydrolysis and susceptible to oxidation and reduction (Janasson et al., 1996; Ketrane et al., 2009).

Several importance of the use of phosphonate inhibitors in the field with reference to aminotri (methylene phosphonic acid) (ATMP) have been highlighted (Tantayakom et al., 2005) to include;

- The economic viability of the scale inhibitors which stem from their ability to inhibit scale at low concentration.
- Their stability over a wide range of temperature and pH.
- Their versatility of use as scale inhibitors to mitigate diverse forms of scale.

- The relative ease with which their concentration in the produced fluid can be determined, thereby giving information on retreatment time for the well.

The essentiality of phosphorus as a nutrient for the growth of aquatic algae and other biological organisms has been elucidated. However, further reported is that excessive use of phosphonates would introduce uncontrolled phosphorus into the natural water bodies like lakes and reservoirs with resultant algae blooms and eventual degeneration of water quality (Li et al., 2016). Many chemicals such as organic phosphonates, organic phosphates and low molecular weight ester derivatives of these molecules with desired secondary properties have been widely used as scale inhibitors in oil and gas applications (Wylde et al., 2010). Nevertheless, ongoing efforts are geared towards green scale inhibitors such as polycarboxylic acids and polyacrylates and their copolymers which are eco-friendly (Ghosh et al., 2012). The need for replacement presumably stemmed from their corrosive and bacterial fouling characteristics which necessitates their application in a mixture of other additives. At high concentrations of these chemicals, they become too acidic and affect seaweed and constitute environmental concerns; as a result, they have become increasingly restricted for use (Kumar et al., 2010). Structural representation of different organo-phosphonate scale inhibitors with different functional groups and a carboxylic acid inhibitor most commonly used as scale inhibitors are depicted in Figure 3 below.

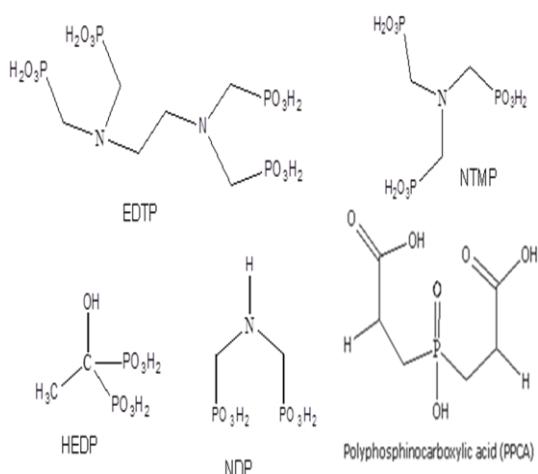


Figure 3: Molecular structures of some organophosphonate-based inhibitors (Adapted from Jones et al., 2003).

The number of phosphonate groups attached to a compound has a significant role in the inhibition efficiency of the molecule. The phosphonate groups strongly adsorb onto the BaSO_4 or CaCO_3 crystalline substrate owing to the high chelating ability of the $-\text{P}(\text{O})(\text{OH})_2$ groups when ionized to PO_3^{2-} (Yang et al., 2001). In contrast, polyphosphinocarboxylic acid (PPCA) has been reported to lower the ionic activity product of scales through either chelating of the metal ions or by decreasing pH (Kumar et al., 2010). Polyphosphinocarboxylic acid is characterized by its reactive carboxylic and hydroxyl functional groups which makes it an effective scale inhibitor and gives it wide application in oil and gas systems. However, Phosphonate molecules are characterized by their multiple functional groups with varying charges which depend on pH as well as in their interactions with available cations (Jones et al., 2003).

Hao et al. (2012), in their study on preparation and adsorption performance of aqueous glyphosate on manganese oxide-powdered

activated carbon (MnO_2/PAC) composite, have reported that the uptake rate and the kinetics of adsorption are essential parameters to consider in designing appropriate adsorption isotherm because they determine the residence time of adsorbed solute. Figure 4 below shows kinetic adsorption of glyphosate solute on porous MnO_2/PAC packed bed, which in general, elucidates kinetic adsorption pathways for most of scale inhibitors.

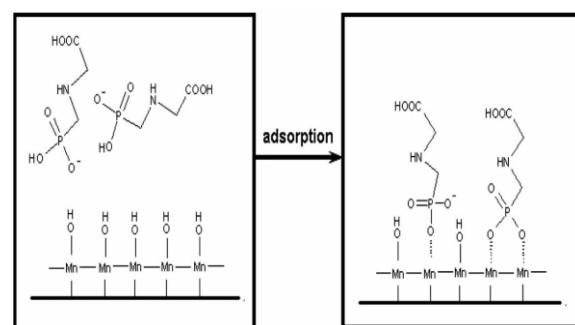


Figure 4: Kinetic of chemical adsorption on porous material (Hao et al., 2012).

With all the above-mentioned characteristics, polyphosphonates and polyphosphinopolymers have been widely and profusely used in oil and gas scale squeeze control due to their ease of adsorption, high scale inhibition efficiency, low economical cost and relative environmental compatibility.

2.1.2 Effect of Formation Variables in Adsorbing Characteristics of Polymer on Adsorbent

Most reservoir sands and sandstones contain a given amount of clay. Clay particles are generally very small fractions of μm size range and contribute both to increasing specific area of the core and to decreasing its permeability (Saldungaray et al., 2001). The specific area explains the high adsorbing capacity of clays toward scale inhibitors, whilst the permeability is

expected to favour scale inhibitor reversible retention.

