A review: the utilization potency of biopolymer as an eco-friendly scale inhibitors

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Abstract
Scale formation is one of the major issues in the petroleum industry. The development of these scale layers could result in production losses and equipment instability because of pipeline blockage, energy leakage, corrosion acceleration and severe accidents which will impact the safety of the production process. The utilization of chemical scale inhibitors (SIs) is considered an economical and successful route for the scale prevention. Two main components of the chemical SIs are phosphonate and polymer. Many of the phosphorous compounds are toxic and very expensive. Besides, portions of the phosphonate compounds are thermally less stable than polymeric scale inhibitors in a harsh environment of high temperature and high pressure (HTHP). This is considered as an issue as a good scale inhibitor should be able to be applied under wide range of temperature and pressure. Therefore, the continuous development in petroleum production imposes the need to develop a novel phosphorus-free scale inhibitor. Meanwhile, polymers have been broadly applied as a scale inhibitor in oil and gas fields because of their enhanced thermal stability and improved environmental compatibility. Polymeric scale inhibitors also show better dispersing efficiency. Today, the biopolymers have pulled in a tremendous consideration from the industry to replace the utilization of synthetic polymer due to their interesting qualities such as their lightness, strong mechanical properties, and appealing functionality. Biopolymers are insensitive toward brine salinity yet are vulnerable to biological degradation. Specifically, these polymers present enormous potential for environmental application because of their biodegradability, chemical adaptability and reactivity, biocompatibility, and nontoxicity. Recently, several new eco-friendly scale inhibitors have been reported in the literature. Hence, this paper provides a review of the utilization of biopolymer as scale inhibitor in the application of oil and gas industry under laboratory approach or field trial application. The types of scales, chemical scale inhibitors (SIs) and biopolymers are likewise reviewed here. The presented work in this paper is expected to enhance the fundamental understanding of scale formation, as well as contribute to the development process of biopolymer scale inhibitors.

Keywords Scale inhibitor · Biopolymer · Eco-friendly · Synthetic polymer · Mineral scale

Introduction

Oil and natural gas are one of the significant components of worldwide energy resources (Da Rosa et al. 2016; Lu et al. 2019). Increased worldwide consumption of oil and gas and the depletion of conventional oil and gas reserves, create challenging conditions for the petroleum production industry. Such conditions include high temperature and high pressure (HTHP) during the drilling and production operations (Fan et al. 2012; Lu et al. 2019). As the oil industry continues to operate in more complex and ultrahigh temperature environments, scale control becomes an ever-increasing challenge (Lu et al. 2019).
Mineral scale formation is a complex problem for oil and gas operations. Scale formation and deposition can occur during certain operations in the production of petroleum such as stimulation, production and transportation (Ituen et al. 2017). The scale formation can cause a total or partial obstruction of equipment and pipes, causing great damage such as corrosion, energy leak, economic loses and severe accidents which will influence the production safety (Amjad 1995; Luo et al. 2015; Macedo et al. 2019; Ramzi et al. 2016; Zeng and Yan 2013b).

Obviously, this scale may deposit in formation matrix, tubing, artificial lifts and surface facilities (Suhadi et al. 2015). These may lead to a severe production issues including: reduction in pipe carrying capacity, increase in operational hazards, localization of corrosion attack, impedance of heat transfer, and increases in operating costs due to down time and system maintenance (Merdhah and Mohd Yassin 2009; Wylde and McAra 2004). In the other hand, the oil industry is currently facing severe restrictions concerning the discharge of oilfield chemicals into the environment (Adewole and Muritala 2019; Baraka-Lokmane et al. 2009; Ituen et al. 2017). Particularly, the restriction includes the use of high levels of phosphonates in terms of release to the environment (Andrianov et al. 2016; Huang et al. 2019; Kumar et al. 2018, 2010; Liu et al. 2017, 2016; Pecnik et al. 2016; Zeng and Yan 2013b). The phosphorus-containing scale inhibitor has some fatal setbacks such as prolong biodegradation in the water (Wang et al. 2014). The inorganic or organic phosphonate in the scale inhibitors increases the phosphorus content in water, leading to heavy eutrophication (Lourteau et al. 2019; Pervov et al. 2018; Yuan et al. 2020; Yu et al. 2018). The application of phosphorus-containing scale inhibitors also has tendency to form calcium phosphates scales (Amjad 1995; Macedo et al. 2019).

Many of the phosphorous compounds are toxic and very expensive, so the development in the petroleum production dictates the need to develop new phosphorus-free scale inhibitor (Frenier and Ziauddin 2008; Gill 1996; Hasson et al. 2011; Kumar et al. 2010; Liu et al. 2016; Lourteau et al. 2019; Mohamed et al. 2017; Pecnik et al. 2016; Senthilmurugan et al. 2019; Yu et al. 2018; Zeng and Yan 2013b). In the high temperature-high pressure (HT-HP) environment, some of the phosphate compounds are thermally less stable than non-phosphonate polymeric scale inhibitors (Senthilmurugan et al. 2019). The usage of many synthetic polymeric scale inhibitors without phosphorus have been reported (Can and Üner 2015; Yuan et al. 2020; Yu et al. 2018). These commonly used synthetic polymer as scale inhibitors are water soluble, which will contact easily with the aqueous environment (Eubeler 2010; Huang et al. 2019). However, due to inorganic origin of the substance, the substance remains undecomposed for a long period of time (Kumar et al. 2018).

Most conventional polymers and scale inhibitors are manufactured without ecofriendly consideration rendering slow degradation of the chemical post-disposal (Hasson et al. 2011; Ituen et al. 2017). The substantial use of non-degradable synthetic polymers for considerable length of time can also makes irreversible harm to the environment (Eubeler 2010; Lamberti 2013; Mahat et al. 2016; Webb et al. 2013). Most of the compounds of the polymeric scale inhibitors are also costly (Pecnik et al. 2016; Yu et al. 2018). Therefore, as the increasing of the environmental concern and regulatory issue, moving in the direction of sustainable strategy, an environmentally friendly inhibitor become one of the major researches focuses nowadays (Adewole and Muritala 2019; Belarbi et al. 2014; Diez-Pascual 2019; Ituen et al. 2017; Kumar et al. 2018; Liu et al. 2017, 2016; Pecnik et al. 2016; Yuan et al. 2020).

The purpose of this work is to provide a review for selecting a potential polymer to be applied as a green scale inhibitor. The review focuses on the utilization of biodegradable-based polymers utilization as scale inhibitors for various types of scales in the oil field. The concept of scale and scale handling techniques and the use of synthetic polymer-based scale inhibitor are likewise reviewed here. Finally, the review also include discussion about current challenges and limitation on the use of biodegradable-based polymer as scale inhibitor.

The concept of mineral scale and its handling techniques

Scales are formed either by mixing of two incompatible brines or the sudden changes in produced fluid conditions, such as CO₂ partial pressure, temperature and pH (Gu et al. 2013). Primarily, there are three steps in the precipitation process, including super saturation, nucleation, and crystal growth (Amjad and Demadis 2015; Crabtree et al. 1999; Fevang 2017; Gill 1996; Hajirezaie et al. 2019; Hasson et al. 2011; Jimenez 2014; Khormali and Petrakov 2016; Kumar et al. 2018; Liu et al. 2011; Olajire 2015).

Supersaturation

Supersaturation is the function of temperature and pressure (Kumar et al. 2018). Supersaturation is the most important reason for mineral precipitation (Mohammed 2007). At the moment when the activity of cations and anions in the solution is concentrated beyond the solubility limits of one or more of the constituents by water evaporation, or perhaps by separation of pure water at ambient temperature, or by a change in temperature, then the solution becomes supersaturated (Hasson et al. 2011). Supersaturation is important for scale to form but the phenomena alone is not sufficient to
trigger precipitation since nucleation only start if the solution contains both cationic and anionic species and supersaturation condition occurs (Amjad and Demadis 2015; Kumar et al. 2018).

**Nucleation**

During the nucleation stage, a formation of unstable clusters of atoms includes cations and anions within the supersaturated solution collides to form ion pairs (micro-particle) (Crabtree et al. 1999; Fevang 2017; Hajirezaie et al. 2019; Khormali and Petrakov 2016; Kumar et al. 2018). Next, the formation of micro-aggregates which act as a small center of crystals, embryo, and micro-nuclei (Kumar et al. 2018). In the smaller pores, the probability of the ions collisions is small due to the smaller number of ions present (Hajirezaie et al. 2019). There are two pathways for nucleation: homogeneous and heterogeneous (Amjad and Demadis 2015; Gill 1996; Kumar et al. 2018; Olajire 2015).

