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The Potency of Biopolymer as a Green Scale Inhibitor

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Abstract. Scale formation is one of the major issue in petroleum industry. The development of these scale layers results in production losses and equipment instability because of pipeline blockage, energy leak, corrosion acceleration and severe accidents which will impact the safety of production. Scale precipitation exists due to the progressions of thermodynamics conditions or the fluids incompatibility. This paper provides a review about the utilization of biopolymer as scale inhibitor whether under a laboratory approach or field trial application. The types of scales, chemical scale inhibitors (SIs) and biopolymers are likewise reviewed here. The utilization of chemical SIs are considered as an economical and successful route for the scale prevention. Two main component of the chemical SIs are phosphonate and polymer. A large number of the phosphorous compounds are toxic and very expensive. Besides, a portion of the phosphonate compounds are thermally less stable than polymeric scale inhibitors in the harsh environment which has high temperature and high pressure (HT-HP). Therefore, the development in the petroleum production directs the need to develop novel phosphorus-free scale inhibitor. While polymers have been broadly applied as a scale inhibitor in oil and gas fields because of their enhanced thermal stability and better 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.

Keyword: scale inhibitor, biopolymer, eco-friendl

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1 Introduction

Mineral-scale formation is a complex problem for oil and gas operations. Scale formation and deposition can occur during certain operations in petroleum production such as stimulation, production and transportation [1]. 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 [2]–[6]. Scales are formed either by mixing of two incompatible brines or the sudden changes in produced fluid conditions, such as CO_2 partial pressure, temperature and pH [7]. Primarily, there are three steps in the precipitation process, including achievement of super-saturation, nucleation, and growth of the nuclei to form particles [8]. The scale deposition products in oilfield are mainly consisted of calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, iron, silicon sediment other insoluble solids.

Scales are managed using techniques that ensure that the remediation is quick/fast and does not damage the reservoir, tubing or wellbore [1]. Mitigation of scale in oil field involves either removing the deposits intermittently with chemicals/acids or by mechanical scrapping, continuous injection of scale inhibitors into production tubing or squeezing slow release scale inhibitor into the producing formation [9]. The widely used technique for controlling scale deposition is by dosage a chemical scale inhibitor [1], [10]. Scale inhibitors are the substances that react with the potential scale-forming chemicals to stabilize them or suppress the crystal growth [1]. Adding chemical scale inhibitor is an economical and simple effective route for the prevention of scaling [4].

The mechanism for the chemical 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 dissolution of the precipitate and release of the inhibitor molecule back into solution [9]. A multitude of chemical and thermodynamic factors are involved in inorganic scaling in oil and gas production [11]. There are many factors that affects the deposition of scale, such as: fluids incompatibility, super saturation, changes of the temperature and pressure, ionic strength, evaporation, and pH [4], [12], [13].

2 Types of Scale Inhibitor

The most common and effective solutions to reduce and preventing scales deposition in oil field is the use of scale inhibitors [1], [5], [14]–[17]. 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 [18]–[20]. 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 [9]. Determination of inhibitor concentration is very important in reality because low concentration of inhibitor does not work well and high concentration of inhibitor may result in waste and even cause water pollution [21], [22]. 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 [22].

There are two major chemical types of the scale inhibitor, including phosphonate and polymer based scale inhibitors. Although the phosphonate and sulfonate containing scale inhibitor 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 [23]. Phosphonates are not large enough to cause a distortion, mostly because they have less molecular weight than the crystal [24]. Furthermore, the use of phosphonates based scale inhibitors have been reduced due to environmental problems (eutrophication of sea areas, rivers and lakes) and tendency of these compounds to form calcium phosphates scales [2], [3], [6], [25]. 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 [9], [26].

Besides, polymers have been extensively applied as scale inhibitor in oil and gas fields, because of their enhanced thermal stability and better environmental compatibility [2]. In the high temperature – high pressure (HT-HP) environment some of the phosphonate compounds are thermally less stable than polymeric scale inhibitors [9]. But, the substantial use of non-degradable synthetic polymers for considerable length of time can also makes 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 years, some biopolymer have been assessed as an eco-friendly scale inhibitors in the petroleum production and the outcomes acquired have been viewed as exceptionally promising [2]. 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 materials 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 biopolymers material plan, and feature new, advanced, and functional materials developed from these sustainable polymers to be applied as scale inhibitor.

