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Green Antiscalants and their Efficiency: A Review

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ABSTRACT

Formation of scales cut across almost all industries where minerals find their way into waters utilized in production either directly or indirectly especially when such waters are subjected to changes in temperature, pressure, pH, supersaturation, hydrodynamics etc. Scaling causes incrustation as a result of heated surfaces, reduces life span of equipment and facilities where they occur. It also predisposes personnel to accidents and brings about economic losses and raises environmental concerns when they are non-biodegradable. In view of these threats of scaling, efforts have been directed towards tackling scale formation in the past and presently by using various methods which include the use of antiscalants also known as scale inhibitors to prevent scale formation or disperse scales when they are already formed. The challenge of these Antiscalants used in time past include non-biodegradability, toxicity, and bioaccumulation even though they are effective Antiscalants. Hence, there is need to make antiscalants that are readily biodegradable, non-toxic with no bioaccumulation and also efficient Antiscalants. Antiscalants meeting these three criteria are said to be green Antiscalants. In this review article, antiscalants, types, scaling mechanism and efficiency of some green antiscalants were x-rayed. This article would serve as a guide for future research on scales and related topics.

Keywords:
Green antiscalants, mechanism, scaling kinetics, phase transition, types

1. INTRODUCTION

In recent times, scaling is one of the main challenges being encountered in the treatment of wastewater from industries. Contained in these waste waters are mainly salts of inorganic materials which causes scaling on the surface of equipment; damaging equipment and eventually leading to a wastage of energy [1] The formation of calcium carbonate scale is a major production challenge in water treatment plants that are handling significantly large volume of water [2]. Even water-cooling technology and desalination operations are also affected by the calcium carbonate scale formation [2, 3]. Cooling circuits used in industries become clogged as a result of deposits of calcium trioxocarbonate (IV) ($CaCO_3$) deposits. This $CaCO_3$ find their way into the tubes of condensers on PVC used as packing in the cooling towers. The scales gradually increase and also form very hard layers which increases resistance to heat transfer invariably reducing the efficiency of the cooling circuits even in kraft pulping but highly increases energy consumption in industries where cooling circuit is highly used; industries like nuclear plant, thermal power plant, etc. This eventually leads to reduction in the life-span of the tubing and associated equipment with increment in operational cost as well as costs of preventive and curative maintenance [2,4-8]. Calcium sulfates are also scales that have also affected oil and gas industry as well as plants used for the treatment of water [8]. In fact, a lot of oilfields are facing serious challenges due to formation of scales in the facilities used for oil production. The attachment of scale deposits onto the surfaces of equipment used for production and its gradual growth, reduces flow assurance due to flow pipe and tubing diameter reduction. The scale growth also affects surface equipment. When the crystal growth is not inhibited or dissolved, it eventually leads to total blockage of pipes and tubing causing production shut down and economic losses to the affected companies [7,8-9]. According to reports “Many wells have been abandoned prematurely as a result of poor management of scaling and corrosion.” [10, 11]. As such, precipitation of calcium carbonate is of great concern to a lot of researchers in many disciplines ranging from medical sciences (e.g. osteoporosis), most scientist in industries (e.g. incrustation as a result of heated surfaces), in homes (formation of scales on fabrics during laundry; using washing machine), our environment is not left out (e.g. natural waters undergo pH-buffering), even in paper and pulp (e.g. in pulp mills, calcium ion is one of the main ions causing incrustation in combination with carbonate and oxalate [12]. In fact, calcium carbonate deposition on surfaces is a well-known problem; often referred to as scale cost billions of dollars to the economy of the whole world [5]. The formation of scales resulting from industrial processes in the United Kingdom alone where heating of water takes place or water is used as a coolant is estimated to cost half a billion dollars annually [13]. This review article gives a summary of concept of scales and scaling, factors responsible for scale formation and deposition, types of scales, plants used for making scale inhibitors also known as antiscalants and their efficiency, mechanism for scale formation, significance of scale formation and future direction. This article can be a source of secondary information.