Research on uptake of nitrolo-tris methylene-phosphonic acid (NTMP) by kaolin, halloysite and montmorillonite monitored by liquid phase ^{31}P NMR spectroscopy have ascertained that in the presence of Ba^{2+} or Ca^{2+} a significant increase of the amount of desorbed phosphorous was recorded. It was further maintained that a weak interaction between scale inhibitor and rock formation contributes to its release in contrast to a strong interaction between scale inhibitor and formation rock (Jordana et al., 2012). In another research to understand rock/phosphonate inhibitor interactions and effect of metal ions on scale inhibitor retention, it has been claimed that phosphonate precipitation increased, with major precipitation occurring near the front of the core upon inhibitor pill solution making contact with core material (Mason et al., 2008).

The effects of increased temperature and flow rate have been reported to cause higher equilibrium concentrations and faster dissolution kinetics for a diethylenetriamine penta(methylene phosphonic acid) (DTPMP)/sandstone interaction study (Yan et al., 2015). However, Dantas et al. (2011) have reported that increase in temperature due to exothermic behaviour of adsorption causes a decrease in adsorption capacity.

Zaitoun and Kohler (1987) have claimed that a change of pH, temperature, brine composition and polymer charge density can modify polymer adsorption characteristics on a given porous material. They further stressed that at neutral pH,

the surface charge of natural sands and sandstones is negative, and thus, an increase in polymer anionicity raises charge repulsion with the rock and reduces the adsorption tendency. However, report has shown that positive surface charge on SiO_2 at low pH based on the kinetics of dissolution could exist (Kosmulki, 2006). It has been reported that solution pH is the most important factor affecting the molar ratio of Ca to ATMP in a precipitation squeeze treatment with a marked increase in solution pH giving rise to increase in the amount of Ca-ATMP precipitated (Tantayakom et al., 2005). Kosmulki (2011) reported that the charges on various solid surfaces in aqueous solutions are dependent on the pH. Furthermore, he maintained that in aqueous solution of 1-1 electrolyte, the pH dependent charges on the solid surface govern the adsorption of ions.

2.1.3 The Effect of Molecular Weight on Scale Inhibitor Adsorption

Flood et al. (2007) in their report have stated that the strength of Sodiumpolyacrylate (NaPA) scale inhibitor binding increases with its molecular weight. Adsorption of high molecular weight macromolecules has been reported to be largely irreversible, with significant desorption claimed to be observed only at shear rates exceeding 2000s^{-1} . The adsorption level according to report then becomes directly dependent on the specific area of the rock i.e. on its clay content (Zaitoun and Kohler, 1987). Farooqui and Sorbie (2016) have maintained that the molecular weight of scale inhibitors is deemed to be one of the factors upon which both adsorption and

precipitation processes depend on. They additionally asserted that the concentration of the polymer in the return curve of PPCA scale inhibitor used in their research was relative to the molecular weight distribution (MWD) effects and also in its ability to prevent scale formation.

2.1.4 Functional Group Reactivity/Pathways to Scale Inhibitor Adsorption on a given Sand Surface

Scale inhibitor molecules have a high tendency to adsorb on a given surface such as sand. Several pathways have been described for this. The first pathway is the linkage of one functional group to a mineral surface which provides a platform to the fixation of the whole macromolecule composed of several thousand monomer groups. The next pathway is reported to be where several weak linkages may produce a very strong attractive force (Zaitoun and Kohler, 1987). This happens if electric repulsion forces between the polyanion and the mineral surface are not high and there exists moderate polymer charge density, minimal brine salinity and neutral pH. It has been reported that the main contribution to the binding energies comes from coulombic interaction as indication shows that coulomb interactions are favourable for the combination of scale inhibitors and calcite (Zeng et al., 2013).

Most polymers used in enhanced oil recovery (EOR) applications are weakly anionic and, surprisingly adsorb onto rocks with negative surface charge. The presence of local positive charges on clay edges (Alotaibi, 2010) or the possibility of hydrogen bond formation with silica has been proposed to explain the high affinity of

polymers for many reservoir rocks. However, Vazquez et al (2011) have reported that the cause of deposition of a solid or a gel-like immiscible liquid on the surface of formation rock was as a result of formation of a soluble inhibitor-cation complex or salt such as inhibitor-Ca complex.

2.1.5 Adsorption on Solid Surface

The surface of sand consists of charged particles that produce field of force as depicted in Figure 5 below. The interactions between these field of forces at the surface of sand and that from the molecule of the scale inhibitor to be adsorbed gives rise to surface adsorption on the sand surface. The surface of sand consists of irregularities which are microscopic in nature and the existence of these irregularities give rise to variations in the magnitude of surface forces (Zhang and Somasundaran, 2006). These surface forces play a significant role in the adsorption of scale inhibitors onto the sand surface. In contrast, Yan et al (2015); kan et al (2004) have reported from Tomson et al (2003), that the primary driving force for adsorption is not related to some specific inhibitor-surface interaction, rather to simple hydrophobic repulsion from solution of macroneutral molecule of calcium-inhibitor complex.

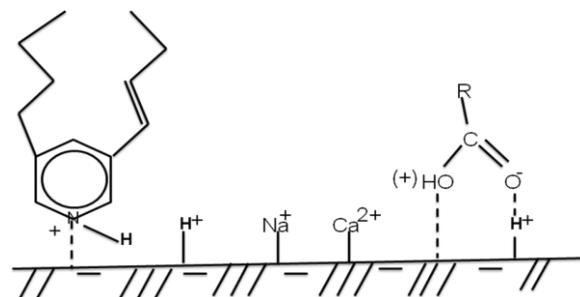


Figure 5: Active component ions on formation rock surface (Strand et al., 2016).

Two main forces of attraction synonymous with adsorption of scale inhibitor molecules onto the surface of sand are; physical and chemical forces. Physical forces give rise to physical adsorption while chemical forces give rise to chemical adsorption. Gupta and Bhattacharyya (2014) described adsorption as one of the fascinating phenomena related to the behaviour of fluids in a force field exerted by the solid surface. They maintained that a solid is a good adsorbent if the internal volume accessible to the adsorbate molecules or ions is high and further stressed that a solid with large pore volume tend to also have a large area.

