Scale Inhibition in Hard Water System

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Abstract The precipitation of an insulating layer of scaling on the walls of the water distribution pipes has serious technical and economic consequences. Various methods were used to prevent the scale formation in water such as the chemical methods in which the germination of the $CaCO_3$ crystals is blocked using the inhibitor. In recent years, a few studies have been focused on the aspects of the surface scaling so that the different mechanisms were proposed to explain the differences between the scaling precipitation in bulk solution and scale deposition at the surface. The water distribution of some Algerian town resulting from the drilling water is supersaturated with respect to calcium carbonate. This causes reducing heat transfer in heat exchanger systems, limiting the efficiency of these

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devices (valves and taps) by decreasing the flow rate in the pipes; this phenomenon is more prevalent at high heating temperature. In this book chapter, we aim to give an overview of the different antiscaling properties in hard water. We also provide the inhibitors used and the researches done on Algerian water.

Keywords Algeria, Calcium carbonate, Hard water, Inhibitor, Scale

1 Introduction

Water plays a central and general role in human activities, development of social economy, and the ecological environment balance. Water contains mineral salts and dissolved or suspended substances. Indeed, during an increase in temperature, removal of dissolved CO_2, an increase in the concentration of certain dissolved salts, or, more generally, a change in chemical equilibrium, dissolved solids can crystallize. A compact and insulating adhesive layer is then formed on the surface of the water pipe. This deposit causes the decrease of heat exchange, the reduction of the partial or total diameter of water pipes, the dysfunction of domestic and industrial installations and equipment, and the inhibition of detergency and ultimately significant financial losses. The primary agents responsible for crystallization fouling are the carbonates and sulfates of calcium or magnesium, barium salts, silicate, and phosphate.

Scaling is essentially linked to the formation of calcium carbonate ($CaCO_3$). Scaling may contain other residues such as algae, calcium sulfate, clays, and the brucite $Mg(OH)_2$. But it is always calcium carbonate that precipitates first, usually in the colloidal form, because its solubility is lower than that of others.

The formation of scale is a very complex phenomenon which can be subdivided into two phases: a crystal of calcium carbonate is formed, and the precipitate is formed around the initiator crystal and then its growth; it is the stack of adsorbed germs that forms $CaCO_3$ growth sites (Fig. 1).

Scaling in natural hard water is a major concern in different facets of industrial processes and domestic installations (Fig. 2). Undesirable scale deposits often cause numerous technical and economic problems such as total or partial obstruction of pipes leading to a decrease in flow rate; reduced heat transfer as scale precipitate is 15 to 30 times less conductive than steel; seizure of valves and clogging of filters; etc. Therefore, it is essential to establish appropriate methods to study this phenomenon and find effective ways to combat it. Among the methods used to inhibit this phenomenon, the use of products to block the formation of tartar by preventing crystal growth (called tartrifuges products): organic molecules such as tannins, humic acids, citric acid, or glutamic acid, there is also chemicals: polyphosphates, phosphonates [1].

The ideal inhibitor would be a compound in a solid form whose solubility would be very low but largely sufficient to ensure a total scaling inhibition. It could thus be

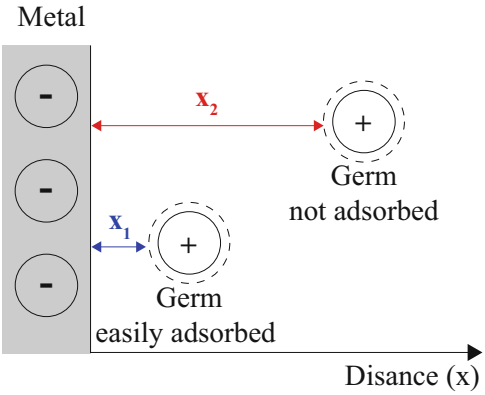

Fig. 1 Adsorption of calcium carbonate germs on a metal wall

Fig. 2 Pipeline obstructed by scale of Ouargla city [2]

brought into direct contact with the water to be treated without having to worry about its concentration, which would be automatically regulated by its solubility. Environmental requirements impose many challenges in the field of water treatment. Thus, the concept of "green chemistry" has been proposed, and the use of "green" chemicals has become a necessity. It is, therefore, of paramount importance to develop "green" scaling inhibitors in order to combat scaling phenomena that have disastrous or even catastrophic consequences [3].

For decades, various attempts have been made to estimate the scaling power of natural waters and characterize the scaling formation mechanisms. These methods can be roughly divided into two categories: electrochemical methods and chemical methods. For the first one, we can use the chronoamperometry, chronoelectrogravimetry, and electrochemical impedance technique. All these techniques are based on the reduction of the oxygen dissolved in the water. Among the

chemical methods, we can enumerate the critical pH method an evaporation method, the LCGE method, the rapid controlled precipitation method, a polymer scaling test, and a continuous test on tubes and others.

2 Scale

In this section, we introduce the definition of scale, the different type of scale, and the influence on industrial processes.

