



The state of the art in scale inhibitor squeeze treatment

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Abstract

The mechanistic understanding of the reactions that govern the inhibitor retention and release, modeling, and the state-of-the-art innovation in squeeze treatment are reviewed. The retention and release are governed by (1) the amount of calcite that can dissolve prior to inhibitor-induced surface poisoning; (2) calcite surface poisoning after ~20 molecular layers of surface coverage by the adsorbed inhibitors to retard further calcite dissolution; (3) less base, CO_3^{2-} , is released into the aqueous solution; (4) formation of the more acidic inhibitor precipitates; (5) phase transformation and maturation of the more acidic inhibitor precipitates; and (6) dissolution of the less soluble crystalline inhibitor precipitates. The trend to advance squeeze technologies is through (1) enhancing scale inhibitor retention, (2) optimizing the delivery of scale inhibitors to the target zone, and (3) improving monitoring methods. Lastly, a prototype yardstick for measuring the squeeze performance is used to compare the squeeze life of 17 actual squeeze treatments. Even though the various squeeze treatments appear to be different, all published squeeze durations can be rated based on the normalized squeeze life per unit mass of inhibitors.

Keywords Scale inhibitor squeeze · Inhibitor retention · Surface poisoning · Adsorption · Squeeze life

List of symbols

a	Gaussian distribution coefficient
a_{elec}	An electrostatic work function that accounts for the increasing resistance of ionization due to the charge on the inhibitor and the effect of ionic strength
b	Gaussian distribution coefficient
$C_{\text{eq}}^{\text{ppt},i}$	Inhibitor concentration (M) at equilibrium with connate brine (temperature, pressure, ionic strength, Ca, pH) and pK_{sp} , i solid phase
$C_{\text{aq}}^{\text{unreacted}}$	Unreacted inhibitor concentration (M), i.e., the inhibitor concentration that return at 1 pore volume
C_{aq}	Inhibitor return concentration (M)

D_i	Dimensionless dispersion coefficient of dissolution of solid phase i
erfc	Complimentary error function
K	Equilibrium constant of a polymeric inhibitor
$K_{\text{intrinsic}}$	Intrinsic equilibrium constant for polymeric inhibitor
MIC	Minimal inhibitor concentration (mg/L) needed to control scale formation
NSL	Normalized squeeze life, which is defined as the volume of water produced per unit mass of inhibitor (m^3/kg)
PV	Number of pore volume where 1 pore volume is defined as the total injection volume (L) (= inhibitor pill volume + overflush volume)
R_i	Retardation factor of dissolution of solid phase i
θ_u	Dissociation fraction of the polymeric inhibitor

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Abbreviations

BHPMP	Bis(hexamethylenediamine) penta (methylene phosphonic acid)
DTPMP	Diethylenetriamine penta (methylene phosphonic acid)
HTHP	High temperature, high pressure
NTMP	Nitrilo tris (methylene phosphonic acid)
mPAA	Modified polyacrylate
PPCA	Phosphinopolycarboxylate
SPCA	Sulfonated polycarboxylate

1 Introduction

Whenever an oil or gas well produces water, or water injection is used to enhance recovery, there is the possibility that scale will form. Methods to prevent scale formation can be divided into physical and chemical prevention methods. A few physical/chemical means to prevent scale formation may include: (1) avoid mixing incompatible water; (2) dilute the produced water, e.g., in control of halite scale; (3) apply pH control, e.g., acid treatment to remove carbonate scale; (4) add a metal chelator to reduce effective concentrations of calcium, barium, or iron; (5) use a water softening agent to remove divalent cations or membrane filtration to reduce sulfate in injection water; and (6) initiate scale formation to reduce the supersaturation. More commonly, threshold scale inhibitors, such as the phosphonates, polyacrylates, polymaleates, etc., have been used to control scale (Rosenstein 1936). Threshold scale inhibitors are chemicals that will delay or reduce scale formation when added in a small, or sub-stoichiometric, amount to scaling water. The fact that the most commonly used scale inhibitors function by inhibiting the formation or growth of the scale crystals means that the inhibitor must be present in the water at the point where the crystals begin to form. Therefore, the inhibitor must be present in the water at the point where the crystals start to form, i.e., the inhibitor must be applied upstream of the problem area. The inhibitor must be present in the water continuously so that it is available to inhibit the growth of each scale crystal as it precipitates from water. Either continuous chemical injection or a “squeeze” treatment, which provides a constant supply of inhibitor to the system between treatments, must be used. Furthermore, the inhibitor cannot be depleted from the solution during the production of water from downhole to surface.

An inhibitor squeeze is performed by pushing the scale inhibitor solution into a producing formation and fixing the inhibitor in the formation. In Fig. 1 is illustrated the conventional squeeze technology where three stages of injections occur. The preflush stage involves the injection of a small volume of fluid that may contain chemicals, e.g., acids, chelating agents, surfactants, biocides, etc., to clean the production tubing and wellbore (preflush). The scale inhibitor pill, containing a scale inhibitor of 0.5%–10% (w/v) in makeup water of either ~1% KCl solution or filtered produced water, was pushed into the formation following the preflush. Lastly, another volume of fluid can be injected as the overflush solution to push the inhibitor pill further into the formation (Hong and Shuler 1987). When oil/gas production begins, the inhibitor is produced along with the formation water. Following the squeeze, scale inhibitor flows back at low concentrations. The return

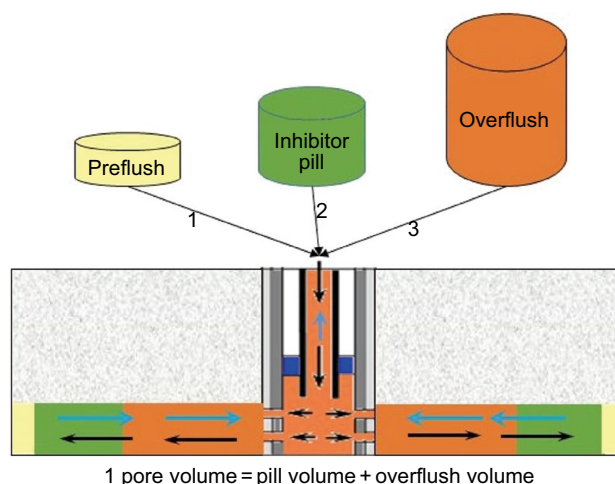


Fig. 1 An illustration of a scale inhibitor squeeze treatment

scale inhibitor concentration increases rapidly and peaks to some value and then declines within a few days to a low plateau concentration, which comprises the bulk of the squeeze duration. The plateau flowback inhibitor concentration usually is sufficient to inhibit scale.

2 Mechanistic understanding of the reactions governing inhibitor retention and release

There is little agreement regarding the primary mechanism by which threshold scale inhibitors are retained in the producing oil or gas well formation because of the squeeze procedure. It is often called a “precipitation” squeeze when an acidic phosphonate pill is injected into a carbonate formation to cause the precipitation of calcium phosphonate. “Adsorption” squeezes often perform in certain noncarbonate (sand) reservoirs whereby a neutralized phosphonate pill is injected into a sandstone formation. The factors affecting the retention and release of inhibitor from the reservoir following a squeeze treatment are certainly more complex than the simplistic description of precipitation versus adsorption reactions. Many researchers have studied inhibitor reactions under various production conditions (Jordan et al. 1995, 1997; Collins 2003; Benton et al. 1993; Sweeney and Cooper 1993; Smith et al. 2000; Lawless and Smith 1998; Lawless et al. 1993; Sorbie et al. 1994; Jordan et al. 1994; Sorbie 2012; Farooqui and Sorbie 2016; Sorbie 2010; Shaw and Sorbie 2015), mostly using empirical equations that are not based upon mechanistic understanding. The present authors advanced the following mechanistic interpretation to explain the phenomena of inhibitor return following a squeeze treatment.

The chemical/physical properties of phosphonates bear many similarities to those of orthophosphate. In calcareous soil, the effective sorbent for phosphate is calcite. At low phosphate concentrations, the phosphate adsorption is strongly favored (Miltenburg and Golterman 1998; Bowden et al. 1980; Cole et al. 1953). At high concentration, phosphate sorption occurs in two steps, the fast chemisorption of phosphate to a limited number of specific surface sites followed by the spontaneous crystal growth on the cluster of surface phosphate ions (hetero-nuclei) (Griffin and Jurinak 1982; Sawada 1998). Understanding of the phase formation and transformation of calcium phosphates was advanced using a new method of precipitation kinetics and stoichiometry (Tomson and Nancollas 1978). Stumm and Leckie (1970) postulate that the reaction occurs in three steps: (1) chemisorption of P to form amorphous calcium phosphate; (2) slow transformation of the amorphous calcium phosphate to hydroxyapatite; and (3) crystal growth of apatite. Mineral salts in nature can form into different amorphous and crystalline phases. For example, vaterite and aragonite are metastable phases of calcite. There are a large number of calcium phosphate solid phases that exist under different conditions: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$, and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (Brown 1973).

The authors have done a series of experimental studies to detail the sequence of reactions that govern the retention and release of scale inhibitors during squeeze. Analogous to the phosphate adsorption/precipitation reactions in calcareous soil, we proposed the following sequence of reactions for phosphonates wherein fixation in the reservoir takes place by adsorption and precipitation of an amorphous phase (Fig. 2). Note that further detail comparisons of phosphonate to phosphate chemistry are reviewed in the supplementary information document. The acidic protons on phosphonates react with the basic carbonate ions of calcite dissolving calcium and bicarbonate and simultaneously raising the solution

pH and calcium concentration. Several dissolved calcium ions form complexes with the partially neutralized phosphonate (Tomson et al. 1994). The primary driving force for phosphonate adsorption is related to simple hydrophobic repulsion from the solution of a macroneutral molecule and not, as is generally presumed, some specific phosphonate–surface interaction. The amorphous phase transforms into a crystalline phase with lower solubility during the shut-in period, accounting for the much better results seen in the field following squeezes with a shut-in period. The long-term flowback concentrations of the inhibitor are the result of the low solubility of the crystalline phase combined with the kinetics and mass transport effects. The effects of temperature, salinity, pH, and inhibitor pill composition on squeeze retentions and returns of several phosphonates and a polymeric inhibitor have been studied and are summarized below.