Sorbie et al. (1993) outlined interactions between inhibitor and sand surfaces to involve three processes;

- Normal adsorption/Desorption.
- Enhanced adsorption/desorption-which is sometimes designated as surface precipitation or surface condensation.
- Precipitation or phase separation process itself.

A clear understanding of the properties of the adsorbent (sandstone) and the adsorbate will contribute to a better mechanistic view of the inhibitor adsorption/desorption behaviour. Most reservoir rocks, when brought into contact with water, develop positively charged edges (Alotaibi, 2010) and become negatively charged at higher pH (Strand et al., 2016; Dove and Craven, 2005). The negative surface charge on quartz (the principal component of sandstone), when immersed in water or at normal pH, is generated by dissociation or de-protonation of the weakly

acidic surface hydroxyl groups (silanols) (Buyuktimkin and Wurster, 2015) as follows:



Eqn. [2.1]

Ibrahim et al (2012) have reported that the surface of quartzitic or siliceous sand has an isoelectric point (or alternatively, a point of zero charge) at pH of about 2, above which the concentration of negative charge on the surface increases. They reported that at intermediate pH values (approximately 4) and at room temperature, the adsorption of inhibitor was found to be lower than at both pH 2 and pH 6 due to a relative weakening of both the hydrogen bonding and calcium binding mechanism. Adsorption is thought to occur through an electrostatic attraction or physical adsorption between the inhibitor and formation mineral (Sorbie et al., 1993).

Report has shown that surface area, most especially, the internal pore surface and pore size distribution and the nature of pores determine the extent of adsorption (Gupta and Bhattacharyya, 2011). The physical size and form of the solid particles, the chemistry of the adsorbent, namely, degree of ionization at the surface, the types of functional groups present and the degree to which these properties change in contact with an aqueous solution are important considerations in determining the adsorption capacity of a solid (Gupta and Bhattacharyya, 2014).

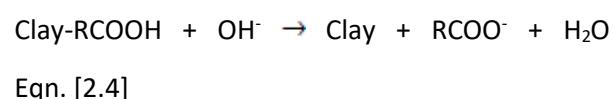
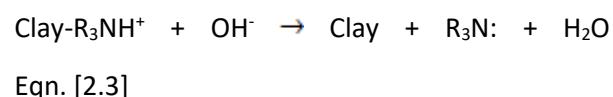
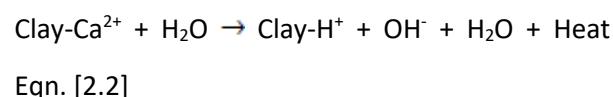
Oluyemi (2013) has reported that adsorption and desorption characteristic of formation in unconsolidated reservoir rocks may be affected

by grain-size distribution, porosity and permeability and eroding effects of particles of sand in motion. He further ascertained that the eroding effects of sand particles can cause a reduction in the amount of inhibitors adsorbed as a result of reduction of the surface area of sand available for adsorption or the stripping off of the already adsorbed inhibitor species from the formation. Similarly, McMahon et al (2005) in their laboratory tests simulating field conditions showed there can be possible reduction in the concentration of inhibitor available to protect steel surfaces. They maintained that large amounts of corrosion inhibitors can be lost from bulk solution by adsorption onto the surface of produced sand grains.

2.1.6 Chemical Adsorption of Scale Inhibitors onto Sand Surface

Chemisorption on sand surface consists essentially of the formation of a chemical compound at the surface of sand and involves an exchange of or sharing of electrons between the adsorbate molecules and the adsorbent. The surface of the adsorbent consists of active functional groups which take part in chemical interactions thereby producing effects that are less reversible and different from that of physical adsorption (Gupta and Bhattacharyya, 2011). Zhang and Somasundaran (2006) in their report claimed that there was a sharp increase in the adsorption of calcium on quartzitic surface and they attributed the increase to chemisorption caused by hydrolysed calcium ions. Chemical reactions for the process of adsorption and

desorption due to enthalpy and entropy change are given below (Ivan et al., 2016).



The desorption of Ca^{2+} from the clay surface and the adsorption of the H^+ onto the negative site of clay in equation [2.2], gave rise to increased pH and, additionally, an exothermic process. The displacement of Ca^{2+} from the solid surface and replacement with H^+ paves way for adsorption reaction of ionized chemical inhibitor as seen in equation [2.3]. Change in pH which could result from brine flooding tends to alter the reaction kinetics thereby causing release or desorption of the inhibitor into the flowing stream for further reaction with Ca^{2+} or any other cation present in seawater used for flooding. For many reservoir rocks, there exists a high affinity for chemical inhibitors due to the presence of hydrogen bonding, electrostatic attraction and hydrophobic repulsion from macro neutral molecules (Yan et al., 2015). The high affinity of these chemicals with weakly anionic groups adsorb onto rocks with negative surface charge and as such cause local positive charges on clay edges (Alotaibi 2010).

2.1.7 Physical Adsorption of Scale Inhibitors onto Sand Surface

Physical adsorption or electrostatic adsorption between the inhibitor and formation minerals has

been reported to be the cause of adsorption (Sorbie et al., 1993). Dang et al. (2014) have reported that physical adsorption occurs when polymer molecules are adsorbed onto rock surface by virtue of a lower overall free energy. They further explained that entropic contribution whereby the liberation of water molecules previously bound to the rock surface or to the polymer due to lower free energy causes an increase in entropy.

Veloso et al. (2014) in their report have claimed that capacity adsorption in physisorption decreases with increasing temperature. They further reported a 7% increase in adsorption capacity obtained from their experimental data subsequent to temperature increase from 30 to 80°C. They suggested that electrostatic interactions or changes in the rock surface could have occurred to facilitate interaction between the rock and inhibitor.

