



Inhibition of Oilfield Scales using Plant Materials: A Peep into Green Future

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Abstract Oilfield scales have been effectively managed using scale inhibitors derived from inorganic and organic polyphosphates, carboxylic acid and carbohydrate based polymers, and ethylene diamine tetracetic acid (EDTA) based compounds. Many of these compounds are toxic and very expensive. Providentially, some of the active functionalities present in these compounds could be obtained from isolates or phytochemicals in extracts of plant materials. This paper examines how scales generate in oil and gas production, and how it has been managed using scale inhibitors. Scale inhibitor materials, their chemistry and use have been highlighted. Some plant materials (having relevant functionalities) which could be used to develop cost effective, sustainable and green scale inhibitors are discussed. Other plant materials which could fit in but are not discussed are critical food substances; hence their application as scale inhibitors can compete with food. In its present form, the ideas so discussed await practical experience which could contribute to local content development. Information presented in this paper could act as a good secondary source of information and reference for current and future researchers in the area.

Keywords adsorption effect, morphology change, oilfield chemicals, plant materials, scale inhibitors.

1. Introduction

Scale formation and deposition can occur during certain operations in petroleum production such as stimulation, production and transportation. When solution becomes supersaturated perhaps due to temperature changes during injection operations, scaling generates [1]. Scales can also be formed when two solutions that are capable of precipitating are brought together. For instance, the contact of calcium ions from dissolved fines with hydrogen fluoride from stimulation fluid is likely to precipitate calcium fluoride scales.



Scale has been seen as any crystalline deposit (salt) resulting from the precipitation of mineral compounds present in water [2]. In the oilfield, one or more types of inorganic deposit alongside with other organic debris, sand, precipitates and corrosion products constitute scales. Common scales encountered in the field include calcium carbonate, iron carbonate, barium sulphate, iron sulphides, gypsum, strontium sulphate and magnesium salts, etc. Details on scales and its chemistry is available in literatures [3, 4].

To prevent or control scaling in petroleum production, scale inhibitors (SIs) are usually deployed. These are substances that react with the potential scale-forming chemicals to stabilize them or suppress the crystal growth [6]. Many SIs are soluble in water, and are said to be hydrophilic [7] and can simultaneously inhibit scaling and corrosion, since scaling hardly occur without simultaneous corrosion and vice versa [8-10]. To achieve specific



needs, oil-soluble and coated SIs have also been developed [11-13]. Scaling rarely occurs in a simultaneously non-corrosive environment, and vice versa, hence SIs are frequently applied in combination with corrosion inhibitors [9, 14-15].

A major reason for scale prevention is for flow assurance and continuous production from existing reserves that produce brine [6]. Many wells have been abandoned prematurely because scaling and corrosion are poorly managed [16]. In this study, oilfield scaling, scale inhibitors and their mechanisms of action are highlighted. The functionalities present in effective oilfield scale inhibitors are identified. Some plant materials that possess similar functionalities as the effective SIs are also earmarked as potential scale inhibitors for the near future. Research is currently being designed to experimentally assess the efficiency of the plant materials identified here and will be communicated in due course. This paper can serve as a secondary source of information for readers and researchers in the field while pointing a directing finger to the possible future of oilfield scale management.

2. Scaling in oilfield

2.1. Scale formation

Movement of oil/gas from formation to the surface is usually associated with brine, water and changes in temperature and pressure. These factors may cause dissolved salts to precipitate and form scales (self-scaling). In practice, brine is sometimes injected into the formation to enhance oil recovery and balance pressure in producing wells. The brine may precipitate in the formation or in the borehole resulting in scaling. Sea water is rich in brine, hence their reaction with formation water in some offshore fields can produce deposits. The deposited scale builds up on the surfaces of the producing well tubing leading to flow problems in reservoir, pumps, valves and other facilities.

Common oilfield scales include calcite (calcium carbonate, CaCO_3), barite (barium sulphate, BaSO_4), gypsum (CaSO_4), celestite (strontium sulphate, SrSO_4), halite (sodium chloride, NaCl), fluorite (calcium fluoride, CaF_2), pyrite (iron sulphide, FeS_2) and zinc sulphide (ZnS). Zinc sulphide and calcium fluorite scales are sometimes referred to as exotic scales and are associated with high temperature/high pressure (HT/HP) wells.