2. SCALES AND SCALING

Various authors have described and defined scales in various ways. Some of these definitions are; Scales are inorganic precipitates [14]. It involves the precipitation of metal carbonates, sulfates, oxides and hydroxides from solutions caused by temperature changes, evaporation or pressure decrease [15]. Any crystalline deposit (salt) emanating from the precipitation of mineral compounds present in water can be regarded as scale [11]. Scaling is the deposition of various salts inorganic or organic materials due to supersaturation of salt-water mixtures [1]. Inorganic fouling is also referred to as scaling since it is due to the formation of mineral deposits on the membrane surfaces as the feed water becomes supersaturated by inorganic salts in water purification using reverse osmosis [16]. Scales are also described as incrustations formed mainly at the surfaces of heat exchangers, within pipes, on the surfaces of membranes used in distillation or reverse osmosis; tremendously decreasing the optimal performance of desalination units, heat exchangers, as well as oil and gas facilities [15]. In summary, scaling is the process that gives rise to precipitation and deposition of scales while scales are the end products of the scaling.

2.1. Factors Responsible for Scale Formation and Deposition

The factors usually responsible for scale formation and deposition vary slightly form industry to industry, well to well, age of well, etc. In the cooling system of electric power plants, the precipitation of $CaCO_3$ out of solution and/or its deposition is caused by the following factors; changes in temperature, concentration of solutes/ions/minerals, water residence time, the quality of circulating water (the concentration of bicarbonates and calcium and other suspended matters, varying hydrodynamic condition, construction materials e.g., materials used for the condenser, materials used for the housing the condenser (e.g., concrete), polyvinyl chloride (PVC) packing etc. [18]. In the oil and gas industry, formation of scales and its deposition can occur in any or all of these petroleum production operation such as stimulation operation, production and even during transportation mainly as a result of supersaturation of solution arising from changes in temperature, reduced pressure usually due to loss of CO_2 which also give rise to reduced acidity, pH, mixing of incompatible waters such as sea water which contains a lot of sulphates SO_4^{2-} with formation water which is rich in Ba^{2+}, Sr^{2+}, etc., reaction equilibria, evaporation, exposure time, waterfloods/waterflooding [1,7,11], presence of hydrocarbon [14]. In general, factors responsible for scale formation and/or deposition can be summarized as hydrodynamics condition, kinetic and thermodynamic changes, physicochemical incompatibility of fluids [17].

2.2 Types of Scale

Olajire (2015) concentrated on oilfield scales which he classified as “pH sensitive or dependent scale deposits” and “pH independent scale deposits”. The former are scales in which their precipitation out of solution or/and deposition is based strongly on changes in the pH of the solution (brine) among other factors while the latter’s precipitation out of solution or/and deposition is not strongly determined by changes in the pH of the solution (brine). Some of the pH dependent scales include; the carbonates e.g., $CaCO_3$ and sulfides e.g., ZnS and PbS and they are soluble in acidic pH. Some of the pH independent scales include; sulphates of barium ($BaSO_4$), calcium ($CaSO_4$) and strontium ($SrSO_4$) [1, 7]. Scales of Zinc sulfide ZnS and calcium fluoride CaF_2 are a times called exotic scales because they are usually found in wells with high pressure and temperature. Calcium carbonate and halites are also referred to as self-scaling scales but calcium carbonates result from loss of CO_2 and pressure while halite results from a decrease in well temperature and evaporation of solution (brine). Barites ($BaSO_4$ barium sulphate) are usually precipitated as a result of mixing incompatible liquid (e.g., formation water and sea water) [11]. Jafar Mazumder (2020), also considered some of the scales from the oilfield and classified them as; carbonates and sulphates of calcium and magnesium, oxides and sulphides of iron etc. Most of these scales dissolve in either water (e.g., NaCl) or corrosive medium (e.g., $CaCO_3$, FeS, FeO, etc.) but some are neither soluble in water nor in corrosive medium [1, 18, 19]. Naphthenates were also discovered to be among the scales deposited in oil and gas production especially in the production of heavy crude. They are usually deposited as the soft sodium naphthenate or as the hard calcium carbonate naphthenate emulsion at the oil and brine interface during production [7]. Steve Strba classified the primary oilfield scales as follows; calcium carbonate precipitated due to pH and temperature dependent and these is a reverse solubility, strontium sulphate precipitated due to incompatibility of ions in solution, barium sulphate is precipitated due to incompatibility of ions in solution, iron oxide precipitated as a result of corrosion products and iron sulphide scales are produced as a result of sour wells or wells having high hydrogen sulphide [20]. Iron Sulfide scales are generally found being precipitated out of solution in oil and gas well known as sour wells due to the high contents of hydrogen sulfide (H_2S) in such wells. The H_2S usually react with the iron in the production facilities at a favorable brine pH, pressure and temperature to precipitate FeS. The iron sulfides scales vary in form either as the soft pyrrhotite or as the hard pyrite or monosulfide such as troilite, pyrrhotite, and the mackinawite or as disulfide as in the iron pyrite and marcasite, based on variations in brine pH, formation minerals e.g., presence of hematite ore in the sedimentary rocks etc., iron-to-sulfur ratio, pressure and temperature, exposure time etc. Zinc Sulfide scales and lead sulfide scales are less soluble in water when compared to the scales of iron sulfide. PbS and ZnS solubility increases as the salinity and temperature increases, an indication that the PbS and ZnS are usually precipitated at low temperature [1, 21, 22].