2.1.7.1 Adsorption through Hydrogen Bonding Mechanism

Dellostritto et al. (2016) have ascertained that the understanding of the structure of the H-bond network at the quartz-water interface is vital for a complete analysis of the behaviour of the system. They additionally claimed that the surface charging of quartz is highly dependent on ion concentration as well as cation species with cations promoting negative surface charge as a function of pH. It has been reported that surfactants with carboxylic, phenolic, hydroxyl, and amine groups form hydrogen bond with solid surfaces species. The bond formed between the surfactant functional groups and the mineral

surfaces is reported to be stronger than that formed between the mineral and interfacial water molecules for adsorption due to hydrogen bonding to take place (Zhang and Somasundaran, 2006).

2.1.8 Adsorption Isotherm

There exists a relationship between the type of isotherm and the nature of the adsorbent. The pore size distribution of the adsorbent is a function of the type of isotherm obtained for a given adsorbate. At equilibrium, the concentration of the solute or adsorbate in the bulk liquid to the concentration of the adsorbate on the solid phase defines the adsorption isotherm (Salvaraju and Pushpavanam, 2009).

It has been reported that in adsorption/desorption squeeze treatment applications, the nature of the isotherm depicts the behaviour of the inhibitor return profile (Jordan et al., 1994). Reports have depicted that the nature of adsorption isotherm is influenced by (i) inhibitor species itself, (ii) the formation brine composition and pH, (iii) application pH and temperature and (iv) the nature of adsorbing surface i.e. surface charge, reservoir mineralogy and wettability (Jordan et al., 1994; Vazquez et al., 2011). Bassioni (2010) maintained that electrostatic interaction by means of ion-pair formation, ion exchange, hydrogen bonding or complex formation on the surface of formation rock with saturated adsorption plateau gives rise to adsorption. He further stressed that anion-anion interaction which leads to formation of a second layer may as well cause increased adsorbent concentration. The reason he gave was

a reduction of the adsorption enthalpy and consequent increase of the system's entropy.

Boels et al., (2012) have maintained that the presence of calcium during adsorption process causes a transformation in the equilibrium adsorption isotherm from Langmuir to Freundlich type with much adsorption capabilities. They further claimed that calcium increases the rate of adsorption. Langmuir model was originally developed to describe gas adsorption onto activated carbon based on the assumptions that (i) the adsorbent surface has energetically uniform sites for adsorbate ions, atoms and molecules, (ii) no adsorbate-adsorbate interactions are present, (iii) the same mechanism is followed throughout the process, (iv) at the maximum adsorption, the surface is covered with only a monolayer (Gupta and Bhattacharyya, 2014).

2.2 Theory and Techniques

There are two methods by which oil field scale inhibitors are administered into oil wells. These two methods are continuous injection and squeeze or batch injection. Continuous injection as the name implies involves the continuous injection of chemical inhibitors into the oil well system by means of electric pumps or gas driven chemical pumps. This method is used for prevention of scales in areas such as top sides, chokes, valves and production tubings where squeezing will not be possible. Other well/reservoir enhancement or treatment chemicals like corrosion inhibitors, hydrate and wax inhibitors as well as seawater can also be applied through continuous injection. Li et al

2019 in their experimental study on the kinetic behaviour of natural gas hydrate have reported that continuous seawater injection can keep the balance between productivity and sand production through controlling production pressure. Alternatively, squeeze treatment is viewed as the most technically favourable and economically viable options for scale treatment in both conventional and subsea oilfields. Squeeze or batch treatment is applied as a one off treatment designed to inject scale inhibitor into the near wellbore region accompanied by brine overflush which is injected to drive the scale inhibitor further into the formation. Upon shut in to allow the scale inhibitor to adequately adsorb onto the formation fabric over a period of time, the production of the well is put back into operation. The diagram in Figure 6 below shows a schematic field application of the squeeze procedure applied in the laboratory.

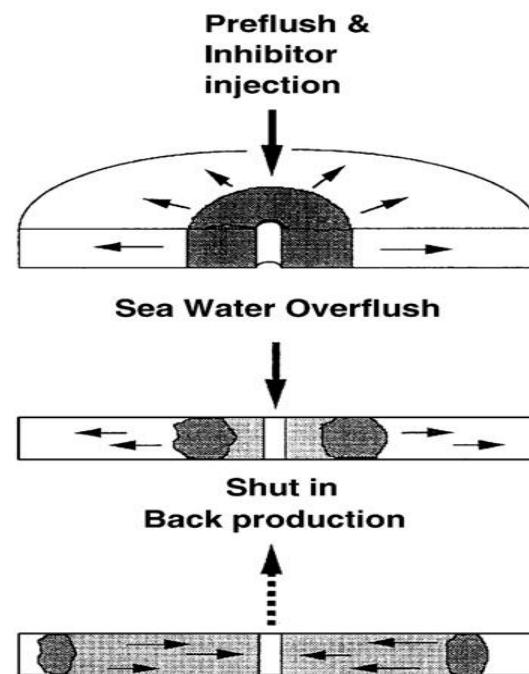


Figure 6: Schematic view of scale treatment procedure (Baraka-Lokmane and Sorbie, 2010).

The laboratory sand pack core holding assembly method using a bench top assembly is shown schematically in Figure 7 below and is used to evaluate the adsorption rate, the adsorption amount and rate of desorption of the chemical inhibitors.