2.1 Scale inhibitor speciation

It is necessary to predict the simple acid–base and complexation equilibria of inhibitors and divalent metals, such as calcium, magnesium, barium, and iron, to predict the fate of inhibitors in diverse fluid compositions. It is also essential to understand the effects of temperature, pH, and ionic strength on these equilibria. The water or brine pH can be deduced from the surface measurement of brine composition, temperature, pressure, and production volumes (Kan and Tomson 2012; Kan et al. 2019). Previously, several of these equilibria have been described to be within experimental error by an electrostatic-type equation (Al-Thubaiti et al. 2004; Friedfeld 1997; Frostman et al. 1998; Tomson et al. 1994). Xiao et al. (2001) have systematically developed the parameters using electrostatic theory (Tanford 1967) to address the solution speciation of polymers, e.g., phosphinopolycarboxylic acid (PPCA) (Xiao et al. 2001). It is proposed that the equilibrium constant for the ionization of any functional group can be considered as consisting of two parts. The first is a constant related to the breakage of the covalent bond between the oxygen and the hydrogen of a particular acid group, RO-H, which is represented as $K_{\text{intrinsic}}$. The second is a variable that is related to the fact that as a polyprotic molecule becomes progressively ionized, there is increasing electrostatic energy (a_{elec}) required to separate a proton from the increasing negative charge on the molecule. The second term is treated as an electrostatic part and should be readily calculated from the electrostatic theory and the dissociation fraction (θ_i). Therefore, the overall equilibrium constant can be described as the product of these two terms $K = K_{\text{intrinsic}} \cdot e^{a_{\text{elec}}\theta_i}$. The unit of polymer concentration used in calculating PPCA speciation is expressed as the acrylic acid monomer (A), which may be extended to polymers of different sizes. The stoichiometry of the calcium salt is

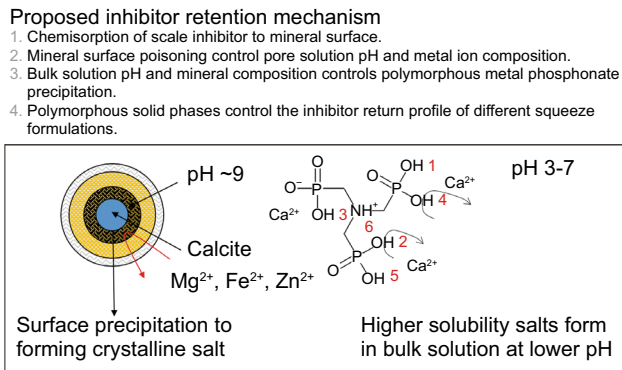


Fig. 2 The proposed reaction sequence that determines inhibitor retention

expressed as three Ca and two acrylic acid trimers. A similar solution speciation scheme for a sulfonated polycarboxylate scale inhibitor has also been developed by Zhang et al. (2017a).

The complexation of Ca^{2+} and inhibitors is mostly electrostatic in origin. At 1.0 M ionic strength and 70 °C, the stability constants for the complexation of Ca^{2+} with a dinegative phosphonate ion are $10^{1.12}$, $10^{1.24}$, and $10^{0.76}$ of three phosphonates, where the three phosphonic acids are amino tri(methylene phosphonic acid) or NTMP, diethylenetriamine penta(methylene phosphonic acid) or DTPMP, and bis-hexamethylene triamine penta(methylene phosphonic acid) or BHPMP, respectively. These stability constants are comparable to the stability constants of Ca/methyl and aminomethyl phosphonates [see Smith and Martell: Critical stability constants (Martell and Smith 1974)]. The average stability constant of Ca with twelve common monophosphonates is $10^{1.55 \pm 0.14}$ at 0.1 M ionic strength and 25 °C. It should be noted that the stability constant for $\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4^0$ is similar, about $10^{1.3}$ at 1 M ionic strength and 25 °C.

2.2 Calcite dissolution kinetics

The squeeze inhibitor pill solution typically does not contain divalent cations since mixing a cation with inhibitor pill may form inhibitor pseudoscale and causes damage to the reservoir. Hence, the dissolution of calcite from the rock is considered the primary source of the cation to induce scale inhibitor adsorption and precipitation. The rate and extent of calcite dissolution are significant factors that control the fate of scale inhibitor retention in the subsurface. Numerous papers have shown that the calcite surface is poisoned when low concentrations of phosphonate are adsorbed onto calcite (Kan et al. 2003). A two-compartment dissolution kinetics was observed by monitoring the calcite dissolution kinetics in the presence of the NTMP. According to the speciation constants, the first two protons on NTMP are strongly ionizable in water. It was observed that calcite dissolution was very fast when in contact with an acidic NTMP. The fast dissolution corresponds to the neutralization of the first two NTMP protons. With the progress of calcite dissolution toward equilibrium, nearly complete inhibition of calcite dissolution was observed after 200 s reaction time, which is presumably caused by surface poisoning of calcite with adsorbed phosphonate. Thus, one may conclude that the acidic phosphonate will dissolve calcite or other minerals to stoichiometric equivalents of at least 1 calcite per phosphonate during squeeze before the dissolution is inhibited by surface poisoning. Establishing this baseline of “no inhibition” of calcite dissolution is important to any model of an inhibitor solid reaction. Once Ca^{2+} is present in the aqueous phase, electronically neutral calcium phosphonate

will adsorb onto the mineral surface. After a few layers of calcium phosphonate are built-up on the surface, calcite dissolution is inhibited. At this point, the solution is near equilibrium at a lower pH than typically observed of a calcite saturated water of ~9 pH. The lower pH environment permits the formation of the more acidic/amorphous calcium phosphonate phases.

2.3 Adsorption of phosphonates to mineral surface

Kan et al. (1991, 2004a, 2005a) extensively studied the adsorption of phosphonate onto sandstone, calcite, and barite surfaces. At low concentration, the neutral, or nearly neutral, Ca-phosphonate solution complex is adsorbed on the mineral surface and it can be characterized as a Langmuir isotherm. Surprisingly, the adsorption isotherms to different solid phases are similar, supporting the idea that the driving force for adsorption is simple hydrophobic repulsion from the solution of a macroneutral molecule. At saturation, only ~7% of the calcite surface is covered with phosphonate. Presumably, these are the kinks, step edges, or other imperfect sites. It has been observed that when the active site on the mineral surface is covered due to adsorption of the scale inhibitor, further dissolution of calcite is inhibited and this observation dictates the inhibitor retention and solid-phase crystallinity.

2.4 Solubility products of scale inhibitor solids

Calcium phosphonates also exhibit polymorphism behavior, which is similar to the polymorphous nature of calcium phosphates. When high concentration of phosphonates is in contact with a cation, such as Ca^{2+} , the initial precipitate is most likely amorphous due to the random nature of phase separation of a macroneutral molecule. This initial precipitate transforms into a well-defined crystalline phase after dissolving excess phosphonate out of the amorphous phase during the inhibitor flow back (Kan et al. 1994). It was proposed that the formation of the amorphous precipitate contributes to the initial retention of the scale inhibitor following a squeeze treatment. The dissolution of the crystalline phase precipitate controls the long-term inhibitor return concentration.

A large number of papers were published to characterize the solubilities of the metal phosphonate and metal-polymer precipitates. Using the solution speciation models, we can establish the solubility products of various metal phosphonate and metal-polymer salts and their ionic strength and temperature dependences by correlating the laboratory-measured solubilities to the equations (Kan et al. 1994; Friedfeld 1997; Frostman et al. 1998; Xiao 2000). Ca^{2+} and Fe^{2+} are the predominant cations in connate water that can precipitate with scale inhibitors.

We typically observed the formation of a high solubility amorphous phase of metal inhibitor salt when mixing the inhibitor with calcium at high concentrations (Oddo and Tomson 1990; Kan et al. 1994; Friedfeld 1997; Frostman et al. 1998; Xiao 2000). Even at $\text{pH} < 2$, Al-Thubaiti et al. (2004) observed an acidic calcium phosphonate phase, which exhibits a gel-like appearance (Al-Thubaiti et al. 2004). The amorphous material will eventually develop into a crystalline phase with a much lower solubility, often by flowing brine over the metal inhibitor salt via a membrane filter to remove the readily dissolved amorphous Ca-phosphonate salt. The crystallinity of both Ca-NTMP and Ca-DTPMP solid phases have been confirmed by XRD analyses. The solubilities of Ca-NTMP and Ca-DTPMP are very similar, while Ca-BHPMP is significantly more soluble than that of Ca-NTMP. The solubility of Ca-PPCA is lower than Ca-BHPMP and higher than Ca-NTMP. The solubility product of Fe(II)-NTMP is many orders of magnitude lower than Ca-NTMP. Therefore, the solubility of Fe(II)-NTMP may also play a significant role in controlling the fate of phosphonate during production, even though the iron concentration is typically much lower than the calcium concentration in brine (Friedfeld 1997). There is little systematic research done for the sulfonated polycarboxylates or polyvinylsulfonate forming inhibitor solids. The sulfonated polymers are known to be very poorly adsorbing on rock material surfaces, and therefore, a poor candidate for squeeze treatment due to their inertness with Ca^{2+} (Collins et al. 1999; Chen et al. 2012b).