2.3 Scale Inhibiting Mechanism

A proper understanding and maintaining of all the conditions that causes inorganic salt precipitation (scales) such as changes in temperature, changes in pressure and chemical composition (e.g. CO_2, pH) generally referred to as scaling thermodynamics [14] will help to inhibit scale formation [23]. In general, $CaCO_3$ is regarded as the predominant scalant [4]. As such, we will consider $CaCO_3$ equation of reaction.

Equilibrium reaction for $CaCO_3$ precipitation is:

$$Ca^{2+}{}_{(aq)} + 2HCO_3^-{}_{(aq)} \leftrightharpoons CaCO_{3\,(S)} + H_2O_{\,(l)} + CO_{2(g)}$$

From the equation, a decrease in pressure will favor precipitation of $CaCO_3$ due to loss of CO_2 from the solution. An increase in temperature will also favor the precipitation of $CaCO_3$. Hence increase in pressure with a simultaneous decrease in temperature will favor dissolution of CO_2 into solution; making the medium more acid (that is, pH moves from alkalinity to acidity). With this condition, the equilibrium will shift to the left (reactant side) and increase the solubility of $CaCO_3$. This is the principle applied in process control methods in the management of scales (to control and prevent scale formation especially $CaCO_3$ [23] but excluding the sulfides scales as they tend to be precipitated at low temperature [1, 21, 22]. However, “Carbonate scale” formation is often alleviated (reduced or removed) by the use of chemicals used as additives in water treatment. Before reviewing the chemical control method of scales, there is need to highlight some of the postulations on mechanism for scale formation usually referred to as scaling kinetics [23, 284].

2.4 Mechanism for Scale Formation

Scaling occurs either by bulk or surface crystallization [16, 25]. Lateral growth of deposited scale on membrane surface giving rise to reduction in flow rate and eventual blockage of membrane is called surface crystallization. Formation of crystal particles in the bulk phase via homogeneous crystallization which may be deposited on membrane surface as sediments or particles leading to the formation of cake that reduces flux or flow is called bulk crystallization. When supersaturated scale forming situation occurs, scale growth and agglomeration takes place [16, 25]. A critical look at the aforementioned, movement (kinetics) is involved. Hence, we will look at scaling kinetics.