Homogeneously formed scale particles do not necessarily deposit or grow onto a surface and hence, could flow through the system without causing too many depositional issues (Olajire 2015). During homogeneous nucleation, water, supersaturated with respect to a mineral, will give rise to the agglomeration of scale-forming ions due to random collision of the ions in motion (Gill 1996). The seed crystals subsequently grow by ion clusters (nuclei) adsorbing onto imperfections on the crystal surfaces—extending the crystal size (Crabtree et al. 1999; Gill 1996). The size of the nucleus grows larger with the addition of other scale-forming ions and once the nucleus grows larger than the critical size, precipitation will occur (Gill 1996). The energy for seed crystal growth is driven by a reduction in the surface free energy of the crystal, which decreases rapidly with increasing radius after a critical radius is exceeded (Crabtree et al. 1999).

In a heterogeneous nucleation process as shown in Fig. 1, crystal growth tends to initiate on a pre-existing fluid-boundary surface (Crabtree et al. 1999). The scale that forms by heterogeneous nucleation builds upon solid surfaces causing problems such as increased pressure and restriction of fluid flow in the formation, pipelines and surface facilities. The scale formation also potentially prevent production equipment such as downhole sub-sea safety valves or the heat exchangers/motors on pumps from operating as expected (Crabtree et al. 1999; Olajire 2015). The predicament may be caused by any isomorphous material which is used as a substrate for the growth of the scale-forming precipitate (Gill 1996). Heterogeneous nucleation sites include surface defects such as pipe surface roughness or perforations in production liners, or even joints and seams in tubing and pipelines, or a high degree of turbulence. Thus, the accumulation of scale can occur at the position of the bubble point pressure in the flowing system (Crabtree et al. 1999). This explains why scale deposits rapidly build on downhole completion equipment.

**Crystal growth**

At the crystal growth stage, the microparticles combine in micro crystals that serve as crystallization centers for the remainder of the solution (Khormali and Petrakov 2016; Kumar et al. 2018). Crystal aggregates start growing continuously by further adsorption of additional scaling ions in the solution and precipitate or attach to the solid surface.
Chemical scale inhibitors are an economical and simple effector to suppress the crystal growth (Ituen et al. 2017). Adding a solution to the near-wellbore area, is common on upstream of oil and gas industry (Suhadi et al. 2015). The widely used technique for controlling scale deposition is by dosages of chemical scale inhibitor (Iwu et al. 2017). Scale control inhibitors play a major role in flow assurance (Wilson and Harris 2010). Scale inhibitors are the substances that react with the potential scale-forming chemicals to stabilize them or suppress the crystal growth (Ituen et al. 2017). Adding a chemical scale inhibitor is an economical and simple effective route for the prevention of scaling (Luo et al. 2015).

Chemical scale inhibitors can be broadly categorized into two types—Thermodynamic and Kinetic Inhibitors. Thermodynamic inhibitors are complexing and chelating agents which bind to the scaling species and prevent crystal formation and deposition. They need to be added in stoichiometric proportions (based on the number of moles of scaling ions present). Hence, they are limited to waters containing low concentrations of the salts. Kinetic inhibitors do not prevent the formation of scaling crystals but work by delaying or retarding the rate of precipitation. They can be dosed at concentrations far below the stoichiometric level required for sequestration or chelation and hence they are known as threshold inhibitors. They affect the kinetics of the nucleation and crystal growth of scaling species, as well as permitting supersaturation without scale formation. Threshold inhibitors are dosed continuously at low concentrations, typically 2–20 ppm. Threshold scale inhibitors are thus applicable in most scaling situations (Senthilmurugan et al. 2019).

The mechanism for the threshold scale inhibition is that the inhibitors get adsorbed on the growth sites of the nuclei, blocking active growth sites, keeping them in the embryo stage and thus preventing their future growth and dispersing them. The inhibitor molecules wrap around the nucleus surface and effectively protect them from further growth. The adsorbed polymer molecules act as immobile impurities on the crystal surface and inhibit crystal growth by reducing the rate of step movement across the crystal surface (surface diffusion). Thus, the scale inhibitor functions in sub-stoichiometric amounts by interfering in the nucleation or the crystal growth process through adsorption at the active sites blocking or restricting further growth. As a result, the onset of crystallization can be delayed and crystallization rates are reduced. This leads to the dissolution of the precipitate and release of the inhibitor molecule back into the solution (Senthilmurugan et al. 2019). A multitude of chemical and thermodynamic factors are involved in inorganic scaling in oil and gas production (Gudmundsson 2018). Many factors that affect the deposition of scale include fluids incompatibility, supersaturation, changes of the temperature and pressure, ionic strength, evaporation, and pH (Baraka-Lokmane et al. 2009; Luo et al. 2015; Mohammed 2007).

**Types of mineral scale**

The most popular types of mineral scales in the petroleum industry are calcium carbonates (calcite), strontium carbonates and barium carbonates, barium sulfate, calcium sulfate, magnesium hydroxide, calcium phosphate, calcium oxalate and silicates (Azizi et al. 2019; Gu et al. 2013; Li et al. 2017; Menzri et al. 2017; Olajire 2015; Ramzi et al. 2016; Rhudy 1993; Yuan et al. 2020). Other less common scales have also been reported such as iron oxide, iron sulfides and iron carbonate and calcium naphthenate from acidic crudes (Mohammed 2007; Olajire 2015). Among them, calcium carbonate and calcium sulfate are considered the most frequent, prominent and terrible (Azizi et al. 2019; de Souza et al. 2019; Fevang 2017; Gu et al. 2013; Kırboğa and Öner 2012; Mady and Kelland 2017; Mohammed 2007; Ramzi et al. 2016; Viloría et al. 2010; Yuan et al. 2020). Carbonate, hydroxide, oxide, and sulfide scales may be removed by acidizing, whereas sulfate, phosphate and ferricyanide scales are not soluble in acid. The latter is very difficult, if not impossible, to remove by means other than mechanical (Chilingar et al. 2008). In the case of calcium scale, the better the inhibition means that there is a more negative charge of the inhibitor atoms that enhances the adsorption of calcium ion (Zakaria et al. 2020).

**Calcium carbonate scale (CaCO₃)**

Calcium carbonate has been identified as the main problem associated with industrial scaling or deposition. It is considered as one of the most insoluble crystalline solids that have been the subject of extensive research in the decades. A large number of studies have focused on the mechanism and the parameters that affect the formation of calcium carbonate polymorphs in aqueous supersaturated solutions (Natsi et al. 2019). Calcium carbonate scaling is a function of pH, temperature, calcium cation concentration, and bicarbonate anion concentration (Chilingar et al. 2008). The two major driving forces causing CaCO₃ deposition in the oil and gas...
industry are reduction in pressure and high temperature during production (Aljeban et al. 2020). Yet, as reported by Suhadi et al. (2015), it is once found in the Zamrud field, Indonesia that the key problem causing CaCO$_3$ scale is not coming from incompatibility of produced water and injection water for waterflood. The problem is caused by the incompatibility of formation water coming from different sands since the perforated zones are commingled production.

The precipitation of calcium carbonate (CaCO$_3$) is shown in Eq. 1. Calcium bicarbonate (Ca(HCO$_3$)$_2$) is very water-soluble, but calcium carbonate (CaCO$_3$) is not (Kelland 2009). Calcium ions react with bicarbonate ions, and form calcium carbonate deposit under a certain condition. As pressure decreases during production, CO$_2$ is released and CaCO$_3$ precipitates (Aljeban et al. 2020; Chilingar et al. 2008).

\[
\text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CO}_2 \uparrow + \text{H}_2\text{O} + \text{CaCO}_3 \downarrow \quad (1)
\]

Pressure drop leads to the loss of carbon dioxide (CO$_2$) as gas-phase forms from the aqueous solution. The continuous release of CO$_2$(g) from fluid due to pressure drop disturbs the equilibrium of the system and increases the chemical driving force of the forward reaction of Eq. (1). Consequently, the reaction moves toward the right side of Eq. 1 and facilitates the increased precipitation of CaCO$_3$. The solubility of CaCO$_3$ decreases with temperature increase; hence CaCO$_3$ crystallization frequently occurs at high temperature (Aljeban et al. 2020). Chemicals that dissolve and chelate calcium carbonate can break this reprecipitation cycle. In brines with high iron (II) ions, it is possible to obtain iron carbonate deposition in addition to calcium carbonate scale.