Kan et al. (2004b) studied the adsorption and precipitation of a phosphonate, NTMP, to calcite. The crystal growth phase yields a constant solubility product of 24.11 ± 0.22 by assuming a stoichiometry of $\text{Ca}_{2.5}\text{HNTMP}$ at pH 9. The measured solid-phase Ca/phosphonate ratio is 2.31 ± 0.42 . Interestingly, the 4.5th root (i.e., per ion) of the solubility product of this new calcium phosphonate salt is equal to 5.34. The 9th root of the solubility product of hydroxyapatite is 5.42. It is remarkable that the solubility of the calcium phosphonate formed at pH 9 is similar to that of the hydroxyapatite, which support our hypothesis that phosphonate reaction with Ca^{2+} is similar to that of phosphate. We expected the proposed solid phase to be the most thermodynamic stable phase for phosphonates since the most basic form of calcium phosphate (hydroxyapatite) is also the most thermodynamic stable phase under many environmental conditions. In addition, the pH of the boundary layer of a calcite surface is approaching 9, and therefore, the existence of the crystalline solid on the calcite surface is plausible. It has been shown that this solid phase controls the long-term slow release of phosphonate following an inhibitor squeeze in numerous oil and gas wells (Tomson et al. 2004), and similar results are expected in other subsurface calcareous deposits.

2.5 Comparison of inhibitors

When four different inhibitors (~0.6% active for NTMP, DTPMP, BHPMP, and PPCA, respectively) were reacted with calcite, the mass of inhibitor that precipitated are in the order of NTMP (81%) > DTPMP (72%) > BHPMP (42%) > PPCA (26%). The observed bulk solid-phase Ca/inhibitor stoichiometries are 1.45, 3, 2.4, and 0.54 for NTMP, DTPMP, BHPMP, and PPCA (in terms of monomers), which are significantly lower than the stoichiometric ratios of the pure inhibitor calcium salts. These observations imply that more soluble solid phases with a lower Ca stoichiometry are formed. The solution is undersaturated with respect to calcite due to the inhibitor poisoning of calcite dissolution. It has also been shown that the calcium-inhibitor ion products compare favorably, within expected error, to the amorphous phase solubility products for the three calcium phosphonate and calcium PPCA salts. Therefore, the equilibrium phosphonate composition can be well represented by their amorphous solubility products (Kan et al. 2004a, b, 2005a; Tomson et al. 2004).

2.6 Impacts of inhibitor pill water chemistry

It has been observed that the water chemistry of the inhibitor pill controls which inhibitor solid-phase forms and the quantity of phosphonate that will be precipitated after inhibitor injection (Al-Thubaiti et al. 2004; Frostman et al. 1998; Kan et al. 1994, 2004a, 2005a; Tomson et al. 1994, 2006, 2008; Xiao et al. 2001). The acidic pill was instantaneously neutralized by carbonates, and the bulk of phosphonate was deposited as soon as enough cations are present for precipitation. The pore solution pH increased during the dissolution of minerals, and this surface environment favors phosphonate precipitation. More phosphonate is precipitated near the entrance to the formation when the pill is more acidic. Less phosphonate was precipitated and at further away from the entrance point for the more neutralized pill. Much more phosphonate flowed back when the neutralized pill is used compared with the acidic pill, indicating that less phosphonate is retained when the pill is neutralized. Therefore, it is proposed that the acid protons of an acidic NTMP will rapidly react with calcite to dissolve ~2.1 mol calcium per mole phosphonate. After the pill solution is partially neutralized, phosphonate will adsorb to the calcite surface and form a multimolecular layer on the calcite surface, as long as the calcium phosphonate ion product is below the crystalline calcium phosphonate solubility products. Additional precipitate will form due to phase separation until the amorphous calcium phosphonate solubility is reached. Phosphonate would deposit a monomolecular layer of calcium phosphonate on the new calcite surface when the residual phosphonate in solution was pushed further into the formation.

2.7 Squeeze modeling

A thorough review of reservoir transport modeling and its applications under various production scenarios are beyond the scope of this review. The primary squeeze model used by the industry is based on a reservoir flow simulators, such as Eclipse, coupled with the Freundlich type isotherms to match the observed inhibitor return to different production scenarios (Mackay and Jordan 2003; Kaur et al. 2016; Jordan et al. 2016a; Vazquez et al. 2009). Since the Freundlich isotherm is not a mechanistically based reaction model, the model is difficult to guide future field operations based on the curve fitted parameters (Vazquez et al. 2012; Sorbie 2010). Due to the empirical nature, nearly all efforts to model and predict the squeeze return concentrations require extensive testing and tweaking of the model to match the data observed from both core flood testing and at field site. The deviation between the model prediction and observations is often attributed to the differences in transport mechanisms (Spooner et al. 2014). The inhibitor squeeze return described by such models divorced from mechanical science, and therefore, improvements are too marginal. Such an effort may be significantly improved with a better chemical model

to predict the processes of both the retention of the scale inhibitor in the formation and the release of inhibitor during production after the inhibitor squeeze.

Analogous to calcium phosphate, Kan et al. proposed that the shape of the inhibitor return curve is controlled by the dissolution of various Ca-inhibitor solid phases (Kan et al. 2005b). We have identified three calcium-inhibitor solid phases of different stoichiometries, namely (1) amorphous phase, (2) middle phase with intermediate solubility (Zhang et al. 2016b), and (3) crystalline phase. These principal mechanistic understanding of calcium phosphonate with calcite and core material from these earlier studies were used to derive an inhibitor squeeze model, SqueezeSoftPitzer™ (Fig. 3).

It is assumed that both phosphonate and polyacrylate inhibitor return can be characterized by dissolution from three calcium-inhibitor solid phases. The dissolution is influenced by connate water pH and brine composition. To characterize the commonly observed large unreacted peak concentration, a peak function is used, followed by an advective–dispersive type of equation (Eq. 1) was used to model the return of three solid phases.

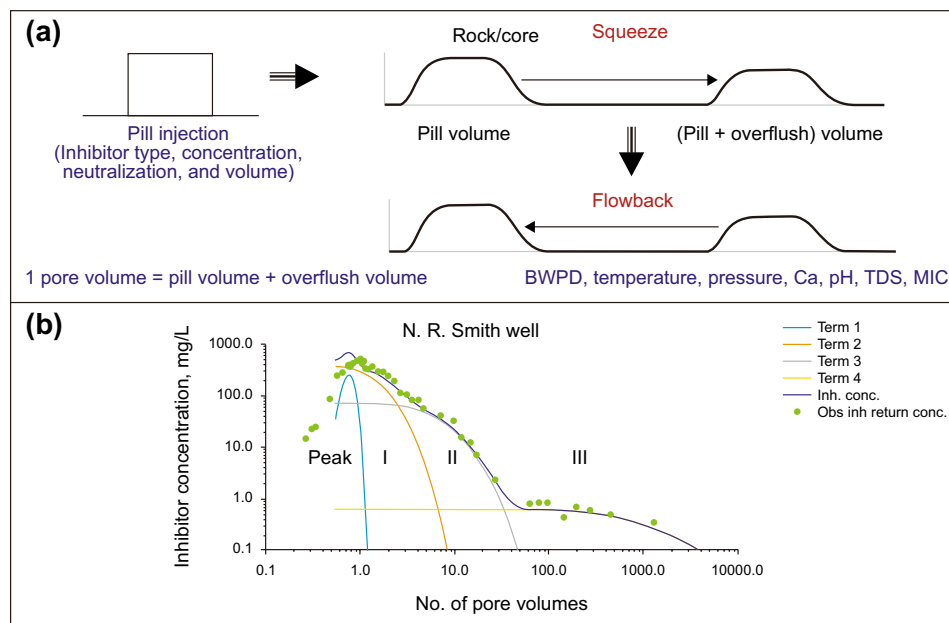


Fig. 3 **a** A schematic illustration of the process of squeeze and inhibitor flow back during a squeeze treatment, where the retention of inhibitor is affected by the inhibitor type, concentration, degree of neutralization and volume of pill and overflush. Inhibitor return concentration is controlled by the solubility of several phases of inhibitor precipitate, and the connate water pH, Ca concentration, TDS, temperature and pressure and the volume of produced water flow rate and the minimum inhibitor concentration needed for inhibition. **b** The simulation of inhibitor return based on Eq. 1, which is composed for four terms, a peak to represent the unreacted inhibitor that flows back immediately following the return and the solubility controlled returns of three inhibitor solid phases. The solid lines are drawn based on Eq. 1 using the condition of a squeeze test at N. R. Smith Well in San Patricio County, Oden, TX

$$C_{aq} = C_{aq}^{unreacted} \cdot a \cdot e^{-\frac{1}{2} \left(\frac{PV-1}{b} \right)^2} + \sum_{i=1}^{i=3} C_{eq,i}^{ppt} \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left(\frac{R_i - PV}{2 \cdot (D_i R_i PV)^{\frac{1}{2}}} \right) - \frac{1}{2} e^{\frac{1}{D_i}} \cdot \operatorname{erfc} \left(\frac{R_i + PV}{2 \cdot (D_i R_i PV)^{\frac{1}{2}}} \right) \right\} \quad (1)$$

The dimensionless terms, a and b , are used to characterize the peak function; the three D_i values are determined by fitting and represent the inhibitor spread from one region to the next. The dimensionless R_i terms represent the duration in terms of pore volumes, PV, where 1 PV is defined as the volume of squeeze treatment, i.e., the sum of the pill and overflush volumes. The squeeze treatment volume represents the extent of squeeze chemical that travels in the formation or in the laboratory core flood. The first term in Eq. 1 represents the return of the unreacted phosphonate, and the second term is the summation of inhibitor returns from three Ca-inhibitor solid phases. For example, the conditional solubility products of $10^{-21.3}$, $10^{-22.6}$, $10^{-24.2}$ at 158 °F and 1 M ionic strength represent the solubilities of the three Ca-NTMP solid phases. Dissolution from the three solid phases are identified as Regions 1, 2 and 3 in Fig. 3. The parameters used in Eq. 1 are explicit functions of temperature, ionic strength, brine pH and Ca concentration, and the inhibitor pill acidity, concentration, and pill and overflush volumes. The calculations use the speciation model of Tomson et al. (1994) for different inhibitors. Also included in SqueezeSoftPitzer is the minimum inhibitor concentration (MIC) predicted from our inhibitor model (He et al. 1996, 1999; Dai et al. 2019). The following three sets of algorithms were included in SqueezeSoftPitzer, where the thermodynamic equilibrium constants and Pitzer equations are used to model the connate water chemistry.