2.5 Scaling Kinetics

Scaling kinetics starts with movement which is the collision of ions leading to formation of ion pairs when all factors for scale formation are favorable. The nucleation can be regarded as the major beginning of scaling and it is strongly dependent upon saturation and temperature of solution. It can be said to be the emergence of a new phase within a homogeneous and supersaturated solution resulting from ion pairing and aggregation of the paired ions. These aggregates of ion pairs forming a nucleus can either grow to develop into a crystal (microcrystals) or simply re-dissolve and go back into solution as ions. Nucleation is simply the formation of the centers of nucleation i.e. formation of micro-crystals in the substrate and in the fluid bulk. The number of new crystals formed per unit volume per unit time in a solution is defined as the nucleation rate [23]. The crystals formed then increases in size by accepting and incorporating the other diffused ion pairs emanating from the supersaturated solution into its active sites through surface diffusion. This is followed by arranging/alignment of the ion pairs into the crystal lattice which give rise to the growth of the crystals. It should be noted that a balance of surface and volume free-energy terms governs the paired ion aggregation and growth [26]. It is important to also state that nucleation can be primary nucleation if there was no foreign material from the onset of particle formation (nucleation) and the process is homogeneous while secondary nucleation is a nucleation that occurs in the presence of foreign material from the onset. Also, growing crystals emerging from existing crystals can be called secondary nucleation [27]. The secondary nucleation mechanism is often classified as either contact nucleation or fluid-shear nucleation. The rates of primary nucleation are dependent on the presence of foreign matter, the containment vessel walls, temperature and levels of supersaturation [23].

2.6 Phase Transition

The unique stoichiometry and spatial arrangement of lattice molecules is referred to as a crystal phase [23]. Phases with similar unit cell stoichiometry but different spatial arrangements are called polymorphs, taking calcium carbonate ($CaCO_3$) as an example, its three main polymorphs are vertebrate, calcite and aragonite; in order of increasing thermal stability at temperature above 70ºC. Severtson et al., 1999 concluded that supersaturation, temperature and liquor constituents are the most important parameters that controls nucleation, crystal growth and phase transition mechanism.

2.7 Agglomeration

Crystal growth (paired ions increasing in size or numbers) leading to formation of microcrystals which agglomerate with other microcrystals to form macrocrystals which get adsorbed to the surfaces of the containers holding them while the microcrystals remain in the bulk solution. It should be noted that agglomeration is the continuous increase in size of the macrocrystals as a result of the additional scaling ions emanating from solution; marking the beginning of a scale film on a surface which eventually grows into a deposit [23, 28]. This particle agglomeration or adherent interparticle collisions give rise to the coagulation of the crystals both in the solution and on the containing vessel surfaces as adsorbed scale deposits especially when the flow rate of the liquid is low and favors the scale deposition. In summary, Severtson et al., 1999, postulated that the scaling process involves nucleation (resulting from ion pairing and aggregation of the paired ions), crystal growth, agglomeration and adsorption (scale deposit formation). Jafar Mazumder (2020) on the other hand from his review postulated that the process for scale formation usually involve these stages:

2.7.1 Initiation

When factors that affects the formation of any of the scales are favorable on a particular surface, the initiation process begins which involves the coming together of oppositely charged ions (cation and anion) to form ion pairs within the induction time of such ion pairs. The induction time usually vary from a few seconds to a week(s); depending on the scales in question and their prevailing condition. The induction time is inversely proportional to the degree of supersaturation or the temperature of the surface where the scale formation occurred [1].

2.7.2 Transport

After the occurrence of the initiation in the bulk solution, the movement of the scaling substances “from the bulk liquid to the surface over the periphery layer begins to take place”. Diffusion, sedimentation, and thermophoresis physical phenomena affects the transport of the scaling substances to the surfaces [1].

2.7.3 Deposition

The scaling substances (salt ions) which are being transported from the bulk liquid gets to the surface and interact with the other salt ions particles that are already on the surface as well as the surface itself (where it will be attached to) as a result of electromagnetic forces to form a nucleus on the surface. This process is known as nucleation formation. This nucleus formed, gradually grows into scale layers as long as the surface conditions remain favorable [1].

2.7.4. Removal

With increasing deposition of the scale particles, the scale grows to a stage in which the electromagnetic forces of attraction holding the scale particles together and to the surfaces weakens and the scales begins to "break off" from the scale deposits especially due to the liquid bulk viscosity and its velocity gradient with respect to the scales and the level of roughness of the surface. This "breaking off" of the scales from the surface is known as removal performance. The removal process is a dissolution, erosion and spalling mechanism [1].