A laboratory study showed that common carbonate scale inhibitors, such as phosphine polymeric acid (PPCA) and bis-hexamethylene triamine-penta(methylene phosphonic) acid, were not effective at preventing ferrous carbonate precipitation, but citrate ions did perform well. However, other calcium carbonate scale inhibitors are effective on iron (II) carbonate. Corrosion inhibition will also help reduce iron(II) carbonate scaling (Kelland 2009). One of the most common methods to mitigate calcium carbonate scale in the oil and gas industry is to apply scale inhibitor treatment through continuous injection or squeeze treatment. The principal inhibitor types used in order to control deposition in the oil and gas industry are polyphosphates, phosphonates, poly carboxylic acid and polyelectrolytes (Aljeban et al. 2020).

Higher dosage of scale inhibitor is necessary for achieving high inhibition efficiency on calcium carbonate deposition at a higher temperature and neutral pH (Ohimor et al. 2019). Calcium carbonate scale formation may be prevented by any one of the following techniques (1) lowering the pH until the stability index becomes zero or slightly negative; (2) adding a scale inhibitor; (3) removing the calcium ion by any one of the following means: (a) Ion exchange, in the case of freshwater. (b) Precipitation. (c) Chemical treatment: chelation, sequestration, and peptization. (d) Dilution to lower the solubility limit (Chilingar et al. 2008).

Generally, the decrease in the scale inhibition efficiency as the temperature increased seemed to be because of two phenomena:

1. A higher temperature led to a reduction of the adsorption capacity of the crystal nucleus and improved the desorption process. In this situation, the growth rate of the crystals will be accelerated, and the crystals aggregated to form larger particles.

2. The second one was that the reverse solubility of CaCO$_3$ decreased with increasing temperature (Zahlan et al. 2019). When the pH value was lower than 7, with the increase in pH, the scale inhibition efficiency of hyperbranched structure (HBP) on CaCO$_3$ was basically stable. Instead, when the pH is higher than 10, the scale performance of HBP declines swiftly (Huang et al. 2019).

Based on the results of a study carried out by Aljeban et al. (2020), there is a low calcium carbonate risk from the reservoir to wellhead under tested conditions. Although the high reservoir temperature favors calcium carbonate formation in downhole, the low pH reduces the risk of calcium carbonate formation at downhole conditions. Harsher calcium carbonate deposition is evaluated at the conditions of phase separator/degasser units due to the higher pH of produced water after released CO$_2$ from the fluid. Calcium carbonate scale can also deposit in transport flowline, especially at high temperature during summer in the desert area, along with higher pH of the produced water. The addition of scale inhibitor prevents the calcium scale formation by suppressing the formation of nuclei in the supersaturated solution or by interfering with crystal growth and thus reducing their ability to adhere to the equipment surfaces. The presence of scale inhibitor and adsorption at specific sites of the growing crystals may result in changes in crystal morphology as can be seen in Fig. 2 (Chew and Mat 2015).

**Calcium sulfate (CaSO$_4$)**

Calcium sulfate scales are normally caused by the commingling of two different water (mixtures), e.g., one containing sulfate ion and the other containing calcium ion. Calcium sulfate scale also may occur when temperature is raised sufficiently to decrease the solubility of calcium sulfate to the point where precipitation occurs (Chilingar et al. 2008). Calcium Sulfate (CaSO$_4$) is precipitated due to super saturation of Ca$^{2+}$ and SO$_4^{2-}$-ions that can
be created due to changes in pH, pressure, temperature or due to mixing of the brines. Among the CaSO$_4$ species, CaSO$_4$.2H$_2$O or gypsum is stable in the solid phase at a lower temperature below 50 °C which has been observed frequently in wells treated with CO$_2$ flooded-EOR technique. As a result, mineral scaling, especially calcium sulfate(gypsum) deposition has been a serious flow assurance problem in oil and gas production leading to production shut down because of formation damage or equipment failure (Ibrahim et al. 2019).

When mixing incompatible waters cannot be avoided, one may follow one of the following procedures: (1) allowing precipitation, and then filtering out precipitates; (2) adding a scale inhibitor; (3) removing the barium, strontium, or calcium ion by ion exchange in the case of freshwater; (4) sequestering or chelating the barium, strontium, or calcium

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Fig. 2 SEM micrographs of calcium carbonate formed after 20 h incubation, in the presence of 5 mg/L active of a and b PMA, c and d AA/MA copolymer, e and f PAPEMP (Chew and Mat 2015)
Barium sulfate (BaSO₄)

Barium Sulfate is one of the most difficult types of scales to inhibit in oil and gas production systems because of its physical hardness and its chemical and thermal stability. It is commonly inhibited with either phosphonate or polymeric scale inhibitors (SIs) deployed at sub-stoichiometric concentrations (Shaw and Sorbie 2015). Barium sulfate scales are normally caused by the commingling of two different water (mixtures), e.g., one containing sulfate ion and the other containing barium ion (Chilingar et al. 2008).

Mixed scale

Scales can often be layered and of mixed composition, for example, containing both carbonate and sulfate scales, at the appropriate field conditions. They can be oily and may even contain other deposits such as asphaltenes making remedial chemical treatment more complicated. If the asphaltenes contain overly inorganic scale deposits, they can render aqueous scale dissolvers ineffective (Kelland 2009). In the case of mixed precipitation, three possibilities may occur:

1. The first salt can act as a foreign body and reduce the energetic barrier of the second precipitating salt, therefore, the germination time of the second compound is reduced
2. Precipitates may have morphologies that are different from those obtained with the pure body formation reactions
3. The presence of a co-precipitation salt can affect the thermodynamic of the solution and subsequently influence the germination kinetic of other salts (Zarga et al. 2014).

Mixed scale consisting of the mixed salts is formed once their saturation limit exceeds beyond a certain threshold limit (Koutsoukos and Kapetanaki 2016). Despite the fact that both the calcium carbonate and the calcium sulfate systems precipitating out of the respective supersaturated solutions have been extensively investigated as separate systems, the number of studies of mixed precipitates formation is limited due mainly to its complexity (Koutsoukos and Kapetanaki 2016; Zarga et al. 2014).

Categorization of scale inhibitors

The most common and effective solutions to reduce and prevent scales deposition in an oil field is by the use of scale inhibitors (Chen et al. 2019; Huang et al. 2019; Ituen et al. 2017; Liu 2011; Menzri et al. 2017; Ramzi et al. 2016). Scale inhibitors are basically the water-soluble chemicals that inhibit or delay the scale formation by sequestration/interfering with nucleation and/or crystal growth of inorganic scales (Azizi et al. 2019; Azman 2014; Fevang 2017). Selection of a chemical scale inhibitor depends on the precipitating ions and the degree of supersaturation, determined by the concentration and solubility at the given conditions (Senthilmurugan et al. 2019). Determination of inhibitor concentration is very important in reality because the low concentration of inhibitor does not work well and high concentration of inhibitor may result in waste and even cause water pollution (Kumar et al. 2018; Yuan et al. 2020). In addition, scale inhibitors must be chemically active yet compatible with reservoir conditions. Thus, reservoir temperature, pressure and brine composition critically affect the stability of the inhibitors (Kumar et al. 2018) (Table 1).