Calcites are self-scaling deposits caused by loss of CO_2 (resulting in removal of carbonic acid) from the water phase to the hydrocarbon phase due to fall in pressure. Barite is formed by mixing of incompatible waters, e.g. sea water (high sulphate content) and formation water (high barium content). Halites are also self-scaling deposit caused by fall in temperature and evaporation of the solution through the wellbore, and occur in both high temperature and low temperature wells. Waterfloods with ground waters of high calcium and sulphate compositions can easily precipitate and deposit anhydrite or gypsum. Iron sulphide is associated with wells with high hydrogen sulphide content and can also result in corrosion of tubulars.

2.1. Scale management techniques

Scales are managed using techniques that ensure that the remediation is quick/fast and does not damage the reservoir, tubing, or wellbore. The location of the scale could determine the technique to be employed. For instance, scales in the wellbore can be removed mechanically or by chemical dissolution. To select a scale-removal technique, the type and quantity of the scale needs to be known. It is also important to know the physical composition and its texture. The cost associated with the technique employed should be considered. Familiar techniques with minimal costs include milling, fluid jetting, chemical or acid dissolution and use of inhibitors. Milling involves the use of electronic detonation cap which may be placed at appropriate location in the wellbore. Fluid jetting involves washing to attack the soluble deposit with appropriate chemicals and is closely related with acid washing which hydrochloric acid is used. The susceptibility to corrosion is a disadvantage of acid washing over fluid jetting though the rate of dissolution is usually higher. The use of substances (scale inhibitors) that interact with the scales and prevent further growth of the scales is considered the simplest, practical and cost effective technique [17].

3. Scale inhibitors and inhibition

The addition of some substances to the scaling medium to reduce the growth or further buildup of scales is referred to as scale inhibition. The substances are called scale inhibitors or antiscalants. Two major classes of SIs are known,



namely, thermodynamic and kinetic inhibitors [6, 17-18]. Complexing and chelating agents which are suitable for specific scales are classified under thermodynamic SIs. Kinetic SIs act by stereospecific and non-specific mechanisms [6]. Largely, scale inhibitors (SIs) act either by adsorption effects or by morphologic changes of the growing sites [19]. When the inhibitor molecules occupy nucleation sites that would have been preferred or occupied by the scale-forming species, the crystals lack active sites to adhere to the surface, and their nucleation is prevented. Such inhibitors are called adsorption SIs and are said to act by adsorption effects. On the other hand, the SIs can change the morphology of the scale-forming species thus preventing them from forming crystals. Such inhibitors are said to act by morphologic change. The mode of action of a SI depends on its molecular characteristics and the nature of the substrate [18].

When designing scale inhibitors, some factors are usually considered. The inhibitor should as much as possible be stable to temperature increase and heat. Increase in temperature with distance travelled by the injected fluid (which SI is added) should not easily breakdown or degrade the inhibitor. This requires that the chemical structure be complex and the melting point be high [19]. In addition, since the chemistry/chemical composition of sea water and formation water vary with region, a SI should be compatible with these two systems. Hence, a SI that performs well in a given region may not do so in another [20].

The deployed volume and concentration of the SI is also important. Like corrosion inhibitors, the inhibitive potential of the SI depends on the amount and concentration applied. Generally, the higher the concentration, the higher the inhibition efficiency of most scale inhibitors [21, 22]. However, for a SI to be considered to be good, effective scale control should be achieved at reasonably low inhibitor concentration [6].

For SIs that act by adsorption effect, adsorption-desorption equilibrium properties of the SI should be balanced so as to allow the chemicals to be released into the production water in a slow and homogeneous manner. Homogeneous release ensures that all parts of the surfaces is contacted by the inhibitor. When the release is fast, this is difficult to achieve.

Changes in environmental conditions such as pH, temperature, fluid hydrodynamics, presence of other chemicals and brine composition can also influence the performance of a scale inhibitor. Factors such as brine supersaturation and the presence of divalent cations, such as Ca^{2+} and Mg^{2+} ions or even Zn^{2+} [16], can lead to incompatibility between the brine system with the chemical, hence reducing its concentration in solution and its scale inhibition performance [23].