3 Phosphonate-Based Scale Inhibitors

Conventionally, chemical scale inhibitors are classified as inorganic scale inhibitors [10]. 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-hydroxiethane-1, 1-bis (phosphonic acid) (HEDP), phosphonobutane 1,2,4-tricarboxylic acid (PBTS) etc,; polymers (Polyacrylic acid, Polymethacrylic acid, Polymaleic acid, Polymethyl methacrylate, Polyethyl methacrylate, Polyisobutyl methacryalte etc.) and co-polymers of phosphonates, carboxylates, and sulfonates [5], [10], [18], [27]–[30]. Phosphonate-based organic compounds have been already widely used as the highly effective scale and corrosion inhibitor, but has the drawbacks of causing environmental pollution or bears serious environment risk of water eutrophication [21], [31]. In addition, many of the classic phosphonate SIs, such as diethylenetriaminepentakis (methylenephosphonic acid) (DTPMP) and aminotris (methylenephosphonic 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 [32]. Therefore, an intense research effort is being undertaken to look for the replacement of phosphorus products by more environmentally friendly products [31].

4 Biopolymer Based Scale Inhibitors

The use of inorganic compounds could have toxic effects towards environment [37]. Oil industries are facing severe restrictions concerning the discharge of oilfield chemicals into the environment [38], [39]. Therefore, environmental friendly scale inhibitor are needed [37]. 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 [8], [37], [39].

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 the future [40]. 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 [14], [41]–[47]. 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 [48].

Biopolymer are polymers obtained from natural sources either chemically synthesized from a biological material or entirely biosynthesized by living organisms. It has been studied widely in recent years [49][49], [50]. The biopolymers are nontoxic and less expensive [51]. There are many source of biopolymers either from plants, algal, fungal, bacteria, protein or animals. Particularly, they includes 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, carboxymethylinulin, copolymers of β-cyclodextrins, carboxymethylstarch and starch-g-poly (acrylic acid) have been evaluated as green scale inhibitors and the results obtained have been considered very promising [2]. Scale inhibitor should as much as possible be stable to temperature increase and heat, and should be compatible with the sea water and formation water system [1]. One newly developed biodegradable inhibitors consisted from starch-based biopolymer, citric acid, HEDP, acrylate copolymer and isothiazolone has been field-tested. The results showed effective calcium and magnesium scale inhibition [10]. A chemical is defined as being “green” if the chemical possesses three qualities: non-toxicity, non-bioaccumulation and easy biodegradation [1], [22], [38], [52], [53].

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 [48]. Among them, agricultural residues are emerging as a source of raw materials which provide renewable and environmentally friendly alternative biomass resources [43]. The most promising approach involves the development of polysaccharide-based polycarboxylates which considered as the “greenest” scale inhibitor [1], [29], [44], [54]. Polysaccharide, such as starch, chitosan, inulin, and alginate, is a class of natural polymers and also contains abundant functional groups including hydroxyl, carboxyl and amino groups, resulting in good chelation and dispersion effects [55].

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 [44], [54]. In particular, there is an 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 [29], [56]. 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 [55]. 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 [48].

Table 1. Biopolymer-based Scale Inhibitors cited in this work

Scale Inhibitors	References
Polyaspartic Acid (PASP)	[25]
Polyepoxysuccinic Acid (PESA)	[16]
Sodium Carboxymethyl Cellulose (Na-CMC)	[57]
Carboxymethyl Inulin (CMI)	[13]
Carboxymethyl Chitosan	[2]

5 Conclusion

Current environmental problems have indirectly forced the industry to switch to using chemicals made from eco-friendly. Some biopolymers have been proven to be effective as substitutes for polymer-based scale inhibitors. Further research is still needed because to be used as a scale inhibitor, the biopolymer must have a good temperature stability and scale inhibition efficiency.

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