Synthetic scale inhibitor

There are two major chemical types of scale inhibitor, including phosphonate and polymer-based scale inhibitors. Although the phosphonate and sulfonate containing scale inhibitors are highly efficient as a scale inhibitor, they have some fatal flaws such as difficult biodegradation in the water and eutrophication of the phosphorus-containing scale inhibitor (Wang et al. 2014). Phosphonates are not large enough to cause distortion, mostly because they have less molecular weight than the crystal (Nagle 2015). Furthermore, the use of phosphonates-based scale inhibitors has been reduced due to environmental problems (eutrophication of sea areas, rivers and lakes) and the tendency of these compounds to form

Table 1 Summary of the characteristics of scale inhibitors (Aljeban et al. 2020)

| Inhibitor                  | Temperature            | Scale               | Existing conditions                                               |
|---------------------------|------------------------|---------------------|------------------------------------------------------------------|
| Phosphate                 | Stable up to 90 °C     | CaCO₃; CaSO₄; SrSO₄; BaSO₄ | Soluble in and compatible with high calcium brines                |
| Phosphonates              | Stable up to 170 °C    | Against the various types of scales | In acid form or with any portion of the acidity neutralized by ammonia, amines or alkaline hydroxides |
| Polycarboxylic acid or    | 200 °C or higher       | CaCO₃; CaSO₄; BaSO₄  | Crystal distorters or dispersive, often blended with other types of scale inhibitors at low dosage rates |
| Polyelectrolytes          |                        |                     |                                                                  |
calcium phosphates scales (Macedo et al. 2019; Popov et al. 2016; Zeng and Yan 2013b). Many of the phosphorous compounds are toxic and very expensive, so the development in the petroleum production dictates the need to develop new phosphorus-free scale inhibitor (Frenier and Ziauddin 2008; Senthilmurugan et al. 2019).

Besides, polymers have been extensively applied as a scale inhibitor in oil and gas fields, because of their enhanced thermal stability and better environmental compatibility (Macedo et al. 2019). In the high temperature-high pressure (HT-HP) environment some of the phosphonate compounds are thermally less stable than polymeric scale inhibitors (Senthilmurugan et al. 2019). However, the substantial use of non-degradable synthetic polymers for a considerable length of time can also make irreversible harm to the environment. Given this, the industry at that point direly needs solutions to address the issues induced by the synthetic polymer application. In recent years there has been a strong research focus on biopolymer, which is the polymeric substances produced by living organisms. In recent trends in the field of biopolymers, key understandings of the scale inhibition as scale inhibitors. Therefore, a number of studies have been carried out to improve biopolymer competitiveness in petroleum production and the outcomes acquired have been viewed as exceptionally promising (Mac- edo et al. 2019). Despite their enormous potential, challenges remain for these biopolymer applications. Technical difficulties may exist to effectively process this biopolymer into a material with wanted form and structure. Furthermore, it is additionally conceivable that not every single resultant material from biopolymers will be appropriate for application as scale inhibitors. Therefore, a number of studies have been carried out to improve biopolymer competitiveness in different manners, such as by carrying out molecular design, chemical modification, material hybridization, and process innovation. This issue gives an opportunity to discuss trends in the field of biopolymers, key understandings of the biopolymer’s material plan, and feature new, advanced, and functional materials developed from these sustainable polymers to be applied as a scale inhibitor (Table 2).

Phosphonate-based scale inhibitors

Conventionally, chemical scale inhibitors are classified as inorganic scale inhibitors (Hasson et al. 2011). Commonly used conventional scale inhibitors are derived from four chemical groups; polyphosphates (Sodium tripolyphosphate, Sodium hexametaphosphate etc.); complexions including phosphonates: ethylenediaminetetraacetic acid (EDTA), aminotris methylenephosphonic acid (ATMP), 1-hydroxiethan-1, 1-bis (phosphonic acid) (HEDP), phosphonobutane 1,2,4-tricarboxylic acid (PBTS) etc.; polymers (Polyacrylic acid, Polymethacrylic acid, Polymaleic acid, Polymethyl methacrylate, Polyethylene methacrylate etc.) and co-polymers of phosphonates, carboxylates, and sulfonates (Al Helal et al. 2019; Andrianov et al. 2016; Azizi et al. 2019; Hasson et al. 2011; Pervov et al. 2018; Ramzi et al. 2016; Viloria et al. 2010). Phosphonate-based organic compounds have been already widely used as the highly effective scale and corrosion inhibitor, but have the drawbacks of causing environmental pollution or bears serious environment risk of water eutrophication (Yuan et al. 2020; Zeng and Yan 2013a). Additionally, many of the classic phosphonate SIs, such as diethylenetriaminepentakis (methylene phosphonic acid) (DTPMP) and aminotris (methylene phosphonic acid) (ATMP), show poor biodegradability, which means such chemicals are not allowed for use in regions with strict environmental regulations, such as offshore Norway or Denmark (Mady et al. 2018). Therefore, an intense research effort is being undertaken to look for the replacement of phosphorus products by more environmentally friendly products (Zeng and Yan 2013a).

However, there was a study conducted to synthesize a phosphonate-based green scale inhibitor (SI) that can work in a high temperature environment. Phosphonate-based SI has showed a remarkable impact on sulphate and carboxylate-based scales. Phosphonate-based SI has a better adhesion to rock surface which improves the capability of the SI to further impede scale formation even down to reservoir depth. However, most non-polymeric SI has poor degradability which limits the application especially in countries with stringent regulation such as Norway. Green SI with good biodegradability somehow has low stability at high temperature which motivated the study. In the study, 7 different types of SI had been synthesized by mainly using mono- and bis-finitrile attached to aromatics as the component with the addition of two amino-bismethylene-phosphonate group.

The types of scales tested in this study is calcium carbonate and sulphate. On top of scale inhibition study, analysis on thermal stability, biodegradability in seawater and compatibility test with calcium ions were conducted as well. None of the synthesized scale can withstand high temperature which failed the thermal stability test. In contrast, for comparison sake, commercial SI tested showed a positive impact on scale inhibition and one of the commercial SIs passed the thermal stability test. During the synthesis of the SIs, NMR method was used to verify the reaction. Basically, all the 7 SIs were synthesized by phosphonating amine group. All the SIs synthesized were then tested in high-pressure dynamic tube blocking equipment (Fevang 2017).

A study was conducted on an ultra-high temperature for testing the performance of phosphate-based SI. This study revolved around thermal stability of phosphate-based SI at a temperature around 392 °F. The type of scale used in this study was Calcium Sulfate and Calcium Carbonate. The temperature of 392 °F was selected because the temperature resembles steam flooding application and the testing was
done using dynamic loop test. The newly synthesized phosphonate-based SI was also biodegradable. Brine compatibility test was conducted using a brine solution of 100, 1000 and 10,000 ppm of calcium ion concentration. The same brine concentrations were used for dynamic tube blocking test in the later part. The pH of the solution was adjusted using PIPES buffer. The scale deposition testing was done separately for carbonate and sulfate. Brine compatibility test indicated that there was no flocculation or cloudiness at all the salinities which showed a good compatibility between