The cost of producing, storing and transporting the scale inhibitor should be low. Cheap and efficient SIs are more desirable. Environmental concerns also requires that SIs be biodegradable and non-toxic or at least of low toxicity. The profile of a good and environmentally benign SI has been reported to include excellent scale inhibition, low aquatic and human toxicity, high biodegradability, low water hazard class (minimum of 2), good price/performance ratio and free of phosphorus, nitrogen, and heavy metals[24].

3.1. Chemical scale inhibitors

Scale inhibitors commonly used in the field can be classified into four groups namely inorganic polyphosphates, organic polyphosphates, carboxylic acids based polymers and ethylene diamine tetra acetic acid (EDTA) based compounds. Inorganic polyphosphates; polymetaphosphates or phosphate salts are condensed phosphates. They show effective inhibition and are compatible with a wide variety of water chemistry. However, they are easily hydrolysed and can precipitate calcium phosphates because of temperature, pH, solution quality, concentration, phosphate type and presence of some enzymes [24].

Organic compounds like polyacrylic acid (PAA), polyphosphinocarboxylic acid, sulphonated polymers and phosphonates have been used as SIs. At high temperatures, phosphonates are highly effective in contrast to sulphonated polymers which are more effective at low temperatures [6]. To bridge the gap between these extremes, phosphonate and sulphonate moieties can be copolymerized to do well over a range of temperatures. Organic inhibitors are also easily hydrolyzed with temperature increase and require high doses of application. Also, when Ca^{2+} concentration is high, they become ineffective. Polymers of carboxylic acids have limited Ca^{2+} tolerance but



require higher doses and larger concentrations. EDTA is effective over a wide range of temperature, pH, solution quality and is calcium tolerant, but EDTA is very expensive.

4. Scale Inhibitors from Plant Materials

Environmental concerns and discharge limitations have increasingly triggered SIs chemistry to move towards “green antiscalants” that readily ‘biodegrade’ and have low mobility for minimum environmental impact [24]. The challenge is basically to obtain acceptable levels of performance at cost-effective dose rates. Most conventional polymers and scale inhibitors remain for many years after their disposal without degrading: phosphorus based inhibitors are of more concern. Phosphorus and heavy metal discharges are regulated in many areas of the world, and permissible limits are decreasing. The oil industry is currently facing severe restrictions on the discharge of oilfield chemicals into the environment. More severe environmental constraints have prompted users to assume a rational management of industrial waters and barriers and to take more restrictive steps concerning its disposal.

Although the conventional phosphorous scale inhibitors have first been replaced by less organic phosphorus compounds such as carboxylhydroxymethyl phosphoric acid and dibutylphosphoricdithioic acid, more needs to be done. Also new classes of less toxic compounds not based on phosphorous chemistry have been introduced. These are polymers such as poryacrylates and derivatives and various sulfonic acid homo and copolymers. What then about natural compounds and carboxylated plant polysaccharides such as carboxylatedinulins? Among them are also the “greenest” scale inhibitors which include plant materials and biodegradable polymer and inulin derivatives. Various natural products, especially from plants, contain generous amounts of polyphosphates, carboxylic acid groups, alcohol and aromatic amines, which are potential functionalities for adsorption or antiscaling effect of the chemical SIs mentioned above. Research on the use of plant materials as oilfield chemicals like drilling mud [25, 26], biosurfactants [27] and corrosion inhibitors [28, 29] is very active, but very little has been done to test some plant materials as SIs. Extracts of natural plants materials are environmentally friendly, non-toxic, relatively less expensive, readily and sustainably available and also biodegradable. Nevertheless, this biodegradability limits the storage and long term usage of plant extracts/local materials.