1. Inhibitor return concentration is set to be a function of inhibitor type, inhibitor pill acidity, volume and concentration, and formation water pH, ionic strength, calcium concentration, temperature, and pressure.
2. The MIC is set to be a function of the inhibitor type, scale type, saturation ratio, temperature, pH variation with temperature and pressure changes, and lattice ion ratio.
3. The squeeze life is defined as the time when the return concentration is higher than MIC.

In Fig. 4 are plotted the measured and calculated inhibitor concentrations by SqueezeSoftPitzer from the four different squeeze treatments at four Texas and Louisiana wells. All of these wells have documented scale problems, and the authors' research group was allowed on-site to monitor inhibitor return concentrations during the initial flow back and over the life of the squeeze treatment. NTMP was used

in these squeeze treatments, except that A. E. Guerra well used a mixture of NTMP and BHPMP. The formation type is predominantly sandstone formation with a limited amount of calcite present in the formation. Excellent agreement is observed between the model and field observations, indicating that the proposed sequence of phosphonate/calcite reactions is reasonable. Note that all four inhibitor treatments lasted more than 1 year with an enormous volume of water production. Also note that the return concentrations were at sub mg/L for all four wells, indicating that the actual MIC is quite low for these wells with both calcite and barite scaling problems. The observed MICs of these four wells are often much lower than those that were previously assumed by the producers.

Figure 5 shows the inhibitor return from three squeezes performed and monitored by a production company (Kokal et al. 1996; Nasr-El-Din et al. 2003; Tomson et al. 2008). The field squeeze treatment and return of wells H-1 and H-66 (Nasr-El-Din et al. 2003) present two interesting case studies. The formation is sandstone with less than 1 wt% calcite (Nasr-El-Din et al. 2003). In the two squeeze treatments, a strong acid was added to the inhibitor pill, and it caused high concentrations of Fe^{2+} dissolved from the iron-bearing formation. Also, Ca^{2+} was added to the pill solution. The inhibitor squeeze treatment was proven very successful, with each squeeze treatments lasting over 800 days. Interestingly, both well H-1 and H-66 return curves showed the characteristic three-phase returns, despite that diesel was used as overflush fluid. DTPMP concentration in the return fluids reduced to below 210 mg/L within the first fifteen pore volumes of flow. In both cases, the data exhibits a high solubility phase (phase II, ~ 18 mg/L) between 15 and 800 pore volumes, and the inhibitor return concentration decreased to the lower solubility phase after nearly 800 pore volumes. The squeeze treatments were very successful, with < 30% DTPMP returned after > 800 days production for both wells. The excellent DTPMP retention in the sandstone formation may be attributed to the high Ca^{2+} concentration that was added to the inhibitor pill and high Fe^{2+} concentration that was in situ dissolved from the formation. However, the presence of Fe^{2+} does not appear to influence the phase III return of DTPMP.

Commonly, wells are resqueezed every few months or when the return concentration is no longer readily measured or below designed MIC. By simply tightening up conventional squeeze technology and modest innovation, the typical lifetime of a squeeze has been extended from a few months

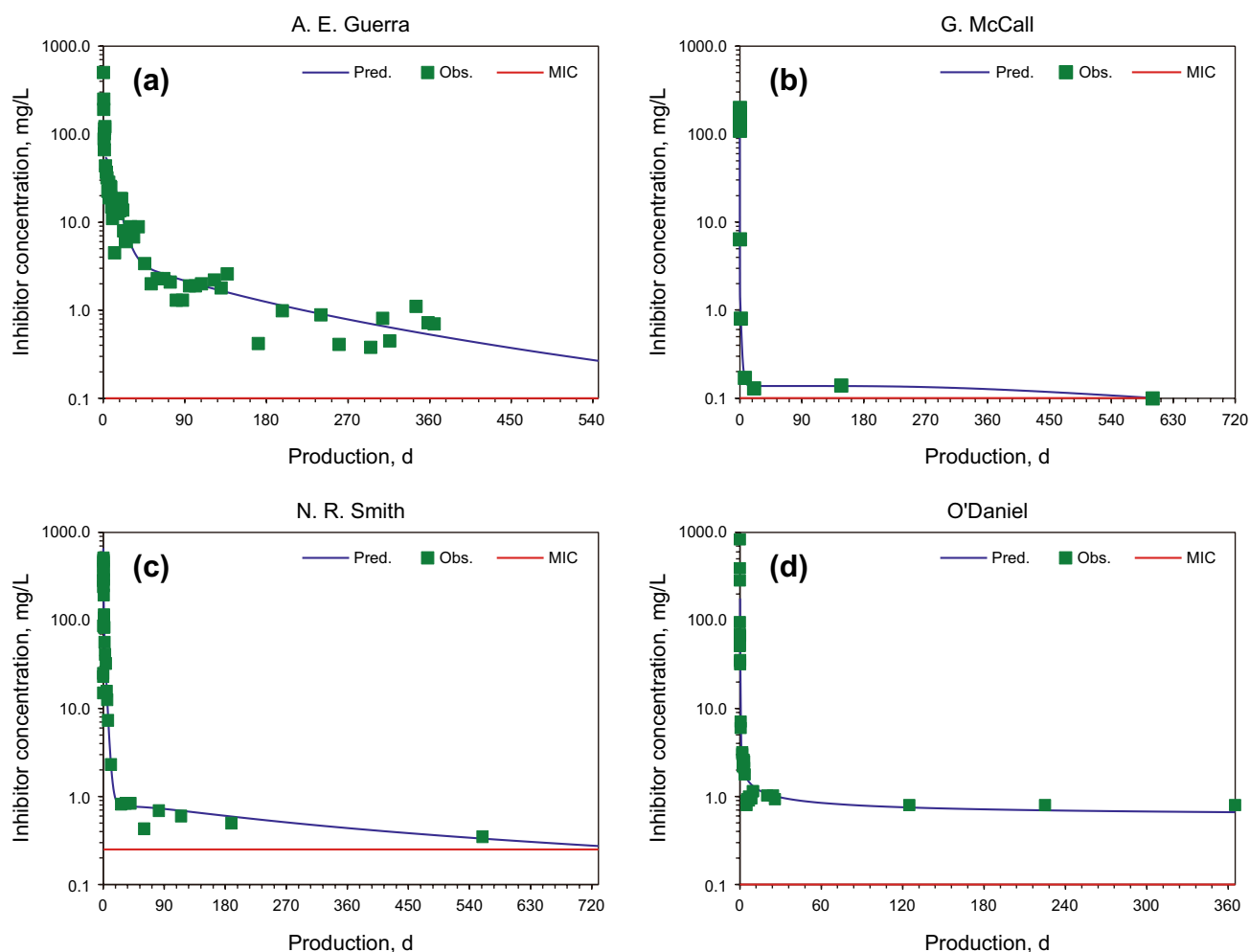


Fig. 4 Plots of four inhibitors return field data with squeeze simulation by SqueezeSoftPitzer model. Additional details of these squeeze treatments are listed in Table 6 and in supplementary information

to one to a few years. For example, the operator pushing the concentration and volume of a conventional NTMP squeeze they have found lifetime over five years (See data in Well A 409, Fig. 5).

From this study, we have demonstrated that the inhibitor return concentrations can be manipulated by varying inhibitor pill chemistry. Typically, the MIC of a particular well condition dictates the success of a squeeze treatment. Methods that can be used to form more soluble phosphonate salts would be useful to manipulate the squeeze process. In this work, it has been demonstrated that a more acidic pill results in a more soluble phosphonate phase. These field inhibitor data support our mechanical model of inhibitor retention following a squeeze treatment. It is essential to identify the controlling mechanism of returning concentrations. Depending on the MIC of particular well conditions, the crystalline phase solubility limit may or may not be sufficient to protect the well. In many common well conditions with low scaling tendency, such as this case study, the MIC is lower than

the crystalline phase solubility limit. In such situations, a squeeze treatment may last for several years of production. However, some wells may encounter more severe scaling potential; then, a squeeze treatment needs to be formulated that extends the phase II return.

3 Advances in squeeze treatments for sensitive formation, horizontal wells, and subsea satellite wells

Many of the adverse effects of squeeze treatment can be prevented by sound management, such as that described in Tomson and Oddo (1996). However, there are real challenges that require innovative treatment methods. Aqueous squeeze treatment may cause formation damage of certain sensitive formations as a result of wettability change, water blocking, clay swelling, or mineral dissolution. Instead of the aqueous squeezes, emulsion, oil, foam, and solids were