| No | Status of study | Scale | Scale Inhibitor | Details | References |
|----|----------------|-------|-----------------|---------|------------|
| 1  | Experiment: static method | CaSO$_4$ | Amino Tris (methylene phosphonic acid) (ATMP) | 0.5 ppm, 100% inhibition at 71 °C | Popov et al. (2016) |
|    | Experiment: static method | CaSO$_4$ | HEDP | 0.5 ppm, 40% inhibition at 71 °C | |
|    | Experiment: static method | CaSO$_4$ | PBTC | 0.5 ppm, 40% inhibition at 71 °C | |
| 2  | Experiment: static method | CaCO$_3$ | Polymaleic Acid (PMA) | 40 °C, pH 8.5, $t=20$ h, 6 ppm, 98.6% inhibition | Chew and Mat (2015) |
|    | Experiment: static method | CaCO$_3$ | Polyaminopolyether Methylene Phosphonic Acid (PAPEMP) | 40 °C, pH 8.5, $t=20$ h, 6 ppm, 93.5% inhibition | |
|    | Experiment: static method | CaCO$_3$ | Acrylic Acid-Maleic Anhydride (AA/MA) | 40 °C, pH 8.5, $t=20$ h, 6 ppm, 97.2% inhibition | |
| 3  | Field Application (DSST in Zamrud Field, Indonesia) | CaCO$_3$ | bis-hexamethylene triamine penta(methylene phosphonic acid) (BHMT-P) | Concentration = 10% diluted with formation water. BHMT-P is suitable for Zamrud field in general and especially well name Example #01 with content of 24 mg/L Ca$^{2+}$, 5 mg/L Mg$^{2+}$, and 0.1 mg/L Fe$^{3+}$ in formation water and Bottom Hole Temperature (BHT) and Bottom Hole Pressure (BHP) are 247 °F and 856 psia, respectively. BHMT-P is not precipitate when it mixed with divalent and multi-valent cation in the formation water | Suhadi et al. (2015) |
| Field Application (DSST in Bekasap Field, Indonesia) | CaCO$_3$ | bis-hexamethylene triamine penta(methylene phosphonic acid) (BHMT-P) | DSST in Bekasap field was also evaluated based-on the successful of DSST in Zamrud field and showed a quite good result. Pumping scale inhibitor, even though 4 months after acidizing, could prolong the lifetime of production | |
|    | Experiment: Dynamic Scale Loop | CaCO$_3$ | bis-hexamethylene triamine penta(methylene phosphonic acid) (BHMT-P) | Ph = 8.5, $T=80$ °C, MIC = 2.5 ppm | |
| 4  | Experiment: static method | CaCO$_3$ | Diethylene Triamine-pentamethylene Phosphonic Acid (DTPMP) | Dose 20 ppm, $T=95$ °C, 93.3% inhibition | Elayatt et al. (2016) |
|    | Experiment: static method | CaCO$_3$ | Diethylene Triamine-pentamethylene Phosphonic Acid (DTPMP) | Dose 20 ppm, $T=80$ °C, 98.8% inhibition | |
|    | Experiment: static method | CaCO$_3$ | Diethylene Triamine-pentamethylene Phosphonic Acid (DTPMP) | Dose 20 ppm, $T=60$ °C, 99.2% inhibition | |
|    | Experiment: static method | CaCO$_3$ | Diethylene Triamine-pentamethylene Phosphonic Acid (DTPMP) | Dose 20 ppm, $T=50$ °C, 100% inhibition | |
| 5  | Experiment: static method | CaCO$_3$ | Polymaleic Acid (PMA) | 70% efficiency with 80 ppm at 80 °C, 61% efficiency with 80 ppm at 90 °C Thermally stable with no precipitation found after exposure to a temperature of 130 °C | Ohimor et al. (2019) |
the SI and brine solution. The novel SI synthesized performed better than another SIs such as BHMT Phosphonate, polymer-based SI such as PPCA and sulfonated polymer. The synthesized SI was found to be 25% biodegradable using OECD 306 test. However, there was no toxicity found in the chemistry (Lu et al. 2019).

A novel phosphonate scale inhibitor for geothermal application was being delineated in a study. Similarly, geothermal brine has calcium carbonate resembling reservoir brine which causes the scale deposition to occur. However, unlike the reservoir temperature range, geothermal wells temperature is way higher which causes thermal destabilization of the SI that led to the study. Commonly, geothermal temperature is higher than 250 °C while the working range for phosphate-based SI is 170 to 200 °C. In this study, the phosphate-based SI was aged for 24 h at a temperature of 250 °C and pressurized with nitrogen as a safety precaution to prevent boiling. The software ScaleSoftPitzer was used to predict the scaling tendency.

The scaling tendency was studied by plotting with saturation index. Dynamic Scale Loop Test was used to study the scaling tendency by the measured differential pressure from which the minimum inhibitor concentration (MIC) was obtained. The effect of thermal stability was tested when the aged sample and pristine SI MIC was compared. Result of no difference between the 2 MICs indicate the aged sample capability does not deteriorate due to high temperature. The coil for the flow was set at 250 °C, 250 psi, flow rate of 10 mL/min, im coil length and 1/16” internal diameter coil. Prior to the dynamic loop test, calcium tolerance test was conducted to ensure that the novel phosphonate has no incompatibility reaction with brine with no scaling ions. This was an important measure as the scale formed later must be identified from which the source was.

The product was tested at a dosage of 10 to 1000 ppm at a temperature of 120 °C for over 24 h. Precipitation during the tolerance test would be considered as fail. The findings indicated SI was not adversely affected during the thermal stability test. Dynamic loop test indicated no spike in differential pressure and the MIC recorded was 5 ppm which was lower than Vs-Co polymer that has MIC of 50–100 ppm and low molecular weight PPCA that had an MIC of 10 ppm. The MIC for aged and pristine sample were 5 ppm indicated quantitatively, the SI passed the thermal stability test. The SI passed calcium tolerance test at all temperature (McCabe and Heath 2019).

The next study was conducted on limitation of SI used in oilfields. The limitations were specified to performance against barite and calcite scale, thermal stability, brine compatibility and tolerance toward ions dissolved in brines. The effectiveness of an SI was tested using Dynamic Scale Loop (DSL). Prior to the testing, all the samples were aged for 24 h at a temperature range from 110 to 170 °C except for brine compatibility test in which, an unaged sample was used. The minimum effective dosage (MED) was tested for each chemical with and in absence of iron (iron tolerance). The dissolution of iron has negative profound effect on phosphonate SI than polymer. The blend of Hydroxyethylidene Diphosphonic acid (HEDP) and Diethyleneetriaminepenta (methylene Phosphonic) (DETPMP) SI was adversely affected by the presence of iron where the efficiency had been reduced by 10 folds. Increment in carbonate ions forced an increase in dosage of SI required (around 7–14 times) as well where the increment in dosage became more drastic with addition of iron (around 10 to 20 times).

For barite scale test, some SIs registered a needed dosage of twice while some was halved except for Ethanolamine (MEA) phosphonate which did not have any effect in impeding barium scale. For DSL test, End Capped Sulfonated Polymer needed 2–3 times of the dosage for carbonate scale inhibition as the temperature was increased. The rest of the SIs required no additional dosage despite increase in temperature for DSL carbonate scale test. The thermal stability test, all SIs passed the test successfully except for MEA Phosphonate and Biodegradable Phosphonate at a temperature of 170 and 150 °C, respectively. Aging required more SI dosage for Barium based scale around twice the amount except for Neutralized DETPMP which required four times the amount (Fraser er al. 2016).

**Polymer-based scale inhibitors**

In addition to phosphates and phosphonates inhibitor, polymeric inhibitors have been used extensively. These inhibitors are based on different function groups such as polymaleic acid (PMA), polyacrylic acid (PAA), polyphosphino carboxylic acid (PPCA) (Obied et al. 2015). Currently, the addition of water-soluble polymers are also widely used and proved as effective scale inhibitors in oil fields (Can and Üner 2015; Huang et al. 2019; Liu et al. 2017). However, many of the polymeric scale inhibitors still have phosphate functional groups in their molecule structure (Huang et al. 2019). Thus, a lot of copolymers and homopolymers containing carboxylic, hydroxyl and sulfonic groups have been developed to replace the phosphonate-based inhibitor (Can and Üner 2015; Yuan et al. 2020). The kinds of these inhibitors are polymethyl acrylic acid, hydrolytic poly maleic anhydride, sodium polyacrylate, acrylic acid and acrylic acid amide copolymer, maleic anhydride and ethylene copolymer and so on (Liu 2011). Besides, the polymeric scale inhibitors have advantages including high solubility, good fluidity, strong complexion of their functional groups to calcium, magnesium or barium ions (Huang et al. 2019).

However, there is a kind of polymer inhibitor that does not hydrolyze in the water, generate precipitate and be limited with some conditions like temperature when applied.
Biodegradable polymer based scale inhibitors

The use of inorganic compounds could have toxic effects toward environment (Lourteau et al. 2019). Oil industries are facing severe restrictions concerning the discharge of oilfield chemicals into the environment (Boak and Sorbie 2010; Olajire 2015; Wilson et al. 2010). Therefore, environmentally friendly scale inhibitor is needed (Lourteau et al. 2019). In the past few years, green inhibitors have been developed and applied because of the non-toxic nature and do not pollute the natural water, soil and general environment around platforms and the pipeline systems through bioaccumulation and non-degradation (Boak and Sorbie 2010; Gill 1996; Lourteau et al. 2019).

The diversified use of green scale inhibitors has been sporadic and evolutionary, and the trend seems to adopt a rather reactionary response to the present and potential environmental regulations and to support economic activities of oil and gas industry in future (Mahat et al. 2016). Currently, the demand for the production of environment-friendly material is increasing and the use of bio-renewable resources for the production of biopolymers have gained a great deal of attention from researchers because of their low cost and ready availability (Agustin et al. 2014; Khandanlou et al. 2014; Liu 2011; Liu and Huang 2013; Oun and Rhim 2015; Raval et al. 2016; Verbeek 2012). By doing so, oilfield production subsectors will be able to minimize waste through efficient utilization of raw materials, mitigate health, safety, and environmental issues by avoiding the use of toxic and hazardous solvents (Adewole and Muritala 2019).