2.1 Definition

Water contains a number of dissolved species that can react under specific conditions to form a precipitate. Some of the precipitated salts have a very low solubility which is called poorly soluble salts. The precipitation reaction can be triggered by changes in conditions such as supersaturation, temperature, pH, or pressure. Precipitation results in deposition and scale formation on all surface materials, including pipe walls, heat transfer surfaces, pumps, etc. This process is also called fouling by crystallization (Fig. 3).

Calcium and magnesium carbonates and sulfates are the main agents responsible for the fouling of crystallization, although barium salts, silicates, and phosphate deposition play an important role in some industries. Deposits formed by water, usually observed, include calcium carbonate, calcium and barium sulfate, silica deposits, iron deposits, magnesium, and calcium phosphates. If we extend our area of interest to wastewater, struvite is the main cause of the mineral scale [4]. Scaling is a phenomenon that occurs when a surface is in contact with incrusting water, likely

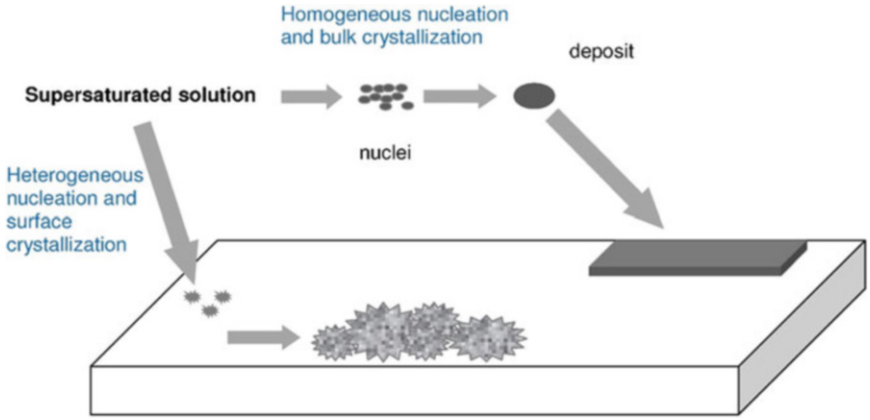

Fig. 3 Schematic illustration of scale formation schemes [6]

to cause the formation of a product of very low solubility in the form of an adherent deposit. In the case of natural waters, the compound likely to precipitate first is calcium carbonate [5].

2.2 *Different Type of Scale*

2.2.1 Calcium Carbonate $CaCO_3$

Calcium carbonate ($CaCO_3$) is the most common compound (in terms of geographical distribution and abundance) in mineral precipitates of biological origin (marine and geological organisms) [7]. It is an essential element of sedimentary rocks [8] and a major constituent of scale that is found in drinking water pipes and in various structures in contact with natural or distribution water. It may be accompanied by various poorly soluble salts according to:

- The origin of the water
- The treatment he has suffered
- Temperature
- The nature and the state of corrosion of the pipes

It is mainly $CaSO_4$, Mg $(OH)_2$, Fe $(OH)_3$, and salts of various metals [9]. But it is always the calcium carbonate that precipitates first, usually in the colloidal form, because its solubility is lower than that of the others [10].

There are three crystallographic varieties of calcium carbonate:

The Calcite Thermodynamically, calcite (Fig. 4a, b) is the most stable polymorph of calcium carbonate, and it comes in many forms in nature. According to the data of the literature, calcite can present 700 different crystal forms always in the same system and also a certain number of twins (intimate association of two or more crystals according to precise plans).

The Vaterite Unlike calcite and aragonite, there is a very little occurrence of vaterite in natural minerals [11]. In fact, exposed to water, vaterite is very unstable and generally recrystallizes in the form of calcite. The most common facies is in lens (Fig. 4c); but we also encounter facies in the form of "roses of the sands."

The Aragonite Aragonite is orthorhombic pseudohexagonal and is usually in the form of a needle (Fig. 4d). It is metastable at ordinary temperature and transforms into calcite at high temperature.

Calcite is the most stable crystalline form at 25°C. Calcite is the least soluble (pK = 8.35). Aragonite is more soluble than calcite (pK = 8.22); it precipitates hot ($T > 60$°C). The vaterite form is the most unstable of the three crystallographic forms of $CaCO_3$ and makes its identification difficult. The solubility of calcium carbonate increases with temperature (Table 1).