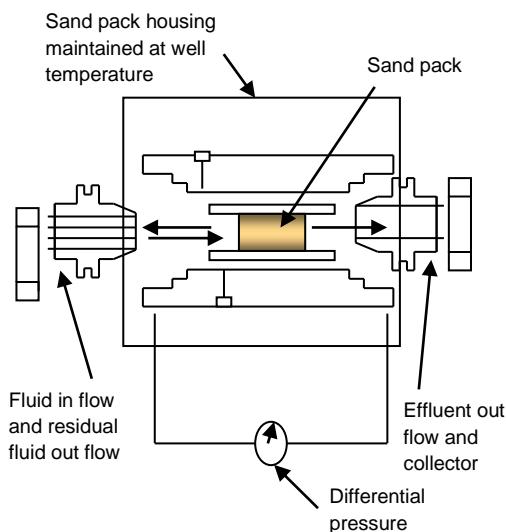


Figure 7: Schematic diagram of sand pack/core holding assembly for Sand pack test (Stamatakis et al., 2006).

This technique involves packing of pre-weighed crushed core samples or sand pack into a core holder assembly. Synthetic sea water (SSW) is flooded into the sample at controlled rate to condition the sand pack and observe the permeability of the SSW into the crushed or sand pack sample. This would be the initial preflush test. Afterwards, synthetic sea water dosed with predetermined concentration of the scale inhibitor is injected into the crushed core sample or sand pack at a determined rate of flow until the inhibitor concentration of the effluent reaches the maximum initial concentration of the injected. The effluent inhibitor solution is collected at intervals of time and the residual

concentration analysed (Yan et al., 2015) to ascertain maximum inhibitor saturation as well as rate of adsorption and the setup is shut in, while maintaining the initial heated test temperature, and allowed to remain over a period of about 24 hours to achieve maximum adsorption onto the crushed specimen or sample.

At the end of 24 hour shut in, the crushed sand pack sample is flooded with synthetic formation water (SFW) at also determined flow rate of say 5mL/h and the effluent collected at intervals of about 1 hour. The concentration of the desorbed inhibitor in the collected effluent portions is analysed using ICP-OES (Yan et al., 2015).

2.3 Conclusion

Squeeze treatment of oilwell production formation with compatible scale inhibitor has proven to be one of the most efficient method of preventing scale formation. Unfortunately, several factors affect the performance of the chosen scale inhibitors. The performance of these scale inhibitors is a function of their rates of adsorption during shut in and desorption during backflow or production resumption. The parameters under which these rates are evaluated are referred to as adsorption and desorption isotherms. These isotherms are affected by a number of factors such as concentration of inorganic ions present in the aquifer water, pH, temperature, the presence of competing ions and irreversible adsorption of scale inhibitors. Different types of formation exist and each formation, combined with the above factors, has an influence on the performance of the scale inhibitors. Most unconsolidated

sandstone formations are potential sand producing reservoirs. The production of these sand particles has been viewed to affect chemical inhibitors squeezed into the formation to enhance the flow of oil and gas through prevention of scale formation. In effect, long scale inhibitor squeeze life has always been a challenge. However, understanding and development of efficient methodology to predict the interaction of scale inhibitors with formation as well as loose sand particles will reduce the economic, environmental and material impact of re-squeezing and production breakdown. A lot of work (experimental, mathematical and simulation modelling) have been carried out to evaluate the behaviour, performance and interaction of the squeezed chemicals within porous media but the role played by the formation loose sand particles has not received much attention. It is important the oil and gas industry begins to focus research attention on this aspect of chemical squeeze to better understand the impact of fine sand production on chemical squeeze performance and to enable better design and field implementation.

References

ABADZIC, D. S. and RYAN, N. J. 2001 Particle Release and Permeability Reduction in a Natural Zeolite (clinoptilolite) and Sand porous Medium. *Environ. Sci. Technol.* 35, 4502-4508.

AGBABOZORGI, S. and ROSTAMI, B. (2016) An Investigation of Polymer Adsorption in Porous Media Using Pore Network Modelling. *Transp. Porous Med.* 115, 169-187.

ALOTAIBI, M. B., AZMY, R., & NASR-EL-DIN, H. A. (2010) A Comprehensive EOR Study Using Low Salinity Water in Sandstone Reservoirs. Paper presentation at the SPE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, USA, 24-28 April 2010. SPE: 129976-MS.

ANDREI, M. and MALANDRINO A. (2003) Comparative Coreflood Studies for Precipitation and Adsorption Squeeze with PPCA as the Scales Inhibitor. *Petroleum Science and Technology; Petroleum Science and Technology*, 21(7-8), pp. 1295-1315.

BARAKA-LOKMANE, S. and SORBIE, K.S. (2010) Effect of pH and Scale Inhibitor Concentration on Phosphonate–Carbonate Interaction. *Journal of Petroleum Science and Engineering*, 70(1–2), pp. 10-27.

BASSIONI, G. (2010) Mechanistic Aspects on the Influence of Inorganic Anion Adsorption on Oilfield Scale Inhibition by Citrate. *Journal of Petroleum Science and Engineering*, 70(3-4), pp. 298-301.

BERNTSEN, A. N. (2012) Scale Effect in Volumetric Sand Production. American Rock Mechanics Association. Paper Presentation at the 46th US Rock Mechanics/Geomechanics Symposium held in Chicago, IL, USA, 24-27 June 2012.

BOELS, L., KEESMAN, K.J. and WITKAMP, G. (2012) Adsorption of Phosphonate Antiscalant from Reverse Osmosis Membrane Concentrate onto Granular Ferric Hydroxide. *Environmental science & technology; Environmental science & technology*, 46(17), pp. 9638-9645.

BROWN, J. M., SHEN, D., SATYA GUPTA, D. V., TAYLOR G., SELF, R. W. (2011) Laboratory and

Field Studies of Long-Term Release Rates for a Solid Scale. Paper Presented at the SPE International Symposium on Oilfield Chemistry held in the Woodlands, Texas, USA, 11-13 April 2011. SPE 140177.

BUYUKTIMKIN, T. and WURSTER, D.E. (2015) The Influence of the Adsorption of Metoclopramide on the Surface Ionization of Fumed Silica. *International Journal of Pharmaceutics*, 478(1), pp. 164-171.