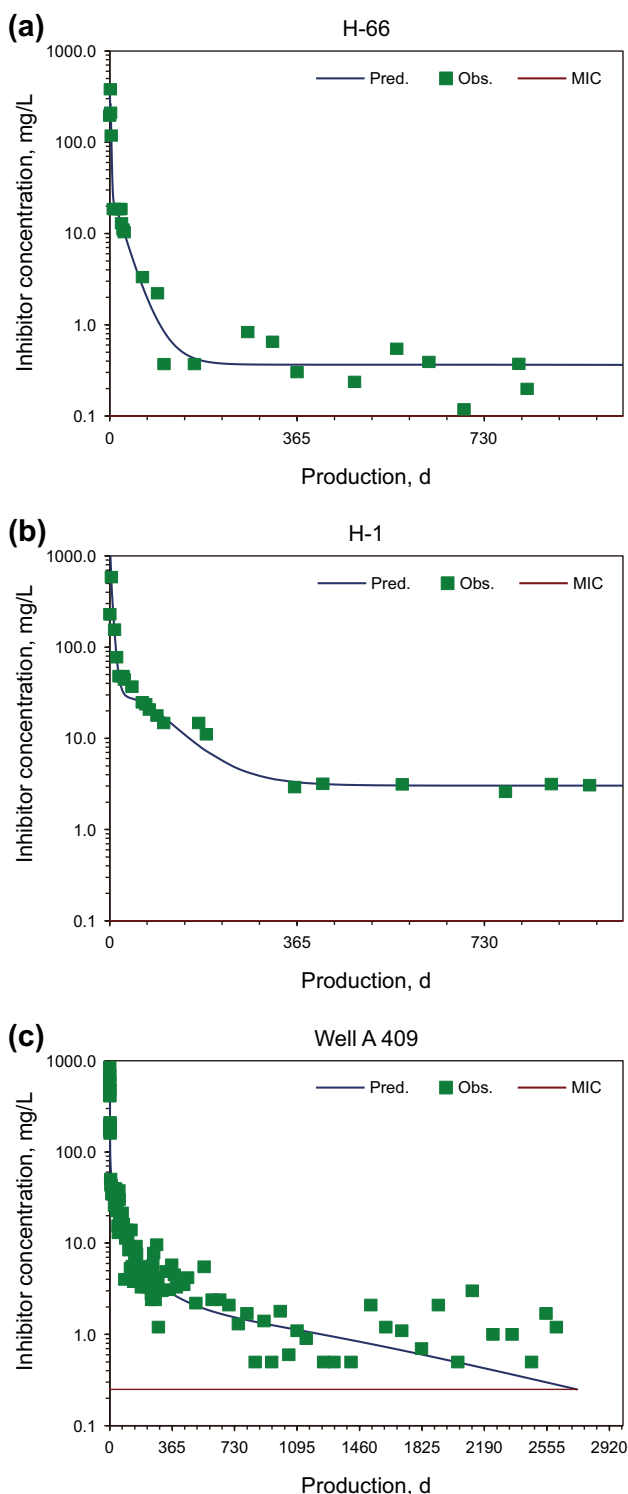


Fig. 5 Plots of three inhibitor return field data reported in literature and squeeze simulation by SqueezeSoftPitzer model. The condition of well H-1 and H-66 squeeze treatment can be found in Tomson et al. (Tomson et al. 2006). Additional details of Well A 409 can be found in Supplementary information

used as media to deliver inhibitors to these sensitive formations. For horizontal wells, the main problem is the placement of inhibitors to the locations where water is produced in their extended production zones and when different zones of water are mixed. Satellite subsea wells usually are subjected to high operational and installation costs. Reentry into a well for servicing can be extremely expensive. Hence, the extended squeeze life treatment will be highly desirable. With the increasing awareness of environmental protection around the world, new chemicals such as environmentally friendly (green and yellow) inhibitors and squeeze enhancers have been developed. Phosphonates and polyacrylates generally adsorb/precipitate better than other polycarboxylates, polyvinylsulfonates, sulfonated copolymers, and green inhibitors.

Typically, the chemical cost of a squeeze is small compared to the costs of downtime and lost production revenue. The conventional squeeze treatment with a water-based scale inhibitor is acceptable for wells at significant water cut. For low water cut wells and to avoid damage to sensitive formations, horizontal wells, and fractured systems, unconventional treatment methods may be needed. Innovative treatment procedures have been developed to overcome these issues and are reviewed below. Lots of research efforts have been focused on improving squeeze efficiency through (1) enhancing scale inhibitor retention (adsorption or precipitation), (2) optimizing the delivery of scale inhibitors to the target zone, and (3) improving monitoring methods.

3.1 Squeeze enhancement chemicals and techniques

The short squeeze life is often associated with a high initial inhibitor return. It has been observed that the squeeze life is inversely related to the mass of inhibitor produced back immediately after the well is put on production. For an ideal squeeze, the injected scale inhibitors shall be retained entirely by the formation rock, and the inhibitor is released back into the pore water at a sufficiently low concentration needed to control scale (MIC). It has been recognized that a well-controlled precipitation squeeze produces longer squeeze life than the adsorption squeezes (Kan et al. 2004b, 2005a). However, only phosphonates precipitate well with a metal cation, such as Ca^{2+} . Polyacrylates and many of the new yellow and green chemicals don't form precipitates unless the pH, cation, and inhibitor concentrations are very high. One attempt to circumvent this problem has been to inject cations, such as Ca^{2+} , in the preflush and overflush solutions. This technique relies upon mixing the two solutions within the interstices of the reservoir. Success has been limited due to the inefficiency of mixing.

Numerous innovations have been done to improve the precipitation squeeze in US patents, which involve the use of

one or a combination of chelating (Carlberg et al. 1989; Faircloth and Lawson 1993), acid-producing (Adam et al. 1994), and base producing (Faircloth and Lawson 1993) chemicals. Carlsberg and colleagues invented a mixed chelate process to improve squeeze by combining chelated calcium and scale inhibitor in the inhibitor pill (Carlberg et al. 1989; Carlberg 1987; Hearn et al. 1988). After a controlled delay, the calcium salt of the scale inhibitor is expected to precipitate. Similar ideas are being developed (Todd et al. 2012), but no published field squeeze results are available in the literature. Several authors described the use of polymeric inhibitors, such as a low molecular weight modified polyacrylic acid (mPAA), in combination with a temperature-sensitive activation and pH neutralizing agents to slowly cross-link the mPAA at reservoir temperature during the well shut-in period (Bonnett et al. 1991; Hen et al. 1995; Hugh et al. 1999).

Quaternary amine type of chemicals is often used in squeeze preflush for clay stabilization. It was observed that such cations might improve scale inhibitor retention during a squeeze. Therefore, quaternary amine types of chemicals are proposed to be used in both preflush and overflush as a bridging agent for inhibitor retention (Selle et al. 2003; Heath et al. 2012; Sitz et al. 2012). Amine groups are also incorporated into the anionic polymer to improve the anionic inhibitor retention in the formation rock in squeeze treatments (Jordan et al. 2011b; Chen et al. 2011). Jordan and his colleagues reported a phosphorus-containing polymer amine chemical (PCPA) which have both the properties of ease of detection from the P tag and desired chemical retention release characteristics from the amine tag and the retention is comparable to that of phosphonate (Jordan et al. 2011b; Sutherland et al. 2018).

The primary functional groups in scale inhibitors are phosphate, phosphonate, carboxylate, and amine. The first transition element cations, from Mn^{2+} to Zn^{2+} have $3d^5$ to $3d^{10}$ subshell electrons. The attraction of these inner electrons to the nucleus leads to an overall decrease in cation radii and an increase in electronegativity as compared to Ca^{2+} . The metal/ligand complex stabilities increase in the order of $Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} \approx Zn^{2+}$, and this order is often referred to as the Irving-Williams order (Irving and Williams 1948, 1953). The complex between phosphate and the metal ion is electrostatic, and the stability constants of phosphate with alkaline earth ions and the first transition series ions are very similar. The complex stability constants between carboxylic acid and metal ions are approximately 1.5–1.9 log units lower than that of phosphate except for the complex with ferrous ion. The stability constant of ferrous acetate is more than two orders of magnitude larger than the corresponding Ca^{2+} complex. Because glycine has both carboxylate and amine functional groups, the ferrous glycine stability constant is also high.

The strong complex between carboxylate and ferrous iron may have some implication in scale inhibition of ferrous salt. For example, Yean et al. (Yean et al. 2005) observed strong inhibition of ferrous carbonate formation by citrate. On the other hand, the stability constants for the amines (glycine and ethylenediamine) with transition metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+}) are much higher than that of phosphate and acetate. It was proposed that by including Zn^{2+} , and possibly Cu^{2+} , or Fe^{2+} , an inhibitor pill could significantly extend the squeeze life because the solubility of transition metal salts of phosphonates and polymers are expected to be much lower than the corresponding alkaline metal salts. From laboratory core flood studies, the authors observed significant improvement in the retention of BHPMP and PPCA. However, this concept has not been tested in field squeeze (Kan et al. 2009).

3.2 Selection of inhibitors for special applications

A group of “green scale inhibitors”, such as polymaleic acid, polyaspartic acid, and carboxymethyl inulin, have emerged for use in environmental sensitive regions (Inches et al. 2006; Bazin et al. 2004). Phosphonates were better than polymeric carboxylate type of inhibitors or green inhibitors to be suited for squeeze application. Phosphate esters and phosphonates are typically less thermally stable than some polymeric inhibitors (Wang et al. 2013). In addition, phosphonates are not allowed in certain regions due to environmental regulations. Jordan et al. (2011b) reported a phosphorus and amine-containing polymeric chemical that performs similar to a phosphonate in squeeze and also is environmentally acceptable in the North sea region. Similarly, another green inhibitor, an amino acid phosphonate, has been developed for this purpose. It is a short-chain monophosphonate type molecule. It shows similar desirable squeeze and return properties as the bis-hexamethylenetriamine pentaphosphonate and is applicable to HTHP and high salinity, high Ca^{2+} environment (Di Toto et al. 2018). Lastly, it was observed that phosphate ester chemicals are more effective at lower temperatures and provided the longer squeeze life for applications in the arctic circle or with CO_2 EOR (Jordan et al. 2016b; Valiakhmetova et al. 2017; Jordan and Mackay 2015).

3.3 Non-aqueous scale treatment

Formation damage is assumed to be caused by wettability change, water blocking, clay swelling, and mineral dissolution associated with aqueous squeeze treatment. Several technologies have been developed to increase scale inhibitor retention on a rock formation at reduced water volume to reduce hydrostatic head pressure and to improve the wettability of the rock for inhibitor attachment. Ghosh et al. tested

an anionic surfactant and an alkaline base in the preflush solution to effectively clean the oil-wet formation rock and improve aqueous inhibitor retention during squeeze (Ghosh and Li 2013; Ghosh et al. 2016).