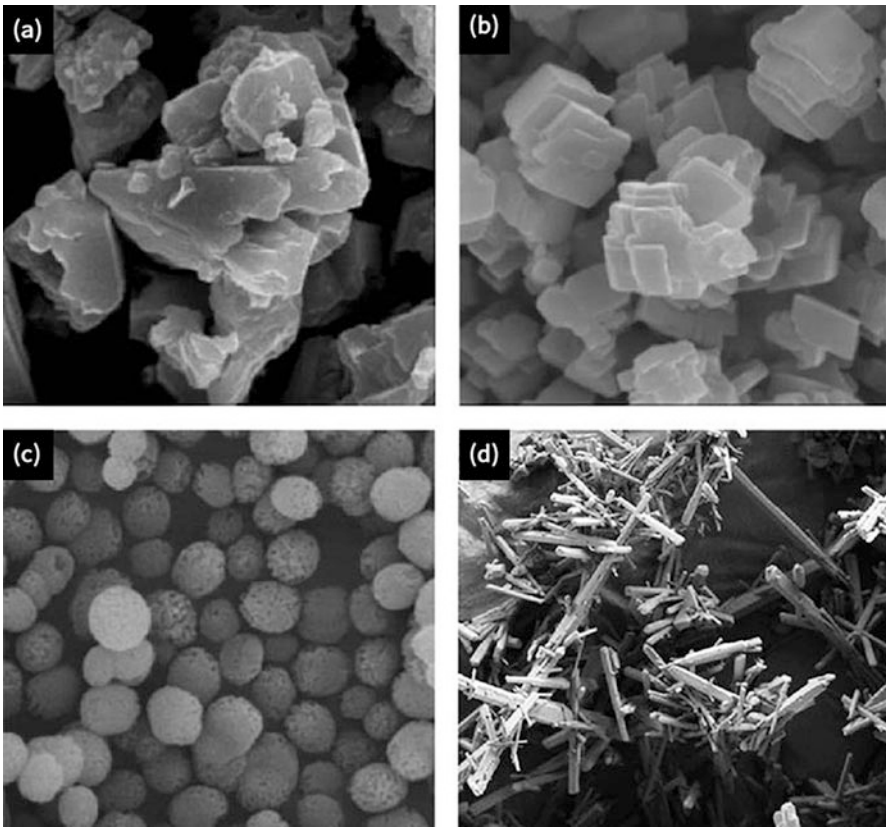

Fig. 4 The SEM images of $CaCO_3$ forms: (**a**) amorphous calcite, (**b**) layered and rhombohedral calcite, (**c**) spherical vaterite, and (**d**) needle aragonite [12]

Table 1 The temperature effect on the solubility of calcium carbonate [12]

	Solubility (mg L^{-1})	
Temperature	à 25°C	à 50°C
Calcite	14.43	14.43
Aragonite	15.28	16.17

Natural waters contain in solution many chemical species at very different concentrations according to their origins. We can classify them into two groups according to:

- The fundamental elements: $CO_{2(free)}$, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-, and Ca^{2+}, which participate in the carbonic and calcocarbonic equilibrium.
- The characteristic elements: Mg^{2+}, Na^+, and K^+ for the cations and SO_4^{2-}, NO_3^-, and Cl^- for the anions. These ions do not intervene in the preceding equilibria except by their action on the ionic strength of the solution.

(a) The carbonic equilibrium

When we dissolve CO_2 in water, we have the following equilibrium:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \text{ with the constant } K_0 = \frac{[H_2CO_3]}{[CO_2]} = 10^{-1.5}$$

At ordinary temperature, so that there is only 3% of carbon dioxide in the form of H_2CO_3

The latter has in solution, the behavior of a diacid according to:

$$H_2CO_3 + H_2O \leftrightarrow HCO_3{}^- + H_3O^+ \text{ with a constant } K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3{}^- + H_2O \leftrightarrow CO_3{}^{2-} + H_3O^+ \text{ with a constant } K_2 = \frac{[CO_3^{2-}][HCO_3^-]}{[HCO_3^-]}$$

If we note: $[CO_{2\ (free)}] = [H_2CO_3] + [CO_2]$

We write the balance:

$$2H_2O + CO_{2\ (free)} \leftrightarrow HCO_3{}^- + H_3O^+ \text{ and we can put } K_3 = \frac{[HCO_3^-][H_3O^+]}{[CO_{2\ (free)}]}$$

$$= \frac{K_1}{\left[1 + \left(\frac{1}{K_0}\right)\right]}$$

In addition, we have the autoprotolysis of water:

$$2H_2O \leftrightarrow OH^- + H_3O^+ \text{ with a constant } K_e = [H_3O^+]\,[OH^-].$$

The previous constants depend on the temperature of the water, the ionic strength of the solution, i.e., the concentration, and the charge of all the ions present (fundamental and characteristic).

(b) The calcocarbonic equilibrium

For water in equilibrium with solid calcium carbonate, the equilibrium:

$$Ca^{2+} + CO_3{}^{2-} \leftrightarrow CaCO_{3(S)}$$

This equilibrium, called calcocarbonic, is governed by the law of mass action, which establishes between the concentrations of the ions Ca^{2+} and $CO_3{}^{2-}$ the following relation:

$$K_s = \left[Ca^{2+}\right]\left[CO_3{}^{2-}\right]$$

K_s depends on the temperature and the ionic strength of the solution. It also depends on the crystallographic variety. Under the usual conditions and at ordinary temperature, the $K_s = 10^{-8.3}$ is often adopted.

If the product $[CO_3{}^{2-}][Ca^{2+}]$ is lower than K_s, it will not be possible to precipitate.

Conversely, for having precipitation of calcium carbonate, it is necessary to have:

$$\left[CO_3{}^{2-}\right]\left[Ca^{2+}\right] > K_s.$$

Generally, in a circuit of water, one can write at any point of this circuit:

$$\left[CO_3{}^{2-}\right]\left[Ca^{2+}\right] = \delta \cdot K_s$$

where δ is the local supersaturation coefficient of water. Indeed, three cases can occur at one point:

$\delta < 1$: the water is locally aggressive.