2.7.5 Aging

The scale aging process begins immediately the deposition of scales starts [1]. In summary, Jafar Mazumder, 2020 stated that scaling or scale formation processes are; initiation, deposition, removal and aging.

However, Hu et al. (2022) outlined that the scale deposition is a crystallization process arising from these four stages; oversaturation, nucleation, crystal growth around the nucleus and the continuous growth of the microcrystals leading to the thickening of the already formed scaled layer [29, 30, 31].

3. SCALE INHIBITING MECHANISM

Antiscalants are chemical substances made used of to prevent the formation and deposition of scales on equipment and facility [7, 8]. The antiscalants help to delay the scaling of salts and particles like calcium sulphate, barium sulphate, calcium carbonate, etc. Having reviewed some of the scaling postulates which gives a summary of the scaling kinetics as ion pairing, aggregation, nucleation, crystal growth, agglomeration and adsorption, the chemical control of scalant or scale formation using antiscalants or scale inhibitors or just additives can be achieved by applying;

(i) Precipitation threshold inhibition method
(ii) Crystal dispersion method
(iii) Crystal distortion mechanism
    One or more of any of these three mechanisms are basically what the usage of the polymeric antiscalants is intended to achieve [23, 32]
(iv) Chelants (Sequestrants) [1]
(v) Fluorescent-Tagged Scale Inhibitors [1]
(vi) Squeeze treatment [7]

3.1. Precipitation Threshold Inhibition

This occurs once the active sites of a crystal or precipitate are blocked by the adsorption of an anti-scalant to prevent the crystal from growing to its peak [4]. Once nucleation occurs after ion pairing and aggregation, active site(s) on the aggregates (crystals or precipitate particles) occurs. These sites provide room for other ion pairs to be accepted and incorporated into the crystals which increases their size leading to crystal growth (microcrystal formation). Precipitation threshold inhibitors act by blocking the active sites of the crystals or precipitate particles they are adsorbed onto thereby preventing crystal growth. A precipitation threshold inhibitor with multiple sites for adsorption are most effective. The crystals with blocked active site(s) remain in solution without obstructing the process flow assurance. Anionic functional group groups are what the precipitation threshold inhibitors basically possess. These anionic functional groups can take the place of the lattice anion sites due to their electronic charge and their geometry which fits into the active sites [23]. Some of the reported inorganic antiscalants used are; sodium hexametaphosphate, sodium salt of orthophosphate, pyrophosphate, tetrametaphosphate, polyphosphate and trimetaphosphate. Though these antiscalants are effective, their drawback is that they are subject to hydrolysis which reverts them back to orthophosphate thereby making them lose their scale inhibiting efficiency on calcium carbonate scales [23]. The organosphosphonates are often used for calcium carbonates [33]; these include; Aminotrimethylenephosphonates (ATMP), aminomethylenephosphonates (AMP), 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC). They also act by getting adsorbed to the crystal active sites. They also have a set back by their thermal stability, calcium tolerance (calcium salt solubility), under caustic conditions their hydrolytic stability [23]. Also reported to be effective precipitation threshold inhibitors are hydroxycarboxylic acids and aminopolycarboxylic acids [23]. Poly Phosphono carboxylic acid (PPCA) is used in the oil and gas for its nucleation inhibiting ability [7, 34].

3.2. Crystal Dispersion

This is the prevention of agglomeration and micro-crystals growth by increasing surface anionic charge and repulsion [4]. While precipitation threshold inhibitors get adsorbed to crystals' active sites, the anionic dispersants act by getting adsorbed to the particle (growing crystals) thereby preventing agglomeration and adsorption from occurring. This is because, once the anionic dispersants get adsorbed to the growing crystals, their anionic character increases giving rise to repulsion and steric barrier between the growing crystals. Hence, increasing the activation energy for agglomeration and adsorption to occur thereby reducing the rate of agglomeration and adsorption leaving the crystals dispersed in a colloidal state instead of forming scales. Synthetic anionic polymers having carboxylate functional groups and molecular weights ranging from 1 000 to 100 000 have been reported to be very effective in dispersing calcium carbonate particles. Acrylic acids, methacrylic acid, and maleic acids are usually used as monomers in which the carboxylate functional groups for the synthetic anionic polymers are derived. Polyacrylic acid, polymethacrylic acid and partially hydrolyzed polyacrylamide are polymers often used as dispersants for calcium carbonate. Polyacrylate-based scale inhibitors predominantly contains acrylic acid and the other components of the polymers like amide, ester, ether, phosphonate or sulfate are in smaller amount [23]. Diethylenetriamine Penta (methylene phosphonic acid) (DETPMP) is used in the oil and gas for its crystal growth inhibition property [7, 34].