Many researchers developed non-aqueous inhibitor treatments, i.e., oil-soluble, amphiphilic solvent solution, invert emulsion and microemulsion systems, to avoid squeeze-induced damages. For example, Frigo et al. (2005) discussed a HTHP system where a gas condensate is anticipated at squeeze condition (Frigo et al. 2005). They used a hybrid aqueous/non-aqueous system where the preflush and overflush in organic solvents were used in combination with the aqueous inhibitor pill for the squeeze treatment. The squeeze treatment of a similar hybrid system was tested in a deep-water well located offshore Gulf of Mexico (Bogaert et al. 2006). The overall squeeze treatment was successful, while injection difficulty was observed with the diesel stage injection of some wells.

Several papers (Yuan 2010; Miles et al. 2004; Kelland 2009; Chen et al. 2004; Heath et al. 2004) provided the pros and cons of these non-aqueous inhibitor treatments. Since the mineral scale is a water phase problem, these non-aqueous scale treatments contain the water-based scale inhibitor formulated so that it is compatible with the oil phase, often as a reverse micelle or water in oil product. The basic chemistry of scale inhibition and inhibitor adsorption is similar to the aqueous treatment. The only exception is that the volume of water used in the procedure is significantly reduced. For example, one oil-soluble inhibitor, designed to be infinitely soluble in hydrocarbons, contains about 8% water. The non-aqueous scale treatment is generally more expensive and might induce formation damage because the chemicals, such as mutual solvents, surfactants, and additives, can induce other damages and costs. In a review of various types of non-aqueous delivery systems, a majority of over 30 treatments produced acceptable treatment life with no measurable change in the productivities (Jordan et al. 2011b). Many of these non-aqueous systems use the same type of scale inhibitors, and the retention mechanism appears to be similar to that of the aqueous system. Lastly, a mutual solvent, e.g., short-chain alcohol or ether, is often used in the preflush to avoid water blockage and improve inhibitor retention. However, such practice can generate mineral scale deposition while the mutual solvent is formulated with seawater or is mixed with the formation water (Arab et al. 2016).

3.4 Foam and gel scale treatment

Foam has been used in the oil industry for many purposes, such as acidizing foam (Kam et al. 2003; Thompson and Gdanski 1993). Foam is a means for mobility control used in enhanced oil recovery (Hirasaki et al. 2011). This concept was not adopted widely because of the lack of understanding

of the mechanism of mobility control with foam and the compatibility of chemicals used in foam technology. There have been many advances in the understanding of foam mobility control. Foam in porous media is a dispersed gaseous phase within a continuous aqueous phase comprised mainly of thin films known as lamellae. The lamellae are stabilized by adsorption of surfactant at the gas/liquid interfaces. Because foam has an effective viscosity much higher than that of gas, it has been investigated as a method for improving sweep efficiency in processes where steam or supercritical CO₂ are injected to enhance oil recovery (Yan et al. 2006). The most crucial advance in understanding that has made foam mobility control practical is the understanding of the condition necessary to generate stable foam. A critical pressure gradient must be exceeded to create stable foam during the flow of surfactant solution and gas through homogeneous porous media. Below this pressure gradient, gas may flow as a continuous phase with only modest mobility reduction. Above this pressure gradient, stationary bubbles are mobilized such that bubble trains have multiple branch points. At each branch point, a flowing bubble divides into two bubbles and thus regenerates bubbles that are lost to coalescence. A successful foam treatment depends on understanding the critical pressure gradient necessary for strong foam. The logistics of producing stable foam at field conditions of high temperature, pressure, salinity, and conducting a gas foaming operation at a remote well site can be a limiting factor in such treatment.

A foamed scale inhibitor and scale dissolver treatment have been tested for a subsea well (Selle et al. 2012). Most of the wells in the Norne field have a long horizontal reservoir section of 500–1000 m productive zones intersecting several formations with significant permeability and pressure contrast. The objective of this foam scale inhibitor treatment is to push the treatment fluid into the low permeability and potentially the most productive zone. The reservoir section is approximately 1300 m long, and around 600 m is perforated, and the formation is the sandstone with a high shale content. The reservoir temperature is about 90 °C, and the reservoir pressure is around 150 bars. Because of the low reservoir pressure, it is not capable of supporting a full water column during back production. The scale inhibitor treatment was carried out, using alternating foam stages and non-foam stages. The post-squeeze evaluation concluded that the foamed scale treatment was successful and was better than a follow-up “conventional” water-based squeeze treatment. The operational challenges were mostly in connection with the ability to pump nitrogen offshore on a vessel. Since the injection fluids contain mostly gas, the technology is seen as suitable for wells with low reservoir pressure and no gas lift system in place.

Besides the foam treatment for horizontal wells, the industry also developed a gelled scale inhibitor treatment

where a shear thinning gelling agent, xanthan gel, and breaker have been formulated into squeeze treatment (Selle et al. 2009). This viscosified shear thinning scale inhibitor system is believed to be able to divert the inhibitor from the higher permeability zone to the lower permeability zone. It is envisioned to be useful for inhibitor placement in horizontal wells. Similarly, Chen et al. (2012a) developed a gelled inhibitor package for high water production horizontal well using an environmentally safe scale inhibitor that meets the north sea regulatory requirement.

3.5 Solid inhibitor treatment

Scale inhibitors in solid form have been used in many unconventional scale treatments. Earlier papers described the use of solid inhibitor in a capsule at the bottom of the well and gravel pack (Bourne et al. 2000). Recently, the scale inhibitor was applied either as a coating or adsorbed on ceramic proppant or as solid inhibitor mixed into the silica proppant. These proppants are then incorporated into the fracture fluids and injected during hydraulic fracturing. Several articles reviewed the pro and cons of solid inhibitor in hydraulic fracture fluids (Gupta et al. 2008, 2010). It is critical to place the solid inhibitors uniformly in the fractures, and the secret relies on proper control of the injection flow rate and pressure. Successful placement of solid inhibitor seems to be the key to produce a very long squeeze life, as shown in these review papers (Gupta et al. 2008, 2010; Szymczak et al. 2013; Shen et al. 2017). The solid inhibitor treatment could potentially be superior to the other types of procedures. However, at least one report showed a significant increase in the cost of solid inhibitors with no proven increase in benefit (Marquez et al. 2011). One drawback of adding the solid inhibitor into the frac fluid is that there is no way to resqueeze, when it is needed. The second issue is the inability to alter or to select the return concentration; the operator is required to take whatever the fluids and flow produces.

3.6 Squeeze treatment during well stimulation

Squeeze treatment can be combined with the acid stimulation process (Jordan et al. 2011a). The key advantages are to put inhibitors before the start of the production to protect the well from scale formation until the water cut has risen to a value where more conventional scale squeeze treatments can be applied. This procedure was used proactively at the early stage of the well development to address the early scale problem of seawater breakthrough at low water cut in offshore wells where treatments are expensive. Such simultaneous treatment has been applied to the Gulf of Mexico and West Africa wells with good squeeze life (Jordan 2012; Patterson et al. 2013, 2014). Lastly, a phosphonate scale inhibitor has been successfully incorporated into a seawater-based,

borate-cross-linked frac fluid for frac pack operations as a preempt measure (Marquez et al. 2011).

3.7 Nanoparticles as inhibitor carriers

Numerous papers have been published on the development of nanosized scale inhibitor for squeeze treatments (Shen et al. 2008; Zhang et al. 2011, 2016a, 2017b; Wang et al. 2013; Ghorbani et al. 2012; Ruan et al. 2016). When colloids, or nanoparticles, of SiO_2 , Fe_3O_4 , carbon, or $\gamma\text{-AlOOH}$ are made in the presence of scale inhibitors, templated, and made negatively charged using surfactants and low molecular weight polyacrylic acids, the materials can carry inhibitors deep into a formation virtually without sticking to the rock. When the flow stops for some time, the nanoparticles and associated inhibitor molecules adsorb to the rock and then slowly release the adsorbed inhibitor at the constant concentration for long periods. When the crystalline nanoparticles were put into a column and flowed with a simulated brine, the DTPMP desorbed at a continuous concentration for over 6000 pore volumes, which might be translated into the equivalent treatment of about 5000 bbl/kg of inhibitor, i.e., an average of ~ 1.0 mg/L of active inhibitor (Zhang et al. 2016a). Therefore, each about 200 kg could treat about a million barrels of produced water, all at a constant concentration. Figure 6 shows the synthesis of the $\gamma\text{-AlOOH}$ (Fig. 6a) and a sulfonated polycarboxylate copolymer (SPCA) nanoparticle synthesis (Fig. 6b) and squeeze simulation return results (Fig. 6c). The negatively charged sulfonated polycarboxylate copolymer (SPCA) favorably adsorbed to the positively charged $\gamma\text{-AlOOH}$ nanoparticle via an ion exchange reaction (Fig. 6b). The primary issues with the nanosized scale inhibitor techniques are the stability of nanoparticles in saline produced water or KCl (Fig. 6b), the effects of pH on inhibitor adsorption, and change of viscosity. According to Yan et al. (2013), boehmite ($\gamma\text{-AlOOH}$) nanoparticles (NPs) were synthesized via an environmentally friendly green chemistry route (Yan et al. 2013). The particle size of the boehmite nanoparticles is approximately 3 to 10 nm. At pH 4.0, the zeta potential of boehmite is approximately +42 mV. Sulphonated polycarboxylic acid (SPCA) and two other scale inhibitors (phosphonate and polyacrylate) were adsorbed to boehmite at pH 5. During SPCA adsorption, hydroxide ion was exchanged and the solution pH was raised to 5.5 pH. The zeta potential of the adsorbed particles was approximately -35 mV with a hydrodynamic diameter of 20–60 nm.