$\delta = 1$: the water is locally at equilibrium.

$\delta > 1$: the water is thermodynamically capable of locally precipitating $CaCO_3$ according to the increasing germination process mentioned above.

The germs of $CaCO_3$ can have varied evolutions:

- The germ will grow and regress and then dissolve.
- The seed will grow and evolve into a crystal. We then go to a phenomenon of sludge generating precipitation.
- The seed will be produced at the level of a metal wall. We will be in a scaling process if the connection with the wall is strong enough.
- The germ will remain suspended in the water and be carried away by the flow.

The solubility of $CaCO_3$ depends on the pH. It is shown in Fig. 5. The solubility of $CaCO_3$ can be increased by the addition of carbon dioxide according to the equilibrium:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3{}^{-}$$

2.2.2 Calcium Sulfate

Calcium sulfate is one of the most common scalants in processes involving seawater, such as desalination. It is also often referred to as nonalkaline scale. Pure calcium sulfate is white in color with a similar resemblance to calcium carbonate. It exists as $CaSO_4{\cdot}nH_2O$. All these forms are more soluble than calcium carbonate and magnesium hydroxide [13]. The most common is gypsum with a monoclinic prismatic

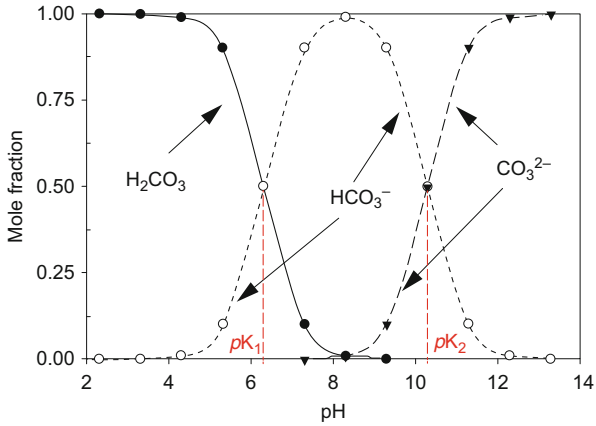

Fig. 5 The distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH [12]

crystal structure, with four or eight molecules in the unit cell. It crystallizes as white crystals according to the following reaction [10]:

$$CaCl_2 \cdot 2H_2O + NaSO_4 \rightarrow CaSO_4 \cdot 2H_2O + 2NaCl$$

Layers of gypsum can settle and form a shell with layers of anhydrite. These relatively thin layers (0.6 mm) of calcium sulfate scale on the tubes of low-pressure boilers can cause a massive temperature drop of 180°C [14]. This had previously been shown by Bansal and Müller-Steinhagen [15] for calcium sulfate fouling on plate heat exchangers.

Crystallization of calcium sulfate is a complex phenomenon influenced by a number of parameters, such as temperature, pressure, electrolytes, and dissolved organic matter, and the presence of other minerals [16]. Research by Bansal and Müller-Steinhagen [15] showed that the measured calcium sulfate resistance of a plate heat exchanger was 50% lower than 85°C compared with 90°C. Temperature also influences the formation of polymorphs. Gypsum is the most formed deposit in all reverse osmosis and cooling systems that use moderate temperatures (up to 50°C), while calcium sulfate hemihydrate and anhydrite are the most formed in applications at high temperature [17, 18]. Calcium sulfate is found in many cooling systems, but since most of these systems operate at pH = 7–9, calcium carbonate is the most predominant scale, and calcium sulfate only precipitates when all carbonate is eliminated [19]. Precipitation of calcium sulfate is insensitive to pH, unlike other calcareous deposits [20]. Calcium sulfate may be in the form of hard rock or soft granules [10].

2.2.3 Magnesium Scales

A number of magnesium scales, such as magnesium hydroxide ($Mg(OH)_2$), magnesium carbonate ($MgCO_3$), and hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$), can be

formed in applications using water. Magnesium hydroxide is commonly known as brucite but may also precipitate as amorphous magnesium hydroxide. Magnesium carbonate is known as magnesite (magnesium carbonate anhydrite) [15].

Magnesium hydroxide is the most common of magnesium scales. The magnesium hydroxide is formed in a series of the following reactions [13]:

$$CO_3{}^{2-} + H_2O_5 \rightarrow CO_2 + 2OH^-$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

Other magnesium containing deposit is magnesium silicate ($MgSiO_3$) and its hydrated form known as talc. Possibly less known magnesium containing minerals also include iowaite [Mg_6Fe_2 $(OH)_{16}$ $Cl_2{\cdot}4H_2O$], new beryite ($MgHPO_4{\cdot}3H_2O$), serpentine ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$), merille [$Ca_{18}Na_2Mg_2$ $(PO_4)_{14}$], and other phosphates [$Mg_3(PO_4){\cdot}Mg(OH)_2$, $Mg_3(PO_4)_2{\cdot}8H_2O$, and $Mg_3(PO_4)_2{\cdot}22H_2O$].