3.3. Crystal Distortion

This is simply the modification of the morphology of a growing micro-crystal to deform it or create an irregular pattern which prevents the formation of the regular crystalline lattice [4]. The main objective in this treatment is to use antiscalants to change or modify or distort the initial regular lattice or shape of the growing crystals to prevent or make it very difficult for other similar shaped crystals from "properly fitting into and locked up into" the crystal lattice. This treatment delay or makes agglomeration and adsorption impossible. Hence, the distorted or modified crystals remain in solution not forming hard layers and not disrupting the flow assurance. The modifiers operate by selectively adsorbing onto the faces of certain crystals or series of faces of crystals thereby modifying or altering their original shapes or surface properties. This modification will give rise to crystals that their incorporation into an already existing deposits becomes very slow or impossible instead they flow along with the solution. Acrylate- and phosphonate-based additives have been reported to have crystal modification or distortion influence [23, 35].

3.4 Chelants

Scale inhibitors either organic or inorganic with chelating properties can effectively prevent scaling. They simply do this by forming coordinate bonds with the metal ions (cation) in solution. That is, the antiscalants (chelating agents) “cage or hold back the cations from pairing up with their respective anions” with their “claws” lone pairs of electrons they donated to form the coordinate bond based on the combining stoichiometric ratio of the anions to the cations. Though a very effective way of preventing scale formation, it is very expensive on large scale [1,7,11,36]. Some examples of chelating agents used as antiscalants are citric acid, ethylenediaminetetraacetic acid (EDTA), Diethylenetriaminepentaaceic acid (DTPA), gluconic acid, etc. [1].

3.5. Fluorescent-Tagged Scale Inhibitor

This is based on using fluorescence to tag or label antiscalants and carryout visual study to understand the mechanism of scaling and antiscaling with particular interest in $CaSO_4$ [1, 37, 38, 39]. A fluorescent-tagged bisphosphonate scale inhibitor 1-hydroxy-7-(6-methoxy-1,3-dioxo-1Hbenzo[de] isoquinolin-2(3H)-yl)heptane-1,1-diyl-di(phosphonic corrosive), HEDP-F) was synthesized and observation was visually done under a fluorescent microscope to understand how the synthesized antiscalant will inhibit the formation of scales of $CaSO_4$ in a supersaturated solution. The visualization revealed that HEDP-F and Ca^{2+} formed an insoluble complex, followed by heterogeneous nucleation [1, 40]. These insoluble particles remain strong but dispersed in solution. It was also observed that the bisphosphonate (antiscalant) did not undergo any noticeable sorption onto the crystal edges or onto other crystal development centers yet it obstructed the sites for $CaSO_4$ crystals dynamic development and retarded $CaSO_4$ scales formation [1, 41]. When another fluorescent antiscalant -1, 8-naphthalimide-tagged polyacrylate (PAA-F) was studied for its antiscaling efficiency and fluorescent properties on $CaSO_4$ the result was similar [1, 37, 38]. This is a deviation from the traditional chemical antiscaling mechanism. As such the mechanism was proposed as fluorescent-tagged scale inhibitors mechanism [1, 39].