The viscosity of the SPCA nanoparticles increases with the increase of $\gamma\text{-AlOOH}$, SPCA or Ca^{2+} concentrations. For example, the boehmite (3%)-SPCA (1.5%) nanoparticles has a viscosity of ~ 300 cp with 100 rpm shear thinning in 1–3% KCl background electrolyte solutions. The injection can be improved due to shear thinning properties, and the viscous

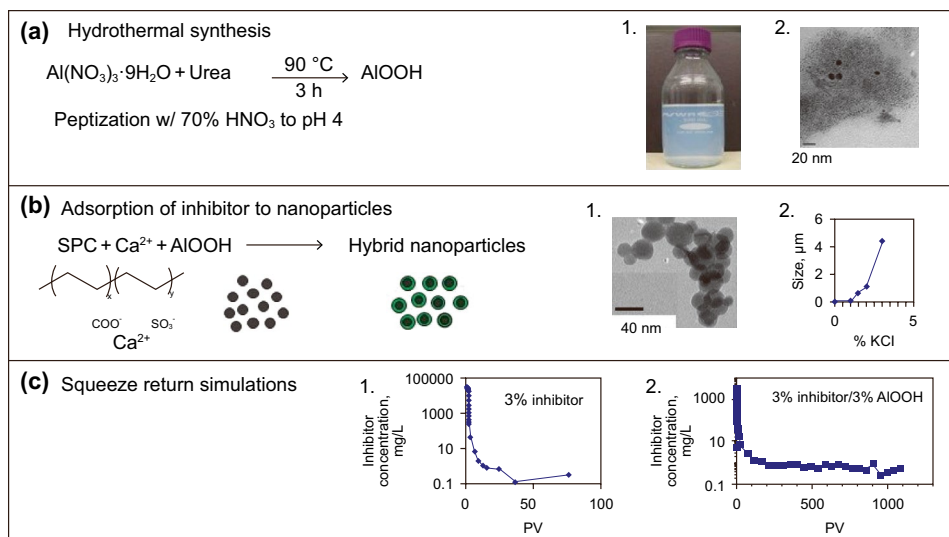


Fig. 6 **a** Synthesis of γ -AlO(OH) nanoparticles; **b** Surfonated polycarboxylate (SPCA) scale inhibitor/ γ -AlO(OH) nanoparticles; and **c** comparison of squeeze return profile of neat 3% SPCA and 3% SPCA in 3% γ -AlO(OH) nanoparticles

fluid may provide more control to inhibitor transport during injection. Inhibitor retention in formations during shut-in may also be improved due to the gelling up of inhibitor nanoparticles during shut-in. Laboratory core flood studies have shown successful injection and return of SPCA/ γ -AlOOH composite material with long squeeze life (Yan et al. 2013, 2014). More than 77% of the SPCA/ γ -AlOOH was retained in the column. In comparison, only 0.7% neat SPCA was retained under a similar condition without boehmite. No significant permeability loss has been observed in solid core test, but it should be carefully evaluated further before field application (Fig. 6c). None of these nanoparticle scale inhibitor squeeze treatments has been tested in the field.

3.8 Inhibition from the injection well

Many offshore wells are under constant seawater injection for pressure maintenance. These injection wells are commonly one or two kilometers from the production well and are in various multi-spot patterns. The flow time from the injection well to the producer varies from days to months for the first breakthrough. If chemicals could be made to flow this distance without being completely adsorbed onto the formation, it would prevent scale throughout the injection, reservoir, into the collection horizontals, up the tubing, and into the surface facilities. This ideal result would have an enormous impact on production for these wells. Similar application would apply to onshore wells, e.g., in West Texas, where the injection to production distances are often only one or a few hundred meters. Some newer chemical classes of scale inhibitors, e.g., polymers, various sulfonates and the carboxymethyl inulins, adsorb weakly to carbonates

and sulfates minerals. Some innovations in nanosized scale inhibitors might be useful toward these goals for use in carrying the scale inhibitor from injection well to production well. Making particles as carriers for such distances and conditions are not yet available, but by analogy with nanoreporters, there is a fundamental reason to expect that such materials could exist (Hwang et al. 2014). Many nanomaterials are made from environmentally friendly inexpensive materials, such as carbon, sand (silica), and iron oxides.

3.9 Importance of inhibitor return monitoring

A combination of observations come together to determine the end of squeeze lifetime: (1) a MIC measured in the laboratory; (2) measurement of residual inhibitor concentrations; (3) observations of changes in scaling ions, scale coupons, and production decline to determine when the scale is formed. Often, the ability to decide any of these factors is challenging (Kan and Tomson 2012). Most analytical procedures are unable to measure polymeric inhibitor concentrations accurately to below about 10 ppm (Boak and Sorbie 2010). It is challenging to develop a scaling rig that can truly represent the downhole condition so that the actual MIC can be measured. The lack of reliable monitoring of inhibitor return and knowledge of true MIC significantly impairs the ability to pinpoint the squeeze lifetime accurately. It can be argued that many squeeze jobs were terminated prematurely, due to a lack of ability to measure trace inhibitor concentrations combined with not knowing the true level of inhibitor concentration needed for protection. For example, the authors worked with DOE (US Department of Energy) to design wells in Louisiana and Texas and demonstrated

effective scale control at 0.1 to 0.2 mg/L of phosphonate inhibitor (Rogers et al. 1990; Street et al. 1989).

Many new inhibitors have been developed for better monitoring and tracking, such as the P containing inhibitors (e.g., phosphorus end cap inhibitor) (Selle et al. 2003) and fluorescence tagged inhibitors (Poynton et al. 2012; Vuori et al. 2016). In addition, there are multifunctional inhibitors such as one with either or both the phosphorus and the amine tags (Montgomerie et al. 2009; Jordan et al. 2011b), where the amine tag increases the scale inhibitor retention. An innovative time-resolved fluorescence (TRF) method has been developed (Johnstone et al. 2014, 2015; Heath et al. 2019) for scale inhibitor analysis. Unfortunately, it is difficult to determine the status of this proprietary technology in the produced water application. Recently, Liu et al. (2016) developed an assay method for inhibitor monitoring in the field. The method developed by Liu et al. is based on correlating the inhibition time of barite under a specific condition to the effective inhibitor concentration and therefore this method is applicable to all inhibitors and blends.

3.10 Proper sampling and accurate analysis

What is often referred to as “routine analytical data,” is of great importance to squeeze design and monitoring. Sampling of the produced water can be the weakest link in the analytical data acquisition, especially for gas or oil wells with low water cuts. Since the routine use of ICP (Induced coupled plasma) instruments in recent years, the measurement of most metals, such as Na, K, Mg, Ca, Sr, Ba, and Fe, has become sufficiently reliable. On the other hand, measurement of the critical anions is often problematic. The produced water pH is critical to predicting carbonate, sulfide, and oxide precipitates and to understanding corrosion and biological processes. pH in high TDS waters is difficult to measure at the corresponding temperature, pressure, etc. needed (Kan and Tomson 2012). The produced water pH is usually determined by a balance between the gas phase acid gases, H₂S and CO₂, and the water phase active anions, HCO₃⁻, CO₃²⁻, carboxylates (such as acetate), HS⁻, S²⁻ and OH⁻ and each of these anions is difficult to measure accurately (for a discussion of these analytical issues, see

corresponding references (Kan and Tomson 2012; Kan et al. 2019; Ness and Sorbie 2019). Also, for many wells the temperature, pressure, and flow rates are not known accurately enough to support squeeze/resqueeze decisions. The authors have developed a matrix tableau of how each measurement error impacts the resultant scale prediction (Kan and Tomson 2012).

4 Case study of observed squeeze life in field squeeze treatments

Many of the new advances in squeeze treatments discussed above have been field-tested. The following is an attempt to objectively compare the squeeze life of the various treatments, including both the conventional aqueous treatments and the unconventional treatments, except for the solid inhibitor treatment. The purpose of this discussion is also to propose a prototype yardstick for measuring squeeze performance and the difficulties encountered.

Table 1 categorizes 17 field squeeze treatments. Even though there are a large number of papers on squeeze performance, only case studies with sufficient documentation are included here. These treatments can be classified by inhibitors, reservoir and well types, treatment enhancers, and carriers. The numbers in parentheses indicate the number of case studies for each category. In Table 2 are listed the specific well information, reservoir temperature, problem encountered, and squeeze treatment used. In Table 3 are listed the corresponding squeeze treatment results, and the rows of data were grouped by the treatment types. All data were converted into SI units of m³, kg, and °C. If there is more than one set of squeeze performance data available in a paper, only the best performing squeeze return data are used in the comparison. In other words, only the best squeeze return result from each treatment is included in the tables. For comparison, several conventional aqueous treatment results are included where the well types are varied. The end of squeeze life is assumed the last data point provided in the paper, and sometimes this is in error.

Many factors affect squeeze life, as discussed before. If seawater breakthrough is the primary concern, the MIC could be very high during seawater breakthrough. In some

Table 1 Summary of literature field squeeze treatments

Inhibitor type	Reservoir type	Well types	Treatment type
Phosphonates (9)	Sandstone (8)	Vertical (4)	Aqueous (8)
Polyacrylates (1)	Carbonate (2)	Horizontal (6)	Oil emulsion (2)
Phosphorus end cap polymer (4)	Unspecified (7)	Subsea satellite (4)	Foam (1)
Amine-containing copolymer (2)		Unspecified (3)	Gel (1)
Polyaspartate (1)			Amine type squeeze enhancers (3)
			Simultaneous Squeeze/stimulation (1)

Table 2 List of 17 field conditions where the complete squeeze treatments were compared in Table 1