CHAKRABORTY, A., SAHA, B. B. and ARISTOV, Y. I. (2014) Dynamic Behaviours of Adsorption Chiller: Effects of the Silica Gel Grain Size and Layers. *Energy* 78, 304-312.

DANG, T. Q. C., CHEN, Z., NGUYEN, T. B. N. (2014) Investigation of Isotherm polymer Adsorption in Porous Media. *Petroleum Science and Technology*, 32:13, 1626-1640.

DANTAS, T. L. P., LUNA, F. M. T., SILVA Jr, I. J., DE AZEVEDO, D. C. S., GRANDE, C. A., RODRIGUES, A. E., MOREIRA, R. F. P. M. (2011b) Modelling of the Fixed-Bed Adsorption of Carbon Dioxide and a Carbon Dioxide-Nitrogen Mixture on Zeolite 13X. *Brazilian Journal of Chemical Engineering*. Vol. 28. No. 03, 533-544.

DELLOSTRITTO, M. J, KUBICKI, J. D. and SOFO, J. O. (2016) Effect of Ions on H-Bond Structure and Dynamics at the Quartz (101)-Water Interface. *Langmuir* 32, pp. 11353-11365.

DOVE, P.M. and CRAVEN, C.M. (2005) Surface charge density on silica in alkali and alkaline earth chloride electrolyte solutions. *Geochimica et Cosmochimica Acta*, 69(21), pp. 4963-4970.

FAROOQUI, N. M. and SORBIE, K. S. (2016) The Use of PPCA in Scale-Inhibitor Precipitation Squeezes: Solubility, Inhibition Efficiency, and Molecular-Weight Effects. Society of Petroleum Engineers. Paper Presentation at the SPE International Oilfield Scale Conference and Exhibition held in Aberdeen, 14-15 May, 2014. Paper Peer Approved on 29 October 2015. SPE 169792-PA.

FIELDER, G. D. (2000) Scale Inhibitor Selection for a High Suspended Solids Produced Water Systems. Paper Presentation at the Proceeding of International Conference on Corrosion Houston Texas NACE Paper No. 00105.

FLEMING, N., BOURNE, H. M., STRACHAN, C. J. and BUCKLEY, A. S. (2001) Development of an Ecofriendly Scale Inhibitor for Harsh Scaling Environments. Paper Presentation at the SPE International Symposium on Oilfield Chemistry held in Houston, Texas, 13-16 February 2001. SPE 65040-MS.

FLOOD, C., COSGROVE, T., ESPIDEL, Y., HOWELL, I. and REVEL, P. (2007) Sodium Polyacrylate Adsorption onto Anionic and Cationic Silica in the Presence of Salts. *Langmuir; Langmuir*, 23(11), pp. 6191-6197.

GARMEH, G., JOHNS, R. T. and LAKE, L. W. (2009) Pore-Scale Simulation of Dispersion in Porous Media. Paper Presentation at the SPE Annual Technical Conference and Exhibition, Anaheim, California, 11-14 November. SPE-110228, 559-567.

GHOSH, B., KUNDU, S. and SENTHILMURUGAN, B. (2012) A New Squeeze Scale Inhibitor for a Sandstone Reservoir with a Stimulation Effect. *Petroleum Science and Technology; Petroleum Science and Technology*, 30(4), pp. 402-411.

GUPTA, S. S. and BHATTACHARYYA K. G. (2014) Adsorption of Metal Ions by Clays and Inorganic Solids. *RSC ADV.*, 4, 28537-28586.

GUPTA, S.S. and BHATTACHARYYA, K.G. (2011) Kinetics of Adsorption of Metal Ions on Inorganic Materials: A review. *Advances in Colloid and Interface Science*, 162(1–2), pp. 39-58.

HAO, C., QIN, L., YAN, Q., QIU Z. & JIANPING, Z. (2012) Preparation and Adsorption Performance of MnO₂/PAC Composite towards Aqueous Glyphosate. *Environmental Technology* Vol. 33, No. 17, 2049-2056.

<http://www.rgu.ac.uk/research/research-governance/research-governance/> Downloaded on 19/03/2017.

IBRAHIM, J., SORBIE, K. S. AND BOAK, L. S. (2012) Coupled Adsorption/Precipitation Experiments: 2. Non-Equilibrium Sand Pack Treatments. Paper Presented at the SPE International Conference on Oilfield Scale held in Aberdeen, United Kingdom, 30-31 May 2012. SPE 155110.

IDAHOUSA, P. E. G., OLUYEMI, G. F., OYENEYIN, M. B. and PRABHU, R. (2016) Rate-Dependent Polymer Adsorption in Porous Media. *Journal of petroleum science and engineering*, 143, 65-71.

IVAN, D., PINEREZ, T., AUSTAD, T., STRAND, S., PUNTERVOID, T. and WROBEL, S. (2016) Linking Low Salinity EOR Effects in Sandstone to pH, Mineral Properties and Water Composition. Paper Presentation at the SPE Improved Oil Recovery Conference held in Tulsa, Oklahoma, USA 11-13 April. SPE-179625-MS, 1-17.

JONASSON, R.G., RISPLER, K., WIWCHAR, B. and GUNTER, W. D. (1996) Effect of Phosphonate Inhibitors on Calcite Nucleation kinetics as a Function of Temperature using Light Scattering in an Autoclave. *Chemical Geology*, 132(1–4), pp. 215-225.

JONES, F., STANLEY, A., OLIVEIRA, A., ROHL, A. L., REYHANI, M. M., PARKINSON, G. M. and OGDEN, M. I. (2003) The Role of Phosphonate Speciation on the Inhibition of Barium Sulfate Precipitation. *Journal of Crystal Growth*, 249(3–4), pp. 584-593.