3.6. Squeeze treatment

This is simply the injection of the scale inhibitors into the producers near the wellbore [7]. Generally, antiscalants have been prepared from both natural and synthetic polymers. Among these polymers used are inorganic and organic compounds such as polyphosphates, carboxylic acids, ethylenediamine tetra acetic acid (EDTA) based compounds, etc. They are effective in managing the oilfield scales but many are expensive and toxic [1,11]. Though phosphorus based antiscalants have been used with reported success in their effectiveness but it takes time before degrading and it also causes eutrophication in water surfaces when it is eventually broken down. Hence, there is strict regulations on its disposal [7,14,42]. Most threshold inhibitors used today contains nitrogen and phosphorus which give rise to water quality problem of contributing to nutrient loading in water bodies”; a major environmental challenge. On the other hand, most conventional polymers and scale inhibitors remain un-degraded for many years after their disposal; phosphorus being the main culprit [11]. Hence, there is a conscious effort to move away from the conventional antiscalants especially the usage of phosphorus and nitrogen in making antiscalants; “red antiscalants” to the making of phosphorus-free antiscalants or “green antiscalants”. Green antiscalant must meet these three criteria; it must be readily biodegradable, have no bioaccumulation and non-toxic in line with PARCOM (Paris Commission) [7]. Usage of cellulose-based antiscalants like carboxy Methyl Inuline (CMI) and its derivatives in making antiscalants have been advocated for [43, 44]. Efforts have been devoted to making green antiscalants which are in line with PARCOM either from plants or their extracts or any other natural source and notable successes in the laboratory have been reported [6, 8, 45]. Plants have been reported to contain a lot of the functional groups which have scale inhibiting properties like alcohols, aromatic amines, carboxylic acids, polyphosphates, polysaccharides, etc. [11]. So far, aspartates and inulin derivatives can be regarded as some of the “greenest” antiscalants [7, 46, 47].