Biopolymer is a polymer obtained from natural sources either chemically synthesized from biological material or entirely biosynthesized by living organisms. It has been studied widely in recent years (Smith et al. 2016; Jainan et al. 2018). The biopolymers are nontoxic and less expensive (Akpan et al. 2018). There are many sources of biopolymers either from plants, algal, fungal, bacteria, protein or animals. Particularly, they include cellulose, starch, pectins, konjac, alginate, carrageenan, gums, chitin/chitosan, xanthan and collagen. In recent years, some biopolymers and their derivatives, such as guar and xanthan gums, carboxymethyl inulin, copolymers of β-cyclodextrins, carboxymethyl starch and starch-g-poly (acrylic acid) have been evaluated as green scale inhibitors and the results obtained have been considered very promising (Macedo et al. 2019). Scale inhibitor should as much as possible be stable to temperature increase and heat and should be compatible with the seawater and formation water system (Ituen et al. 2017). One newly developed biodegradable inhibitor consisted of a starch-based biopolymer, citric acid, HEDP, acrylate copolymer and isothiazolone has been field-tested. The results showed effective calcium and magnesium scale inhibition (Hasson et al. 2011). A chemical is defined as being “green” if the chemical possesses three qualities: non-toxicity, non-bioaccumulation and easy biodegradation (Belarbi et al. 2014; Ituen et al. 2017; Kumar et al. 2018; Li et al. 2017; Olajire 2015).

A project was conducted in testing the potential of green SI where several candidates namely Barley, Sweet Potato, Ginger and Pennywort were among the listed due to their higher inulin, amino acid (tannins), and Riboflavin (B2) content. Upon further screening, Barley and Pennywort were selected for further experimentation due to the availability. There were three tests mainly conducted in the study i.e., compatibility test, calcium carbonate threshold test and optical microscopic examination. Each of the tests was designated for the following purposes; to test the compatibility between the extracts and synthetic brine for precipitation detection, the potential of the SI to reduce scale and determine the critical concentration required to impede scale formation and lastly, to study the effect at morphological lattice scale. For the compatibility test, Barley showed a good compatibility at all range of concentration while Pennywort suffered incompatibility issue at higher concentration. Both extracts showed a better performance than a commercial SI, PASP in compatibility test. However, the trend of scale inhibition was rendered invalid by the author due to improper selection of concentration range (Ahmad 2012).

Globally, over 140 billion metric tons of these natural polymers are generated in form of waste from agricultural, domestic and industrial processing activities every year (Adewole and Muritala 2019). Among them, agricultural residues are emerging as a source of raw materials which provide renewable and environmentally friendly alternative biomass resources (Liu and Huang 2013). The most promising approach involves the development of polysaccharide-based polycarboxylates which considered as the “greenest” scale inhibitor (Fakhreeva et al. 2019; Ituen et al. 2017; Oun and Rhim 2015; Pervov et al. 2018). Polysaccharide, such as starch, chitosan, inulin, and alginate, is a class of natural polymers and also contains abundant functional groups.

For instance, classic carboxylate SIs, such as those based on acrylates and methacrylate, as well as many maleic-based SIs are also poorly biodegradable as a result of the polyvinyl backbone (Mady et al. 2018). The widely used polymer also do not naturally degrade to a large degree when released into the environment (Webb et al. 2013). The polymer can accumulate and persist in the environment may become available for uptake by living organisms (Lambert 2013). As we know, the tendency of scale forming is affected by temperatures, and the polymeric inhibitor has different inhibition ability at different temperatures. Generally, the performance of inhibitor gets to be challenged at higher temperature (Luo et al. 2015).
in including hydroxyl, carboxyl and amino groups, resulting in good chelation and dispersion effects (Yu et al. 2018).

These class of scale inhibitors possess good physical and chemical properties, thermal stability and biodegradability, abundantly available and inexpensive which make them promising compounds for the creation of “green” oil field reagents (Fakhreeva et al. 2019; Oun and Rhim 2015). In particular, there is evidence that biopolymers, particularly polysaccharides and polypeptides, significantly inhibit crystallization of calcium carbonate due to the presence of carboxylic acid group in the structure of this compound (Karaseva et al. 2018; Pervov et al. 2018). Moreover, these natural polymers are inexpensive, widely available, and easily biodegradable compared to common green inhibitor such as PASP and PESA that will be discussed more in the following sub-section (Yu et al. 2018). Making use of this enormous amount of materials in upstream operations of the oil and gas industries will provide a better and more economical alternative for waste management and environmental pollution (Adewole and Muritala 2019). The results of a study done by Boels and Witkamp (2011) shows that the ability of the biopolymers to mitigate precipitation is controlled by their degree of carboxylation (Boels and Witkamp 2011).

Polyaspartic acid (PASP)

Poly aspartic acid (PASP) had been developed in the early 1990s and the properties of being anti-scaling was established and confirmed by various authors (Kumar et al. 2018). Figure 3 shows the molecular structure of PASP. Hasson et al. (2011) recently in a review claimed PASP-based inhibitor to be the most promising and alternative to conventional scale inhibitors (Hasson et al. 2011). The result of the thermal stability test of the PASP before and after exposure conducted by Ohimor et al (2019) to a temperature of 130 °C shows that PASP did not result in precipitate, hence, they are reported as being thermal stable (Ohimor et al. 2019). PASP-based inhibitor is non-nitrogenous, non-phosphorus and the biodegradable properties are excellent. Poly(aspartate)s polymers are made from aspartic acid by condensation (Kumar et al. 2018). The trend tagged PASP shows that, with increase in the inhibitor treatment dose, the inhibition efficiency against the calcium carbonate increased. However, when the treatment dose reached a critical value, the inhibition rate attained a maximum value, after which the inhibition rate exhibited a plateau or a slight decrease tendency. For the calcium carbonate inhibition performance evaluation, the inhibition rate increased sharply higher than 50% with increase in the treatment dose from 20 to 70 ppm. At the optimum dosage of 70 ppm, an inhibition efficiency of 95% on calcium carbonate was obtained. The test was conducted at 80 °C and 90 °C (Ohimor et al. 2019). Additionally, study conducted by Karaseva et al. on the performance evaluation of PASP against CaCO₃ scale indicates that inhibition was greater for higher polymer concentrations (Karaseva et al. 2018).

Another study was conducted on low toxicity and biodegradable SI for barium sulphate and calcium carbonate. This SI was ensured to be hydrothermally stable up to 200 °C and tested at different pH ranges. The ability of the SI was tested using dynamic scale loop tests. The results indicated that the SI managed to withstand the high temperature up to 180 °C but showed a minimal decline in performance at 200 °C for 3 days. However, the results were remarkable enough in HPHT topside squeeze treatment. The brine solution was synthesized using Brent formation water chemistry that contains scaling anions and cations at ratio of 50:50. The first part of the experiment was environmental test which was the first stage of the Harmonized Mandatory Control System (HMCS). There were 3 sub-tests under this test namely toxicity test, bioaccumulation and biodegradation. All the environmental tests were conducted by third party for the author. A chemical must at least pass 20% biodegradability and meeting 2 out 3 highlighted criteria. The criteria for marine toxicity are EC₅₀ and LC₅₀ > 10 mg/L. These terms refer to ability of the chemical to induce harmful effect and kill organisms as the concentration reached 50%. The amount for these criteria must not be less than 50 mg/L or else the chemical is deemed as toxic. The logarithmic of partition coefficient (LogOW) between octanol and water must be less than 3. Since the region where the SI (PCA) would be applied is Norwegian Sector of the North Seam OECD 306 Marine Test must be used. The biodegradability must exceed 60% for a chemical to be biodegradable. The toxicity test was conducted on Skeletonema costatum, Acartia tonsa, and Scophthalmus maximus juveniles which gave the following results, respectively EC₅₀ > 1000 mg/L, LC₅₀ > 100 mg/L, and LC₅₀ > 1000 mg/L, respectively. LogOW is less than and biodegradability test is 68.8%. Thus, the chemical passed all the environmental tests. The next test was Calcium Carbonate Threshold Test in which the range of SI used was from 2 to 7.5 g/mL. PASP was used as a reference for comparison. A 90% inhibition was required to be categorized as a good SI in which the SI has achieved at a concentration of 5 mg/L whereas PASP achieved an 70% inhibition plateau.