JORDAN, M. M., JOHNSTON, C. J. and SUTHERLAND, L. (2016) Impact of Reservoir Temperature on Scale Inhibitor Retention-The Challenge of Ultra-Low Temperature Sandstone Reservoirs. Paper presentation at the SPE International Oilfield Scale Conference and Exhibition held in Aberdeen, Scotland, UK, 11-12 May 2016. SPE-179889-MS.

JORDAN, M. M., SORBIE, K. S., GRIFFIN, P., HENNESSEY, S., HOURSTON, K. E. and WATERHOUSE, P. (1995) Scale Inhibitor Adsorption/Desorption vs Precipitation: The Potential for Extending Squeeze Life While Minimising Formation Damage. Paper Presented at the European Formation Damage Conference held in Hague, The Netherlands, 15-16 May 1995. SPE 30106.

JORDAN, M. M., SORBIE, K. S., JIANG, P., YUAN, M. D., TODD, A. C., TAYLOR, K., HOURSTON, K. E. and RAMSTAD, K. (1994) Mineralogical Control on Inhibitor Adsorption/Desorption in Brent Group Sandstone and their Importance in Predicting and Extending Field Squeeze Lifetimes. Paper Presented at the European Production Operations Conference and exhibition, held in Aberdeen, United Kingdom, 15-17 March 1994. SPE 27607.

JORDANA, R., HOWE, R. F. and GUAN, H. (2012) Retention and Release of Scale Inhibitors in Different Clay Minerals. Paper Presented at the SPE International Conference and Exhibition on Oilfield scale held in Aberdeen, UK, 30-31 May 2012. SPE 156019.

KAHRWAD, M., SORBIE, K. S. And BOAK, L. S. (2009) Coupled Adoption/Precipitation of Scale Inhibitors; Experimental Results and Modelling. Paper presentation at SPE International Oilfield Scale Conference, Aberdeen, 28-29 May 2008. Paper Peer Approved 23 January 2009. SPE 114108.

KAN, A. T., FU, G., TOMSON, M. B., AL-THUBAITI, M. and XIAO, A. J. (2004) Factors Affecting Scale Inhibitor Retention in Carbonate-Rich Formation during Squeeze Treatment. SPE 80230. Pp: 280-289.

KELLAND, M. A. (2009) Production Chemicals for the Oil and Gas Industry. Published by CRC Press, Taylor and Francis Group, 6000 Broken Sound Parkway NW, Suite 300 USA. Pp. 53-91.

KETRANE, R., SAIDANI, B., GIL, O., LELEYTER, L. and BARAUD, F. (2009) Efficiency of Five Scale Inhibitors on Calcium Carbonate Precipitation from Hard Water: Effect of Temperature and Concentration. *Desalination*, 249(3), pp. 1397-1404.

KOSMULSKI, M. (2006) pH-Dependent Surface Charging and Points of Zero Charge: III. Update. *Journal of colloid and interface science*, 298(2), pp. 730-741.

KOSMULSKI, M. (2011) The pH-Dependent Surface Charging and Points of Zero Charge: V. Update. *Journal of colloid and interface science*, 353(1), pp. 1-15.

KUMAR, T., VISHWANATHAM, S. and KUNDU, S. S. (2010) A Laboratory Study on Pteroyl-I-Glutamic Acid as a Scale Prevention Inhibitor of Calcium Carbonate in Aqueous Solution of Synthetic Produced Water. *Journal of Petroleum Science and Engineering*, 71(1-2), pp. 1-7.

Li Dexiang, Ren Shaoran, Xu Yan and Rui Hongxing 2019 Experimental Study on Kinetic Behaviors of Natural Gas Hydrate Production via Continuous Simulated seawater Injection. *Energy Fuels*, 33, Pp 8222-8230.

LI, F., WU, W., LI, R. and FU, X. (2016) Adsorption of Phosphate by Acid-Modified Fly Ash and Palygorskite in Aqueous Solution: Experimental and Modeling. *Applied Clay Science*, 132-133, pp. 343-352.

LIU, B., ZENG, L., MAO, J., REN, Q. (2010) Simulation of Levulinic Acid Adsorption in Packed Beds Using Parallel Pore/Surface Diffusion Model. *Chem Eng. Technol.* 33, No. 7, 1146-1152.

MASON, B. T., KAN, A. T., FU, G., SHEN, D., NASR-EL-DIN, H. A, AL-SAAIARI, H. and AL-THUBAITI, M. (2008) Mechanistic Understanding of Rock/Phosphonate Interactions and the Effect of Metal Ions on Inhibitor Retention. Paper Presented at the 2006 SPE International Symposium on Oilfield Scale held in Aberdeen, United Kingdom, 31 May-1 June. SPE 100494. Pp: 325-336.

MCMAHON, A. J., MARTIN, J. W. and HARRIS, L. (2005) Effects of Sand and Interfacial Adsorption Loss on Corrosion Inhibitor Efficiency. *NACE*

International-Corrosion 2005, Paper No. 05274, pages:1-23.

MOLNES, S.N., TORRIJOS, I. P., STRAND, S., PASO, K. G. and SYVERUD, K. (2016) Sandstone Injectivity and Salt Stability of Cellulose Nanocrystals (CNC) Dispersions—Premises for use of CNC in Enhanced Oil Recovery. *Industrial Crops and Products*, 93, pp. 152-160.

NEVILLE, A. and WANG, C. (2008) Study of the Effect of Inhibitor on Erosion-Corrosion in CO₂-Saturated Condition with Sand. Paper Presented at the SPE International Oilfield Corrosion Conference held in Aberdeen, United Kingdom, 27 May. SPE 114081.

NISRINE, S., AZITA, A. S., AZIZ, O., HENRI, B. (2013) Numerical Simulation of Retention and Release of Colloids in Porous Media at the Pore Scale-Colloids and Surfaces A: Physicochemical and Engineering Aspects-Vol. 427, 33-40.