3.7. Green Antiscalants

Polymers which contain carboxylic acid like acrylic acid, aspartic acid, maleic acid are usually used in making green antiscalants. This is because they are biodegradable, effective at low concentrations, have relatively high thermal stability and are not toxic [6, 48]. Some of the novel green antiscalants are Polyaspartates (PASP), Polyepoxysuccinates (PESA), Polymaleates (PMA) and their derivatives as well as polyaspartate copolymers [8]. Polyepoxysuccinic acid and polyaspartic have also been used in making green antiscalants because they contain neither nitrogen nor phosphorus and are biodegradable. The application of these antiscalants (at low concentrations: 4, 5, 10, 15, 30.2 mg/L), at a temperature of 80 °C and pH 9.0 (for 8-10 hours) in the laboratory gave a good result (90 % and above) for the inhibition of $CaCO_3$ (with concentrations; 500-720 mg/L) [6]. Powdered Gambier extract mixed with benzoic acid and citric acid in the ratio 2;1;2 made up to 1 liter have been used effectively as $CaCO_3$ antiscalants by Reno and Endaryanto [11]. Aloe vera gel and methanol have been used by Viloria and Co. in preparing antiscalants with excellent result. It is thermally stable up to 125 °C. It is not adversely affected by hydrolysis and its functional group can form complex with cations like Ca^{2+}, Mg^{2+} to prevent scale formation [1, 49]. Also, extracts from *Ficus carica L.* (fig tree leaf) (150 mg/L) have been used as $CaCO_3$ inhibitor with about 86% efficiency [1, 50] , *Punica granulum* leaf extract (100 mg/L) have been used as $CaCO_3$ inhibitor with about 60% efficiency [1, 51] , *Punica granulum* hull extract (100mg/L) have been used as $CaCO_3$ inhibitor with about 88% efficiency [1, 51], extract from *Olea europaea L.* (olive) leaf (Biopheols) (50mg/L) have been used as $CaCO_3$ inhibitor with about 83% efficiency [1, 52], Copolymer modified with the palygorskite (50 mg/L) have been used as $CaCO_3$ inhibitor with about 99 % efficiency, Heteropolysa-ccharide sulfonate (PS-NAEP) (100mg/L) have been used as $CaSO_4$ inhibitor with about 95% efficiency, Heteropolysa-ccharide sulfonate (PS-NAEP) (55 mg/L) have been used as $Ca_3(PO_4)_2$ inhibitor with about 55 % efficiency [1]. Modification of collagen (P-MACs) (7 mg/L) have been used as $CaSO_4$ inhibitor with about 100 % efficiency [53]. Extract from *Helianthus annus* (sun flower*)* seed (50 mg/L) have been used as $CaSO_4$ inhibitor with about 100 % efficiency [1, 53], *Helianthus annus* (sun flower*)* seed (50 mg/L) have been used as $BaSO_4$ inhibitor with about 84% efficiency [53] extract from Aloe vera gel (containing anthraquinone and perulic acid) (15 mg/L) have been used as $CaCO_3$ inhibitor with about 80 % efficiency [17], extract from *Paronychia argentea Iam* (containing luteolin*)* (70 mg/L) have been used as $CaCO_3$ inhibitor with about 100 % efficiency [1, 54], soya bean polymer(containing methyl ether of soya bean) (4250 mg/L) have been used as $CaSO_4$ inhibitor with about 93% efficiency [1, 47], polysaccharide from seaweed (4200 mg/L) have been used as $CaSO_4$ inhibitor with about 90% efficiency, polysaccharide from seaweed(K-carrageenan) (3100 mg/L) have been used as $CaSO_4$ inhibitor with about 17% efficiency [1, 47]. Xanthan molecules from *Xanthomonas campestris*, a bacterium which contains polysaccharides was used as antiscalant at concentrations 100- 1000 mg/L and pH 9 to inhibit scale formation of Ca^{2+} and CO_3^{2-} of concentrations of 2664 and 2544 mg/L respectively. Carboxylic acids (citric, maleic, malonic, succinic and tartaric acids) effectiveness as antiscalants on $CaCO_3$ crystallization at room temperature was studied by some researchers from Japan and they concluded that about 13 mg/L of citric acid was effective in inhibiting Ca^{2+} of 800 mg/L from pairing up with CO_3^{2-} to start forming crystals due to adsorption of the carboxylic acid [1, 55]. Reddy and Hoch (2001) stated that at lower concentrations (0.01-0.1 mg/L) citric acid; a linear carboxylic acid was not able to inhibit $CaCO_3$ as low as 76 mg/L unlike the cyclic rigid poly-carboxylic acids like tetrahydrfurantetracarboxylic acid or cyclopentanetetracarboxylic acid which was very effective against scaling and even corrosion. A concentration of about 120mg/L at 70 °C and 160-200 mg/L at 90-110 °C of Pteroyl-L-glutamic acid (PGLU), a derivative of glutamic acid was reported to be very effective in inhibiting $CaCO_3$ crystallization. As such, PGLU could be used as a green antiscalant in the oil and gas reservoir [36]. PASP has been reported to be both an antiscalant (for $CaCO_3$ and $CaSO_4$) [56] and corrosion inhibitor [7, 57, 58]. CMI is an excellent scale inhibitor of $CaCO_3$ and can be applied in food making industries [59]. Characterization is usually by the use of Scanning electron microscopy (SEM), X-ray diffraction (XRD) [6], Dynamic light scattering technique for zeta potential measurement of filtrate [8] were used in characterization of scales in antiscalants or scale inhibition studies.

4. CONCLUSION

Scaling is the precipitation of metal carbonates, sulfates, oxides and hydroxides from solutions caused by temperature changes, evaporation or pressure decrease, changes in temperature, concentration of solutes/ions/minerals, water residence time, etc. In the oil and gas industry, formation of scales and its deposition can occur in any or all of these petroleum production operation stages such as stimulation operation, production and even during transportation mainly as a result of supersaturation of solution arising from changes in temperature, reduced pressure usually due to loss of CO_2 which also give rise to reduced acidity, pH, mixing of incompatible waters such as sea water which contains a lot of sulphates SO_4^{2-} with formation water which is rich in Ba^{2+}, Sr^{2+}, etc., among other factors already highlighted. Scaling especially the precipitation of calcium carbonate affects almost all areas where water is involved or used either for domestic or industrial purposes; causing economic losses to industries, threatens the safety of facilities and personnel and can pose environmental challenges when not properly managed if the “red” antiscalants are used instead of the “green” antiscalants. Hence, one of the ways forward in tackling the challenges of scale formation is to make antiscalants that are green; pocket friendly, eco-friendly, not easily hydrolyzed and can withstand extreme conditions such as high temperature and pressure experienced in deep sea oil production.

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