Well No.	Field	Location	Formation	Production start (yr)	Well type	Water rate, m ³ /d	BHT, °C	Ca concentration, mg/L	Problem	References
1	Ghawar	Saudi Arabia	Carbonate	NA	Vertical	1526	88	4000	Calcite	Kokal et al. (1996)
2	NA	North Sea	NA	NA	Vertical	3498	NA	NA	Seawater breakthrough	Yuan et al. (1993)
3	Forties	North Sea	Sandstone	1995	Horizontal	NA	90	3000	Seawater breakthrough	Collins et al. (2001)
4	Ekofisk/Tor	North Sea	Naturally fractured chalk	NA	NA	NA	130	3400	Seawater breakthrough	Jordan et al. (2004)
5	Varg	North Sea	NA	1998	Subsea well tie back	497	127	21,900	Seawater breakthrough	Jordan et al. (2011b)
6	Campos Basin	GOM	NA	2003	Horizontal	394	90	1616	Seawater breakthrough	Jordan (2011)
7	NA	North Sea	NA	NA	Vertical	1599	NA	NA	Seawater breakthrough	Yuan et al. (1993)
8	Varg	North Sea	NA	1998	Subsea well tie back	1602	127	21900	Seawater breakthrough	Jordan et al. (2011b)
9	Heidrun	North Sea	Sandstone with 25% clay	1995	Horizontal	NA	85	1000	Seawater breakthrough/clay mobilization	Wat et al. (2001)
10	NA	Offshore Angola	NA	2006	Dry tree & subsea	513	NA	1645	Seawater breakthrough	Jordan (2011)
11	Heidrun	North Sea	Sandstone with 25% clay	1995	Horizontal	NA	85	1000	Seawater breakthrough/clay mobilization	Selle et al. (2003)
12	Viking Graben	North Sea	Sandstone/clean	1979	Subsea well tie back	667	98	400	Seawater breakthrough	Mahajan (2006)
13	NA	North Sea	Sandstone with little clay	2003	NA	(790)	NA	400	Seawater breakthrough	Montgomerie et al. (2009)
14	Unyazah-A	Saudi Arabia	Sandstone	1994	Vertical	239	71	717	Calcite	Nasr-El-Din et al. (2003)
15	Forties	North Sea	Sandstone	1995	Horizontal	NA	90	3000	Seawater breakthrough	Collins et al. (2001)
16	Norne	North Sea	NA	2000	Horizontal	NA	85	NA	Seawater breakthrough, low reservoir pressure	Selle et al. (2012)
17	Norne	North Sea	Sandstone	NA	Horizontal	2083	98	NA	Seawater breakthrough	Selle et al. (2009)

Table 3 List of the inhibitor type and mass, treatment types, total water produced, MIC and normalized squeeze life (see Table 2 for the well conditions)

Well No.	Inhibitor	Special squeeze treatment	Inhibitor weight, kg	Accumulative water produced, m ³	Squeeze lifetime, d	MIC as product, mg/L	Normalized squeeze life, m ³ /kg product	MIC, mg/L as active	Normalized squeeze life, m ³ /kg active)	Reference
1	Phosphonate (NTMP)	Aqueous	12,206	351,0445	2300	1	288	0.2	1438	Kokal et al. (1996)
2	Phosphonate	Aqueous	11,950	612,150	175	5	51	1.0	256	Yuan et al. (1993)
3	Phosphonate (DTPMP)	Aqueous	6715	635,950	NA	2	95	0.4	474	Collins et al. (2001)
4	Phosphonate	Aqueous	3180	43,721	NA	NA	14		69	Jordan et al. (2004)
5	Phosphonate (DTPMP)	Aqueous	22,650	301,000	210	1–3	13	0.3	66	Jordan et al. (2011a)
6	Phosphonate	Aqueous	16,650	111,936	210	2	7	0.4	34	Jordan (2011)
7	Polyacrylate	Aqueous	2100	439,725	275	5	209	1.0	1047	Yuan et al. (1993)
8	Phosphorus and amine-containing polymer	Aqueous	26,775	410,000	230	1–3	15	0.3	77	Jordan et al. (2011b)
9	Polyaspartate	Aqueous	16,000	50,000	NA	1	3	0.2	16	Wat et al. (2001)
10	Phosphonate	Acid Perforation wash	8052	333,873	651	2.5	41	0.5	207	Jordan (2011)
11	P end cap polymer	Amine type squeeze enhancer	16,000	52,000	NA	24	3	4.8	16	Selle et al. (2003)
12	P end cap polymer	Amine type squeeze enhancer	11,000	160,000	240	NA	15	NA	73	Mahajan (2006)
13	Acrylate/quaternary amine copolymer	Quaternary polymer squeeze enhancer	15,000	112,500	145	5	8	1	38	Montgomerie et al. (2009)
14	Phosphonate (DTPMP)	Emulsion/oil	20,366	194,531	730	NA	10	NA	48	Nasr-El-Din et al. (2003)
15	Phosphonate (DTPMP)	Oil emulsion/seawater overflush	5757	206,683	NA	2	36	0.4	180	Collins et al. (2001)
16	P end capped polymer	N ₂ Foam	12,740	160,000	NA	2.5	13	0.5	63	Selle et al. (2012)
17	P end capped polymer	Xanthan gel	37,960	500,000	240	5	13	1	66	Selle et al. (2009)

Table 4 The average and range of normalized squeeze lifetime based on inhibitor categories

Type of inhibitors	Average NSL, m ³ /kg	Number of observations
Phosphonate	308 (34–1438)*	9
Polyacrylate	1047	1
P end cap polymer	54 (16–66)	4
Amine-containing polymers	57 (38–77)	2
Polyaspartate	16	1

*The solid phosphonate treatment data is excluded in the average

Table 5 Comparison of the normalized squeeze lifetime based on treatment categories

Treatment categories	Average NSL and ranges in parameters	No of observations
Aqueous	386 (16–1438)	9
Oil emulsion	114 (48–180)	1
Amine treatments	42 (16–73)	4
Foam	63	1
Gel	66	1
Squimulation	207	1

cases, the squeeze life is short because a high MIC is adopted for anticipating seawater breakthrough. As shown in Table 2, the data set is biased and incomplete. Furthermore, most inhibitors reported in the literature are assumed product concentrations. The product concentrations are likely to vary from 5% to 50%, which makes the quantitative comparison even harder. Unfortunately, this is what is available in the public literature. A universal active inhibitor concentration of 20% was used to calculate the normalized squeeze life, and MIC is expressed in terms of active inhibitor concentrations.

From these data, we calculated the normalized squeeze life (NSL, m³/kg), which is defined as the volume of water produced per unit mass of inhibitor. In Tables 4 and 5, the average and ranges of the NSL of different types of inhibitors and different kinds of squeeze treatments are compared. The phosphonate type inhibitors have much longer squeeze life than that of polymeric inhibitors. The conventional aqueous-based treatments still show the highest efficiency, NSL.

The squeeze life demonstrated in the aqueous treatment is reasonably consistent with the historical field squeeze data from the research group of the present authors (shown in Table 6), suggesting that this comparison is reasonable. The most extended squeeze life reported in this review is over

Table 6 List of field squeeze treatment results from the historical data of the authors. The produced water composition and details of the squeeze treatment are included in the supplementary information

Well/field Name	Location	Formation	Well type	Problem	Inhibitor	Treatment type	Inhibitor weight, kg	Accumulative water produced, m ³	Squeeze lifetime, d	MIC, mg active/L	Normalized squeeze life, m ³ /kg active inhibitor
Gladys McCall	Louisiana	Sandstone	Vertical	Calcite	Phosphonate (NTMP)	Aqueous	954	2,861,776	600	0.1	2999
Pleasant Bayou	Texas	Sandstone	Vertical	Calcite	Phosphonate (NTMP)	Aqueous	477	317,975	90	0.1	666
Smith	Texas	Sandstone	Vertical	Calcite	Phosphonate (NTMP)	Aqueous	449	216,064	559	0.5	481
O’Daniel	Texas	Sandstone	Vertical	Calcite	Phosphonate (NTMP)	Aqueous	936	232,228	365	0.8	248
Huff	Texas	Sandstone	Vertical	Calcite	Phosphonate (NTMP)	Aqueous	623	260,358	433	0.7	418
AEG	Texas	Sandstone	Vertical	Barite/calcite	Phosphonate (BHPMP)	Aqueous	150	6964	438	0.7	46
Core flood	Rice	Calcite	NA	NA	Phosphonate (BHPMP)	Zn ²⁺				NA	837
Core flood	Rice	Calcite	NA	NA	Polyacrylate (PPCA)	Zn ²⁺				NA	582
Core flood	Rice	Calcite	NA	NA	Sulfonated carboxylate copolymer	AlOOH nanoparticles				NA	1423

7 years. It was a less challenging system than many of the new production systems.

5 Summary and conclusions

An ideal inhibitor squeeze would have a zero chance of causing formation damage, and the inhibitor returned in the first day to the last day of production would be at the optimum concentration to inhibit scale. Although this goal is still not achievable, considerable advances have been made in both the science of inhibitor retention and release and the technology to deliver the inhibitor under specific well conditions. A yardstick has been proposed that the success of inhibitor squeeze life shall be based on the volume of water produced per unit weight of inhibitor injected. The conventional field squeezes with phosphonate are more efficient than green inhibitors. Exceptionally long squeeze life is attainable with solid inhibitors and nano-inhibitors. The combination of squeeze treatment during stimulation or fracturing stage of a new well presents a possibility to control scale at the beginning of production and for the lifetime of the well. There is a need to develop much more efficient ways to improve the efficiencies of squeeze processes for green polymeric inhibitors. The analytical technique that allows accurate analysis of scale inhibitor concentrations to below the minimum effective dosage in produced water may be one of the keys to extending the squeeze life. Many squeeze lifetimes may be prematurely shortened due to the lack of the confirmation of returned inhibitor concentrations.

The following are the main factors to be considered for squeeze design:

- Type of scale and severity of scaling problem. The lower the scaling tendency, the longer the squeeze life
- Tailor inhibitor return rate above MIC by novel alteration of inhibitor precipitation and adsorption chemistry
- The proper wetting of the rock to maximize inhibitor rock interaction
- Select a chemical with optimum adsorption/desorption properties
- Optimized scale inhibitor pill concentration and pH
- Proper placement techniques to where the inhibitor is needed within water production zones
- Optimized overflush, as much as you can where it still gives a benefit to squeeze lifetime versus the pumping time (especially if from an offshore vessel) and providing that it does not affect the ability of the well to come back online
- Properties of the reservoir (rock mineralogy, temperature, pressure, brine composition) and interaction between reservoir brine, reservoir rocks, and scale inhibitor

- Cost of squeeze treatment, e.g., chemical, labor, non-production-time cost, vessel for offshore operation, etc.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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