The formation of magnesium scales is affected by a number of parameters. The rate of magnesium hydroxide crystallization in seawater depends on temperature, pH, concentration of bicarbonate ions, the development of carbon dioxide, magnesium ion concentration, and total dissolved solids. It has been noted previously that magnesium hydroxide supersaturation is pH dependent and that brucite is formed at a higher pH [21–23]. The effect of temperature is important in the case of nesquehonite, which occurs mainly at temperatures below 42°C, and hydromagnesite, which formed at temperatures between 60 and 90°C [23]. Magnesium hydroxide is a salt of inverse solubility, generally formed at temperatures above 95°C, mainly because of the increased formation of hydroxyl ions at such high temperatures [13].

The two alkaline scales (magnesium hydroxide and calcium carbonate) are closely related, and the presence of magnesium affects the formation of calcium carbonate. It has already been reported that the presence of dissolved magnesium favors the formation of aragonite compared to other polymorphs, with magnesium concentrations in seawater explaining the presence of aragonite rather than calcite when seawater is used [23].

2.2.4 Silica Scales

Large amounts of silicon dioxide and many silicate minerals are present in the Earth's crust, resulting in high concentrations in natural environments. They can be in a soluble form (silicic acid, soluble silicates) or in an amorphous state (colloidal silica) [6]. The solubility of crystalline silica (quartz) is quite low with 5–6 mg L^{-1} at 25°C and pH < 9 with the solubility of amorphous silica ranging from 120 to 150 mg L^{-1} at 25°C and pH $<$ 8–8.5. Amorphous silica is usually classified as dissolved (reactive), colloidal (nonreactive), and particulate (suspended) silica [24]. Ning [25] states that natural waters may contain dissolved and suspended silica concentrations that subsequently form on the surface of boilers, RO membranes, and

cooling towers in the form of deposits and scales that may include layers of glass, gels, powders, or nanoscopic particles virtually "invisible." Fouling of silica in water treatment equipment has been dealt with since the earliest developments in industrial water chemistry. As with the previous types of scales, it was reported that a SiO_2 scale layer 0.5 mm thick results in a 90% decrease in heat transfer [16]. Colloidal silica that enters equipment with the feed water can then settle on the boiler tubes or turbines in the form of silicates including SiO_2, $Na_2SiO_3 \cdot 9H_2O$, $NaFeSiO_6$, or $Mg_6[(OH)_8Si_4O_{10}]$ that are not soluble in water and extremely difficult to remove and therefore resulting in losses in turbine efficiency and capacity [26].

Ning [25] has described that "reactive" and "non-reactive" silica in water has a broad spectrum of molecular sizes ranging from silicic acid monomer ($Si(OH)_4$) to dissolved oligomeric forms, through the colloidal polymer suspensions and optionally in the form of silica $(SiO_2)_n$ of silicate particles, n representing very large numbers. If metal hydroxides such as aluminum, iron, magnesium, and calcium are incorporated during dehydration polymerization reactions, metal silicates are formed. It is widely accepted that the polymerization of silica monomers is the formation mechanism of amorphous silica deposits [6, 27].

According to Ning, monomeric silicic acid (the "reactive silica") is the predominant dissolved silica species found in natural waters with concentrations varying from 1–3 mg L^{-1} in mountain lakes to 50–300 mg L^{-1} in well waters in oil production fields. The silicic acid concentration in seawater is reported to range between 1 and 10 mg L^{-1} and is unregulated in municipal drinking water [25].

2.3 Influence of Scale on Industrial Processes

Scale formation affects most industries, as it can occur in a number of industrial processes, such as heating or cooling, desalination, and oil production. Boilers, cooling towers, pipes, tubes, and other equipment used in water-intensive processes pose serious problems, often hampering the overall process and increasing production costs due to associated maintenance costs [28]. The severity of the problem will vary depending on the composition of the water and the operating conditions. The formation of a deposit or layer can take weeks, even months or shorter, leading to major operational problems. This formation of deposits or scale can lead to reduced flow and heat transfer; this leads to additional maintenance or even equipment failure and increased operating costs, not to mention that the deposits formed on the heat transfer surfaces will significantly degrade the performance of the heat exchangers and can lead to a complete failure of the equipment, the mineral deposits affect the nuclear center; chemical, food and beverage industry; the oil and gas industries.

The major sources of concern are cooling water and associated processes due to widespread use in many industries. During cooling applications, flaking is caused by solids concentration, temperature changes, and pressure drop [10]. The other type of recirculating cooling system is an open recirculating system in which water is continuously reused by cooling probably of the greatest interest here. Such systems

are frequently used in large central utility stations; in chemical, petrochemical, and petroleum refining plants; in steel mills and paper mills; and in all types of processing plants [21]. Unfortunately, these systems also have the greatest potential for all types of problems, including fouling due to the excessive amount of mineral ions present in the water flowing through the system at high temperatures and a compliment constant fouling potential when replacing evaporated steam. The main types of scales that form in these types of systems include calcium carbonate, calcium sulfate, calcium phosphate, and magnesium silicate [21]. The formation of scale is a major problem in areas such as energy production, including geothermal energy. This process offers many advantages because it is renewable, clean, safe, and flexible, but to make production competitive with other energy resources such as natural gas, it is necessary to minimize operating costs. In this case, the mineral deposits not only reduce the capacities of the wells but also the heat exchange zones, thus limiting the degree of use of the heat transported by the fluids [29].