The decomposition of plants extracts by microorganisms can be prevented by addition of biocides and other stabilizing agents. Therefore, some plant extracts could be blended with biocides to obtain effective scale inhibitors. However, Reno and Endaryanto prepared calcium carbonate scale inhibitors by modifying 2 g powdered Gambier extracts with 1 g benzoic acid and 2 g citric acid. The mixture was in a 1 L volume glass, added water up to 1 L mark, heated at 80 °C for 1 h and left for one night [30]. Earlier, Vilorio and coworkers prepared scale inhibitors from Aleo Vera gel and methanol [31]. The insoluble solid precipitable methanol, polysaccharides plus a salt complex in alcohol and organic acids was patented.

Leaf extracts of Fig (*Ficus carica L.*) contains β -amyryne, umbelliferone, bergabten, psoralene, β -sitosterol, p-coumaric acid, lupeol and other organic compounds [32] and have been used to inhibit calcium carbonate scales. Other plants materials reported as efficient scale inhibitors include sea weeds polysaccharides and soybean oil methyl ester [33, 34] olive leaf extract and leaf extracts of *Punicagranutum* [35]. There are also reports on products or compounds from plants and natural products such as humic acid, leucine, citric acid and xanthan used as scale inhibitors [36].

4.1. Potential Plant Materials for Designing Scale Inhibitors

4.1.1. Wood

Wood is principally composed of cellulose, hemicellulose, lignin and extractives [37]. Each of these components contribute to fibre properties, which ultimately impact product properties. Cellulose (structure in Fig. 1) is the major chemical component of fibre wall and contributes 40-45% of the woods dry weight. It is composed of linear chains of D-glucose linked by β -1,4-glucosidic bonds with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps. Lignin, a component of wood, is composed of guaiacylprpane (G) syringylpropane (S) and p-hydroxyphenylpropane (H) subunits (see Fig. 2). Various ether bonds and C-C bonds mainly β -O-4-ether bonds hold the sub units together. G-lignin, GS-lignin and GSH-lignin are all organic polymers present in wood.



Cellulose and lignin are both an organic polymers, hence wood could be regarded as a good source of organic polymers (which have been described earlier as a class of scale inhibitor) which could have chelating sites capable of inhibiting growth of scale crystals by adsorption effects or morphology change