OLUYEMI, G. F. (2013) Chemical Inhibitor Adsorption and Desorption Characteristics of Common Gravel Pack Sands under Static and Dynamic Conditions. Special Topics and Reviews in Porous Media-An International Journal, 4 (2): PP: 159-169.

OYENEYIN, B. (2015) Integrated Sand Management for Effective Hydrocarbon Flow Assurance. In: S. Dennis. First Edition, Development in Petroleum Science. Volume 63. Elsevier. Pp. 129-138.

SALDUNGARAY, P. M., CARETTA, F. and SOFYAN, M. (2001) Formation Fines Stabilization using Surface Adsorption Polymerization: Field Application of an Emerging Technology. Paper Presentation at the SPE Asia Pacific Oil and Gas Conference and Exhibition held in Jakarta, Indonesia, 17-19 April. SPE 68655.

SELVARAJU, N. and PUSHPAVANAM, S. (2009) Adsorption Characteristics on Sand and Brick Beds. *Chemical Engineering Journal* 147: PP: 130-138.

SORBIE, K. S. and GDANSKI R. D. (2005) A Complete Theory of Scale-Inhibitor transport and Adsorption/Desorption in Squeeze treatments. Paper Presented at the SPE International Symposium on Oilfield Scale held in Aberdeen, United Kingdom, 11-12 May 2005. SPE 95088.

SORBIE, K. S., YUAN, M. D., CHEN, P., TODD, A. C. and WAT, R. M. S. (1993) The Effect of pH, Calcium, and Temperature on the Adsorption of Phosphonate Inhibitor onto Consolidated and Crushed Sandstone. Paper Presented at the 68th Annual Technical Conference and Exhibition of the SPE held in Houston, Texas, 3-4 October 1993. SPE 26605.

STAMATAKIS, E., CHATZICHRISTOS, C., SAGEN, J., STUBOS, A. K., PALYVOS, I., MULLER, J. and STOKKAN, J.-A. (2006) An Integrated Radiotracer Approach for the Laboratory Evaluation of Scale Inhibitors Performance in Geological Environments. *Chemical Engineering Sciences; Chemical engineering science*, 61(21), pp. 7057-7067.

STRAND, S., PUNTERVOLD, T. and AUSTAD, T. (2016) Water Based EOR from Clastic Oil Reservoirs by Wettability Alteration: A review of chemical aspects. *Journal of Petroleum Science and Engineering*, 146, pp. 1079-1091.

TANTAYAKOM, V., FOGLER, H. S. and CHAVADEJ, S. (2005) Study of Scale Inhibitor Reactions in

Precipitation Squeeze Treatments. Paper Presented at the 2005 SPE International Symposium on Oilfield Chemistry held in Houston, Texas U.S.A., 2-4 February 2005. SPE 92771.

TUSHER, K. S., MEHAJAN, S. P. and KHILAR, K. C. (2002) Colloid-Associated Contaminant Transport in Porous Media: 1. Experimental Studies. *AIChE Journal* Vol. 48, No. 10, 2366-2374.

VAZQUEZ, O., THANASUTIVES, P., ELIASSON, C., FLEMING, N. and MACKAY, E. (2011) Modelling the Application of Scale-Inhibitor-Squeeze Retention-Enhancing Additives. *SPE Production & Operations*, 26(3), pp. 270-277.

VELOSO, C. B., SILVA, A. N. A., WATANABE, T. T. T. G., PAES, J. F. B. C., DE LUNA, F. M. T. and CAVALCANTE JR, C. L. (2014) Scale Inhibitor Adsorption Studies in Rock Sandstone Type. *Adsorption*. 20: Pp: 977-985.

WANG S., CHUNG K. H., MASLIYAH, J. H., and GRAY, M. R. 1999 Deposition of Fine Particles in Packed Beds at Hydrotreating Conditions: Role of Surface Chemistry. *Ind. Eng. Chem. Res.* 38, 4878-4888.

WUYEP, E.O., OLUYEMI, G. F., YATES, K. and AKINSANYA, A. R. (2019) Evaluation of Interaction between Oilfield Chemicals and Reservoir Rocks. *Natural Resources Research* (online) <https://doi.org/10.1007/s11053-019-09523-3>.

WYLDE, J. J. (2010) Scale Inhibition Application in Northern Alberta: A Case History of an Ultra-High Temperature Scale Inhibition Solution in Fire Tube Heaters. *SPE International Conference on Oilfield Scale*. 26-27 May 2010. Aberdeen, UK: Society of Petroleum Engineers.

YAN, F., ZANG, F., BHANDARI, N., LIU, Y., WANG, L., DAI, Z., ZHANG, Z., BOLANOS, V., KAN, A. And TOMSON, M. (2015) Interaction between Scale Inhibitors and Shale and Sandstone Formations. Society of Petroleum Engineers. Paper

Presentation at the SPE International Symposium on Oilfield Chemistry held in The Woodlands, Texas, 13-15 April 2015. SPE 173769-MS.

YANG, Q., LIU, Y., GU, A., DING, J. and SHEN, Z. (2001) Investigation of Calcium Carbonate Scaling Inhibition and Scale Morphology by AFM. *Journal of Colloid and Interface Science*, 240(2), 608-621.

ZAITOUN, A. and KOHLER, N. (1987) The Role of Adsorption in Polymer Propagation through Reservoir Rocks. Paper Presentation at the SPE International Symposium on Oilfield Chemistry held in San Antonio, Texas, February 4-6 1987. SPE 16274.

ZENG, J.-P., Wang, F.-H. and Gong, S.-D. (2013) Molecular Dynamics Simulation of the Interaction between Polyaspartic Acid and Calcium Carbonate. *Molecular Simulation*, 39:3, Pp: 169-175.

ZHANG, R. and SOMASUNDARAN, P. (2006) Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Advances in Colloid and Interface Science*, 123–126, pp. 213-229.