Fig. 3 Molecular structure of PASP (Popov et al. 2016)
at 5 mg/L. A 99% inhibition was achieved at a concentration of 7.5 mg/L. The next test was Calcium Carbonate Dynamic Scale Loop Test. An important observation was DSL had better inhibition mechanism since there was a constant supply of SI while in static jar test, there was no addition of SI. The growth site for crystal was assisted by the roughness of metal. PCA showed a total inhibition at a concentration of 2.5 mg/L and at 2 mg/L, PCA started giving off some inhibition already.

All these test performances from DSL was unmatched by PASP at any concentration. For Barium Sulphate Dynamic Scale Loop Test, the performance of both PASP and PCA were the same at 4 mg/L. The active growth site was inhibited for barium scale. The next test was hydrothermal stability for Barium Sulphate Dynamic test which actually test the ability of SI to withstand temperature and aquatic environment where in reality, the chemical shall not break down within 12 to 18 months range. At pH of 1 and temperature of 120 °C, the solution was kept for 3 days. The degradation of both PCA and PASP very much dependent on temperature. Conclusively, at a pH of less than 6, as the temperature was increased, the efficiency of both SIs was very much degraded. As the pH increased more than 6, even at a temperature of 120 °C, the performance of SI was maintained. However, for Barium Sulphate Dynamic Scale Loop Test, within unfavorable pH range, increase in temperature up to 140 °C contributed to the loss of performance. However, for pH of 8, even at a temperature of 200 °C, there was no decline in performance for PCA observed (Wilson and Harris 2010).

The next study was conducted on improved biodegradability of polymeric SI. There were seven experiments conducted in the study namely Environmental Tests, Calcium Tolerance Test, Chlorine Stability Test, Calcium Carbonate Jar Test, Calcium Carbonate Dynamic Test, Pilot Cooling Tower Evaporative Unit, and Pilot Cooling Test. Polymaleic acid (MAP) was the SI tested in all the studies.

1. In environmental test, MAP passed the toxicity test of > 2000 mg/L and > 100 mg/L for rat and fish which indicated non-toxicity. The amount of SI concentration required to inhibit algae growth was 380 mg/L which ten times more than required SI, thus rendering the SI to be non-toxic.
2. PASP was used for comparison sake in Calcium Tolerance Test which had the highest tolerance and MAP yielded less than 20 NTU turbidity units compared to PASP and recorded comparable performance with maleic acid terpolymer (MAT)—commercial SI.
3. For the Chlorine Test, MAT and MAP were very resistant toward the Chlorine while PASP failed. 95% of Chlorine remained after 24 h for both MAT and MAP. PASP has 76% remaining Chlorine.
4. For Calcium Carbonate Jar Test, MAP and MAT has similar performance but better than PASP.
5. For Calcium Carbonate Dynamic Test, at a concentration of 4 mg/L, the performance of MAP and MAT were the same, however, the performance of MAT was less at 2 mg/L.
6. The next test was Pilot Cooling Tower Evaporative Unit in which the test resembles the actual field condition. This test actually emulates a situation when water was being evaporated as the fluid stream passes by a high temperature medium. The evaporation of water results in more calcium concentration in the remaining water which arose inhibition efficiency of the SI. Thus, as time passes by, the calcite saturation index shall increase indicating increment in calcium concentration due to evaporation and the response in inhibitor efficiency decrement was recorded. At a 90% inhibition efficiency from 100, the calcite saturation would be recorded. In this particular study, Phosphonobutane-1,2,4-tricarboxylic acid (PBTC) was included which was the main benchmark for pilot cooling tower test. PASP failed from the beginning where the efficiency dropped right away to 80% eliminating the SI, whereas MAT fared better to calcite saturation index, 200. PBTC recorded only 195. The best was MAP where the calcite saturation index recorded was 285, a 45% higher than PBTC championing the test.

The final test which was Pilot Cooling Test, which determine the corrosion and fouling rate by the SI. The corrosion and fouling rate depend on the concentration of calcium water where higher concentration reduced both rates. The concentration of calcium water tested were 50, 150, 300 and 700 mg/L which were corresponding to calcite saturation index of 0.02, 19, 61 and 231. The average fouling rate for each concentration were 6.7 mg/cm²/day, 1.6 mg/cm²/day, 1.4 mg/cm²/year and 1.8 mg/cm²/year, respectively whereas the corrosion rate were 2.20, 0.45, 0.23 and 0.10 mm/y, respectively. The very good fouling rate and corrosion rate are 0.11 mg/cm²/day and < 0.05 mm/y which MAP passed successfully in higher calcium water concentration (Wilson et al. 2010).

**Polyepoxysuccinic acid (PESA)**

PESA has attracted intensive interest, because PESA contains no nitrogen, phosphorus and other nutrition elements in the molecular composition, and is degraded easily, which presents the obvious environmental friendliness. Additionally, PESA has the strong chelating and dispersing abilities of the presence of carboxylic groups along its main molecule chain (Huang et al. 2019). In their study, Popov et al. (2016) and Yue et al. (2014) showed PESA scale inhibitor performance was superior to PASP. Therefore, PESA may...
be used as an alternative to PASP in anti-scaling operation (S. Kumar et al. 2018; Popov et al. 2016; Yue et al. 2014) (Fig. 4).

**Carboxymethyl inulin (CMI)**

The carboxymethyl inulin (CMI) are derivatives from inulin, which is a natural poly fructoside with a glucose unit at the reducing end, extracted from chicory roots. Carboxylate groups are introduced into the polysaccharide by CMI with sodium mono chloroacetate as reagent in alkaline medium. Inulin has an excellent calcium tolerance, thus allowing its application in various oilfield conditions. It is an inherently biodegradable scale inhibitor (SI) with an excellent ecotoxicity profile for fresh and seawater species (Baraka-Lokmane et al. 2009). CMI is produced by carboxymethylation of inulin, the latter extracted from the roots of chicory plants. The performance of the CMI biopolymer was reported to be far inferior compared to that of the phosphonate diethylenetriamine Penta-(methylene phosphonic acid) as CaCO₃ scale inhibitor for oil-field well bores (Boels and Witkamp 2011). A carboxylate derivative of an oligosaccharide, carboxymethyl inulin, has been commercialized as a biodegradable oilfield scale inhibitor, particularly for use in environmentally sensitive areas.99–101 it is a fairly good carbonate scale inhibitor but poorer sulfate scale inhibitor (Kelland 2009) (Fig. 5).

**Carboxymethyl cellulose (CMC)**

CMC is a natural anionic polysaccharide usually used in food, such as ice cream, to stabilize emulsion and in oil and gas industries as a component of drilling mud and water shut-off agent, as well (Ko et al. 2020). The hydroxyl groups in all lipopolysaccharides and polysaccharides can be derivatized to carboxylic acid groups using base and chloroacetic acid. An example is carboxymethylcellulose (CMC). However, solutions of these polycarboxylates can be too viscous for injection purposes. Carboxymethyl inulin is an exception, possibly due to being a fairly low molecular weight molecule (Kelland 2009). Based on a study conducted on the performance of water-soluble polymer which is a form of carboxymethyl (CMC) dispersant and phosphonate inhibitors in preventing complex mineral scales from happening in a highly saturated brine solution, CMC showed a more dominant performance in reducing sulfate and carbonate-based scale. The presence of CMC in the brine solution ensure that all the particles remained in nano-sized range which practically prevented the formation of precipitates. The precipitation of sulfate was controlled better upon combination of CMC and phosphonate solution which the combination surpasses the individual performance of CMC and phosphonate. The performance of the different scale inhibitors was measured using induction time (IT) with respect to saturation index. Induction time refers to the time for a scale deposition to happen after a solution has reached supersaturated state and saturation index (SI) refers to the likeliness of scale formation (Bailon et al. 2015; Horizon Commercial Pool Supply, n.d.). The finding in this study indicated that the SI had a significant impact on IT. For barite (CaSO₄) precipitation, SI of 2.0 registered 18 min of IT while SI of 1.89 registered 138 min which the latter is an acceptable range due to the duration of more than 2 h. The ballpark duration of 2 h is used because the time covers the travel of fluid from bottomhole to surface (Fig. 6).