In many industries, such as mineral processing, increasing scarcity of freshwater and stricter environmental regulations are leading to a mandatory increase in the use of recycled water, leading to more problems with mineral scale formation [30]

3 Scale Inhibition by Chemical Additives

In the face of scale formation problems, several chemical methods based on the use of scale inhibitors have been largely effective [31–33]. Admitting the appearance of crystals as fatal, this treatment directly attacks the time and type of germination. For this purpose, products are used which delay the appearance of the seeds (germination time longer than the residence time of the water in the circuit) and promote the formation of little adherent crystals (homogeneous germination) and/or which decrease the growth rate of crystals [1].

The term “tartrifuges” refers to substances that have one or more of these properties. The tartrifuge effect has been known for a long time. Also, the search for new tartrifuges and their development still remains an approach marked by certain empiricism. For this reason, it is important to specify test conditions in which the effectiveness of a tartrifuge can be appreciated.

3.1 Classification of Different Tartrifuge

The big family of tartrifuges is growing every day, which does not allow us to give an exhaustive list of all the products on offer. However, most of these products can be grouped into families with a common grouping or structure that is the basis of the properties of the tartrifuge. By limiting ourselves to the most classical and the most used, this classification is represented according to Fig. 6.

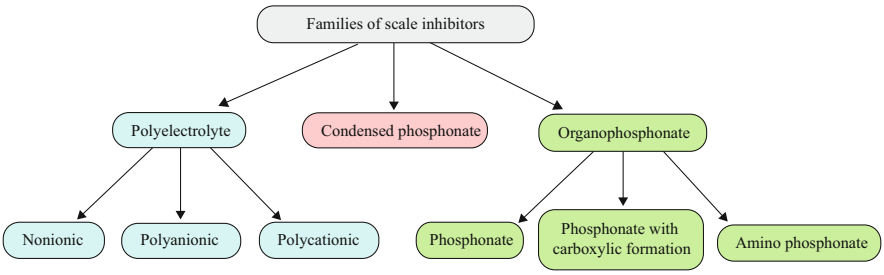

Fig. 6 Classification of different families of scale inhibitors

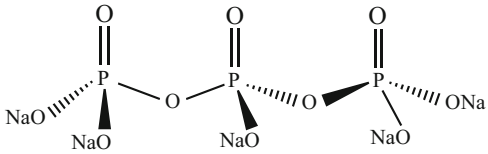

Fig. 7 The structural formula of sodium tripolyphosphate

3.1.1 Condensed Phosphates

These products whose properties are known for a long time and which are widely used in Europe, particularly in the formulation of washing powders, hydrolyze easily above 70°C and give orthophosphate (PO_4^{3-}), which once released into the natural environment is considered to be the main cause of the eutrophication phenomena in aquatic environments. In the late 1960s, these products were replaced by organophosphonates.

Sodium tripolyphosphate is the most used. Its structural formula is given in Fig. 7.

3.1.2 Organophosphonates

They are characterized by one or more groups associated with an organic radical. The most used are:

(a) *Phosphonates*: These compounds have an advantage over polyphosphates since the CP bond of 1.87 Å length is more hydrolysis resistant than the PO bond of 1.5 Å in length, and they are easily biodegradable. On the other hand, they have better stability in the presence of chlorine. The best product is 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP)

(b) *Phosphonates with carboxylic function*: As the name implies, they are composed of two functional groups: $-PO_3H_2$ and -COOH. These acids have remarkable resistance to hot hydrolysis in the presence or absence of bactericides/oxidants [34].

(c) *Amino phosphonates*: These compounds have both a $-PO_3H_2$ group and a nitrogen group [34].

3.1.3 Polyelectrolytes

A number of macromolecules have tartrifuge properties. We can distinguish:

(a) *Polycationics*: the most used correspond to quaternary ammonium compounds, for example, polyethylenimines. They are relatively little used because their effectiveness is low [35].
(b) *Polyanionics* are polycarboxylic or sulfonic acids [34, 35]. Let's mention the polyarilics, the polymetacrylics, the polyvinysulfonic ones, etc. [36–38].
(c) *Non-ionic*: they generally have less efficiency than anionics but much higher than cationic, for example, polyacrylamides [35].

3.2 Additional Work on Scale Inhibitors

Several types of scaling inhibitors, mineral or organic, have proven effective and are already marketed. The inhibiting effect of metal ion scaling (Cu^{2+}, Zn^{2+}) results in the formation of mixed carbonates of calcium and copper $Cu_xCa_{1-x}CO_3$ and zinc and calcium carbonates $Zn_xCa_{1-x}CO_3$. The mechanism of inhibition is based on the dehydration energy of Cu^{2+} and Zn^{2+} ions, which is greater than that of Ca^{2+} ions. This makes it possible to block the growth of the seeds formed [39–41]. Metallic iron ions play an important role in inhibiting scaling [42–45].