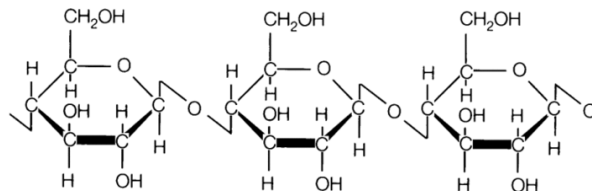


Figure 1: Molecular structures of cellulose

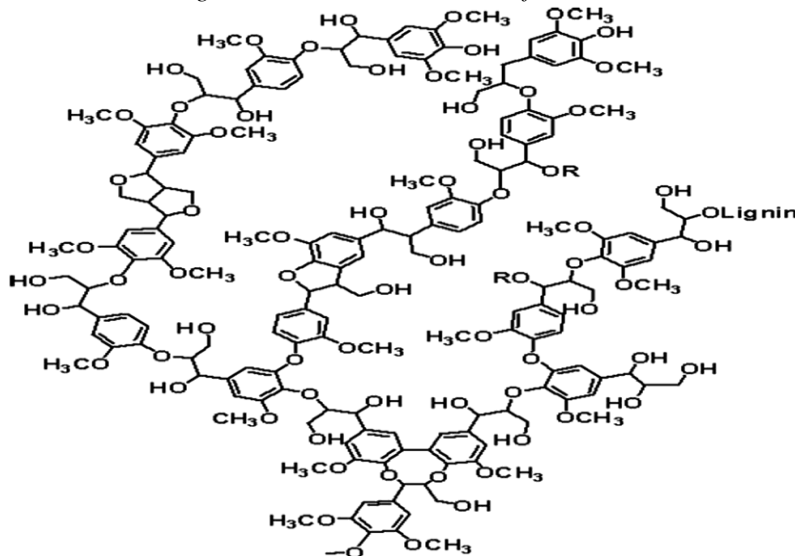


Figure 2: Structure of lignin

4.1.2. Dried hemp

Dried hemp is another potential material for design of scale inhibitor because it also contains cellulose, hemicellulose, pectin and lignin [38, 39]. Hemicellulose in hemp and straw fibres are short and highly branched polymers of pentoses such as xylose and arabinose. It also contains acetyl group and gluconic acid but the degree of polymerisation is much lower than in cellulose ranging from 20 to 300. By attached ferulic acid and P-coumaric residues, hemicellulose can form covalent bonds to lignin. Since hemp belongs to the angiosperm phylum, it contains hardwood lignin of coniferyl alcohol, sinapyl alcohol and minor content of p-coumaryl alcohol. Lignin seems to act like a matrix material within the fibres, making stress transfer on microfibril scale and single fibre scale possible. Having these constituents (cellulose, lignin, hemicellulose, pectin), dried hemp is a good source of organic polymers which might have the potential to be used as a efficient scale inhibitor.

4.1.3. Chicory plant

The main groups of compounds of the chicory root are carbohydrates, including saccharose, glucose and fructose, fructooligosaccharides, polyphenols and inulin whose contents reach an average 21% [40, 41]. Inulin is a soluble polyfructan and belongs to a group of dietary fibre. Its chains consist of up to 100 D-fructofuranose units linked through β -(2,1) glucosidic bonds. Carboxymethylinulin (CMI) is has been reported as a good green antiscalant (scale inhibitor) formed by carboxylation of a natural carbobydrate obtained from the chicory plant. Therefore the chicory plant extracts could find application as scale inhibitor since it is composed of the main constituent inulin to about 60-80%.



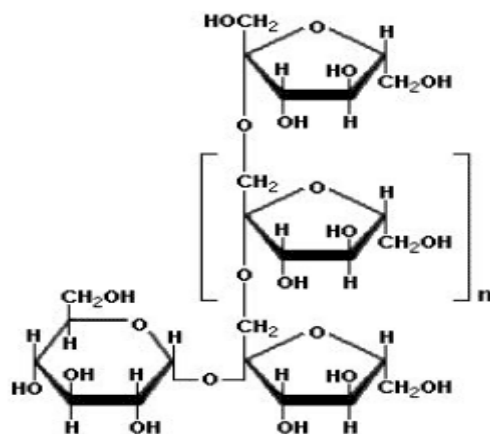


Figure 3: Structure of inulin

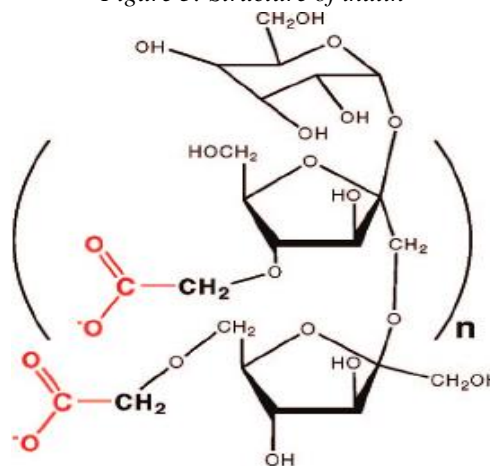


Figure 4: Structure of carboxymethylinulin

4.1.4. Jerusalem artichoke

Another plant which has high inulin content is the Jerusalem artichoke with over 80% (higher than the inulin yield in chicory) [42]. One important aspect for the quality of the inulin is its degree of polymerization (DP). The degree of polymerization of around 10-12 has been reported for standard inulin from chicory and Jerusalem artichoke, although high performance inulin with a DP of 25 has also been produced from chicory. Jerusalem artichoke is also composed of protein fructose and glucose (sugar), and bioactive compounds. Therefore, Jerusalem artichoke (as a good source of inulin) could also be a good scale inhibitor since carboxymethylinulins (CMI) (a good 'green' scale inhibitor) are derivatives of inulin.

Conclusion

Plant materials could be modified obtain cheap, non-toxic and biodegradable scale inhibitors for oilfield application. Some plant materials such as wood, dried hemp, choicory and Jerusalem artichoke are rich in carbohydrates and carboxylic acid based polymers, lignin, CMI, inulin and other compounds. These constituents rare capable of interacting with scale crystals by adsorption effect or causing morphological change on the crystals. Green scale inhibitors can be an area to direct future research interest into just like preparation of other oilfield chemicals is going green.

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