A study conducted using polymer-based SI in a high-salinity reservoir. Sea-water which contains high amount of sulfate has a great tendency in forming scales with calcium, barium and strontium. Conventionally, many SI acts as a chelating agent which prevents calcium-based scale from forming by preventing the formation of supercritical nuclei.
In the study, jar testing and SoftPitzer™ software were used to investigate calcium-based scale formation and the contents of calcium was set to 37,000 mg/L for formation water and sulfate at 4,000 mg/L for sea-water. The mixing percentage of sea water and formation water was varied and the test was conducted at 155 °F and at a pressure of 1000 psi (sea-water and formation water mixing), dynamic compatibility (atmospheric pressure) and 2780 psi for simulation. Many SI were used to prevent calcium sulfate scale and compatibility test were done using bottle testing. The adsorption test for the SI were studied using High Performance Liquid Chromatography (HPLC) and core-flooding method as well. Acrylic homopolymer-based SI was proven to successfully mitigate calcium sulfate scale formation. Dynamic compatibility test was conducted for a duration of 24 h and at an rpm 300. The set of static and dynamic compatibility tests were conducted for the mixture of sea water with formation water and upon the addition of SI. The range of SI concentration were set from 1 to 500 ppm for the minimum inhibition concentration (MIC) determination. The adsorption experiment was conducted at an ambient temperature and SI concentration of 5 to 2000 ppm. The analysis indicated that increase in sea-water percentage increased the formation of calcite and gypsum scale where the maximum was recorded at 70–80% sea water. The amount of calcite and gypsum scale formed was 180 and 3300 mg/L. Based on naked eye observation, the inception of scale formation occurs at a sea water percentage of 10% and after 30 min. The simulation using SoftPitzer™ developed by Rice University indicated similar range despite of difference in pressure. All the results mentioned prior to this were before SI addition. Polyacrylate polymer-based SI was found to be more effective than short chained sulfonated copolymers (SI). At a 50–50 mixing, the MIC for Polyacrylate polymer-based SI was 5 to 20 ppm which was way lower than short chained sulfonated copolymers that recorded 200 to 250 ppm. Polyacrylate polymer-based SI were proceeded for adsorption experiment due to a better performance. Unfortunately, based on HLPC adsorption experiment, it was found that the adsorption was 64–78% which fell in a high tendency category. On the contrary, the permeability of the core plug in core-flooding based adsorption experiment indicated that no formation damage has been recorded. The differential pressure is maintained at 20 psi (Obied et al. 2015) (Table 3).

### Current challenges and limitations on the use of biodegradable polymers as a scale inhibitors

Based on the review of this work, it can be seen that several biodegradable polymers that have been tested have shown good performance. However, the performance is limited by conditions such as temperature and concentration of the polymer itself. In order to achieve high inhibition efficiency, a high concentration of biodegradable polymer is required, unlike that of the synthetic polymer does. Having said that, a decrease in performance was also noticed along with an increase in temperature. Thus, further research is still needed to find scale inhibitors that are not only safe for the environment and non-toxic, but also must be able to work in an ultra-harsh environment (Mazumder 2020).

### Conclusions

Scale formation is the primary problem found in oil and gas production. The formation of scales is affected by many factors, such as pressure, temperature, ion concentrations and pH. Primarily, there are three steps in the precipitation process, including super saturation, nucleation, and crystal growth. Many efforts have been made to prevent the occurrence of scale, one of which is by using a scale inhibitor. This review mainly discusses the theory of scale formation, methods of scale prevention, the use of synthetic scale inhibitors, the use of scale inhibitors based on biodegradable based polymers, the challenges of using biodegradable based polymers as scale inhibitors today. The results of the review show that:

1. Currently, there are many biodegradable polymers that are used as scale inhibitors instead of the synthetic one, such as PASP, PESA, PMA, CMC and CMI.
2. The results show that the environmentally friendly material is able to prevent scale formation even in high effectiveness, however, so far as found, the research conducted is still at the laboratory scale stage.
3. Still, there is still much to be explored in order to find scale inhibitors that are not only non-toxic, biodegradable, cost-effective, but also able to work optimally in an ultra-harsh environment.
| No | Status of study               | Scale type | Polymer                                      | Details                                                                 | References                        |
|----|-------------------------------|------------|----------------------------------------------|------------------------------------------------------------------------|-----------------------------------|
| 1  | Experiment: static method     | CaSO₄      | Polyaspartic Acid (PASP)                     | pH 6.3, 71 °C, 0.5 ppm, 81% inhibition & 3 ppm, 100% inhibition        | Popov et al. (2016)               |
|    |                               |            | Maleic Acid – Acrylic Acid (MA-AA)           | pH 6.4, 71 °C, 0.5 ppm, 100% inhibition & 3 ppm, 100% inhibition       |                                   |
|    |                               |            | Polyepoxysuccinic Acid (PESA)                | pH 6.1, 71 °C, 0.5 ppm, 90% inhibition & 3 ppm, 100% inhibition        |                                   |
|    |                               |            | Sodium Salt of Polyacrylic Acid (PAAS)       | pH 6.3, 71 °C, 0.5 ppm, 43% inhibition & 3 ppm, 100% inhibition        |                                   |
| 2  | Experiment: static method     | CaCO₃      | Polyepoxysuccinic Acid (PESA)                | $T = 24 \text{ h}, T = 80 °C, 30 \text{ ppm}, 90\%$ inhibition         | Huang et al. (2019)               |
|    |                               |            | Sodium Carboxymethyl Cellulose (Na-CMC)      | $1 \text{ ppm, } t = 4 \text{ h, reduced the crystallization from 50\% to 7.4\% only}$ | Goncharuk et al. (2012)           |
| 3  | Experiment (nanofiltration scaling application) | CaCO₃ | Carboxymethyl Inulin (CMI)                  | using Portland carbonate rock, with $T=40 ^\circ \text{C}$, pH 7.82, 23,000 ppm yields SI adsorption 0.64 mg/g and 135,000 ppm, at pH 6, yields SI adsorption 0.89 mg/g (low). The results could be improved by reducing the pH of the injected CMI SI solution and by changing the chemistry, the salinity, and hardness of either main flush or post flush brine | Baraka-Lokmane et al. (2009)       |
| 4  | Experiment: dynamic corefloods |            |                                             |                                                                      |                                   |
| 5  | Experiment: dynamic scale loop | CaCO₃      | Carboxymethyl Chitosan                       | $70 ^\circ \text{C, 1000 psi, minimum inhibitor concentration (MIC)} = 170 \text{ ppm}$ | Macedo et al. (2019)              |
| 6  | Experiment: static method     | CaCO₃      | Polyaaspartic Acid (PASP)                    | $87\%$ inhibition with 80 ppm at 80 °C, 69% efficiency with 80 ppm at 90 °C Thermally suitable with no precipitation found after exposure to a temperature of 130 °C | Ohimor et al. (2019)               |
| 7  | Experiment: static method     | CaCO₃      | Curcumin-citric Acid-aspartic Acid Polymer (PCCA) | $r = 10 \text{ h, } T = 80 ^\circ \text{C, 4 ppm, 99.7\% inhibition}$ | Yuan et al. (2020)                |
|    |                               |            |                                             |                                                                      |                                   |
| 8  | Experiment: dispersion performance test | BaSO₄ | Carboxymethyl cellulose (CMC)                | The particle size dispersed in the presence of CMC remains in nanosized ranges (342 nm after 15-h reaction) | Ko et al. (2020)                  |
|    |                               |            |                                             |                                                                      |                                   |
| 9  | Experiment: dynamic scale loop | CaCO₃      | Monoethanolamine salts of carboxymethyl cellulose (Na-CMC) | $T = 80 ^\circ \text{C, 10 ppm, 30 ppm, 50 ppm, 62–74\% inhibition}$ | Fakhreeva et al. (2019)           |
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Table 3 (continued)

| No. | Status of study | Polymer Details | References |
|-----|----------------|-----------------|------------|
| 10  | Experiment: static method | Maleic acid – acrylic acid (MA-AA) | Senthilmurugan et al. (2019) |
| 11  | Simulation | Maleic Acid—Acrylic Acid (MA-AA) | Mahmoodi et al. (2021) |
|     | Experiment: dynamic scale loop | Maleic acid – acryllic acid (MA-AA) | Senthilmurugan et al. (2019) |
|     | Simulation | Green Scale Inhibitor (details not mentioned) | Mahmoodi et al. (2021) |
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