The most effective is 1,1-hydroxyethylenediphosphonic acid (HEDP) and is active at a concentration of 0.62 μmol L^{-1} (0.2 mg L^{-1}) [46]. A concentration of 9.1×10^{-8} M HEDP is sufficient to completely prevent crystal growth of calcium carbonate for more than 100 h [47].

Rosset and Douville [48] have shown that very low concentrations of organic phosphonate or polycarboxylate inhibitors inhibit the precipitation of calcium carbonate in EL Hamma's borehole water. Effective concentrations of these inhibitors are in the range of 1.1–1.5 mg L^{-1}.

Reddy and Nancollas [49] noted with the Crystal Growth Criterion that HEDP is the best among a range of phosphonates studied, for pure product concentrations of 0.5 ppm. The same result was obtained by Shiliang and Kan [50] when comparing a range of phosphonates as scale inhibitors.

The addition of 0.5–0.6 ppm amino trimethylene phosphonic acid "ATMP" inhibits calcium carbonate encrustation under chronoamperometric conditions [51].

A certain number of organic substances of natural origin have recognized tartrifuge power: this is the case for the metabolites of planktonic algae [52] and humic substances [53].

Abd-El-Khalek et al. [54] studied the antiscaling properties of sodium hexametaphosphate (SHMP) using electrochemical methods as well as a comparison between SHMP and polyacrylic (PPA). This study showed that SHMP is more effective against scale formation than PPA. They also studied the antiscaling properties of the palm leaf extract by chronoamperometry, impedance meter, and optical

microscope. The results showed that this extract could be considered as a precipitation inhibitor of $CaCO_3$ with a concentration of 75 ppm on salt water [55].

Gao et al. [56] synthesized the polyaspartic acid derivative (PASP-SEA-ASP) which showed excellent antiscaling properties in marine waters, with a 100% inhibition rate for the assay of 14 mg L^{-1}. This study demonstrates the potential of PASP-SEA-ASP for scale and corrosion inhibition in domestic and industrial facilities using seawater [56].

Touir et al. [57] based their study on the mechanism of action of sodium gluconate on ordinary steel. They evaluated the effect of temperature on the inhibition rate of sodium gluconate, which becomes more important with increasing temperature, which has been explained by the formation of a stable GS-Ca^{2+} complex.

Henghui Huang et al. [58] investigated the scale inhibition behavior of PESA with linear and hyper-branched structure against $CaCO_3$ and $CaSO_4$ scales that were evaluated using static scale inhibition method, and their ability to retard deposition of $CaCO_3$ was also examined. The experimental results showed that, for $CaCO_3$ and $CaSO_4$, the PESA with hyper-branched structure provides a scale inhibiting efficiency as high as 95.9% and 94.3%, respectively, at an inhibitor concentration of 15 mg L^{-1}.

4 Natural Inhibitors of Calcium Carbonate Scaling

Nowadays, one of the major axes of research is to find economic and environmentally friendly inhibitors. Research is underway for new environmentally compatible inhibitory formulations called "green inhibitors." A chemical is defined as "green" based on three criteria: toxicity, bioaccumulation, and biodegradation [35, 59]. The advance on green scale inhibitors is surprising, and numerous researches and discoveries have emerged. These green inhibitors may be petrochemical derivatives, or using "natural" organic molecules or plant extracts, such inhibitors could be used in various fields such as energy, water, and the food industry.

4.1 Petrochemical Derivatives

In this section, we took the initiative to make a selection of interesting green organic molecules from petrochemicals. In a recent article, Hasson et al. [60] reported that the most promising green scale inhibitors relied primarily on polyaspartic acid (PASP).

Polyepoxysuccinic acid (PESA) is a green scale inhibitor developed in the 1990s in the United States. Static experiments performed by Sun et al. at 30°C [61] showed that at a concentration of 10 mg L^{-1}, the scale inhibition ratio of PESA to $CaCO_3$ at three different concentrations of calcium (40, 100 and 200 mg L^{-1}) was greater than

90%. Liu et al. [62] showed that the anticalcination performance of PESA was higher than that of PASP. Therefore, PESA can be considered as an interesting alternative to PASP in water treatment technology. However, the performances of these molecules in field tests are limited [63, 64], and these molecules deserve to be studied further. However, it should be noted that the inhibition performance of PASP was studied in a pilot cooling water plant by Laborelec (Belgium) [64]. The effectiveness of the tested PASP would be similar to that of low molecular weight polyacrylate, a polymer used in some industrial processes. Laborelec has implemented a PASP scale control in a power plant [60]. PASP was developed in the early 1990s and has many applications, such as scale and corrosion inhibition, water softening, and green chemical formulations for detergent formulations [60]. PASP has non-nitrogenous, non-phosphorous, and biodegradable characteristics, which makes it a good green inhibitor. Indeed, the degradation properties of PASP have been examined by Thombre et al. [65] in the laboratory, Gao et al. indicated by the biodegradability of PASP prepared from poly(succinimide) by 70% thermal condensation in 1 month [66] Martinod et al. [67]. This study describes the effect of PASP on the desquamation of breasts reproducing the composition of the North Sea, where the concentration of Ca^{2+} was 14,225 mg L^{-1}. In addition, PASP significantly reduced the growth rate of $CaCO_3$ crystals by blocking the active sites of growth. Recently, Liu et al. used in diluted mineral water (concentration of Ca^{2+} 253 mg L^{-1}) at 80°C [62].

Carboxymethyl inulin (MIC) is a biodegradable and nontoxic polysaccharide-based polycarboxylate, obtained from inulin by chemical synthesis. It has significant inhibitory effects on the crystallization of calcium carbonate by the presence of carboxylic acid groups in its structure. Verraest et al. [68] investigated for the first time the effect of small amounts of MIC between 0.1 and 200 mg L^{-1} on the crystallization of calcium carbonate and concluded that MIC is a good inhibitor of $CaCO_3$ by changing the morphology of the crystals formed. They also showed that the MIC could influence the growth rate of calcium carbonate seed crystals by using constant composition experiments to study the growth kinetics of constant supersaturation seed crystals. The authors suggested that MIC molecules with a high degree of substitution and a high degree of polymerization were the most effective. Figure 8 presents the structures of some green antiscalant from petrochemistry.

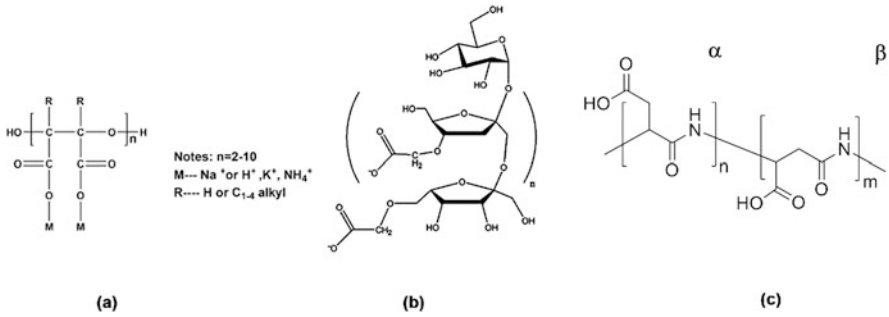

Fig. 8 Structures of some green antiscalant from petrochemistry: (**a**) polyepoxysuccinic acid, (**b**) carboxymethyl inulin, and (**c**) polyaspartic acid

4.2 Natural Organic Molecules

Environmental requirements impose many challenges in the field of water treatment. Thus, the concept of "green chemistry" has been proposed. In their study of the inhibition of the growth of calcite crystals by a humic substance [69], Hoch et al. [70] performed constant composition experiments in a sealed reactor. Solutions with equal molar concentrations of calcium and carbonate have been implicated. They quantified the kinetic effects of humic acid and fulvic acid from different sources on the crystalline growth of calcite by adding seed crystals to a supersaturated solution.

Kumar et al. [71] test the performance of pteroyl-L-glutamic acid (PGLU) scale inhibition by conducting static and dynamic experiments, a specific form of commercially available vitamin M. PGLU is found in almost all leafy vegetables and is essential for many bodily functions, including nucleotide synthesis. Scale inhibition at 100% [72, 73] was obtained by pot experiments at 70°C with 120 mg L^{-1} PGLU. The synthetic waters tested were representative of those found in an oil field at sea. The waters contain high amounts of calcium and bicarbonate. At 90 and 110°C, higher concentrations of PGLU, between 160 and 200 mg L^{-1}, were required to inhibit the formation of the latter result which was confirmed by dynamic tube blocking tests performed at 110°C, where the minimum concentration of PGLU for scale inhibition was 160 mg L^{-1}. The authors suggested using FTIR, XRD, and SEM that scale inhibition occurred by formation of a soluble complex with calcium ions and deformation of $CaCO_3$ crystalline morphology. They concluded that PGLU could be an excellent green chemical for scale inhibition in oil wells.

The authors have shown that certain hydrophobic aquatic organic acids derived from higher plants in the Florida Everglades were able to reduce the rate of calcite growth from a concentration of 0.2 mg L^{-1}. The growth of calcite was almost completely inhibited with a concentration of 5 mg L^{-1} in dissolved organic matter. An SEM study suggested that crystal growth sites were blocked by adsorbent ligands. In a recent work, Gauthier et al. [74] investigated the calcium carbonate scale ability of humic acid in synthetic water (100 mg L^{-1}) at 35°C, purchased as sodium salt. Humic acid also had a significant effect on scaling at a concentration as low as 0.2 mg L^{-1}. The associated efficiency was 78%, as determined by the resistivity response of the FCP. This work may explain the ability of raw rivers to scale, depending on water quality and season, flow [74]. These results could have an impact on many industrial facilities supplied with raw river water, knowing that humic substances are not used as inhibitors in technical applications.

Reddy et al. [75] used the constant composition technique to determine the growth rate of calcite in the presence of citric acid at 25°C and pH 8.55. A solution with constant calcite supersaturation was seeded with calcite crystals synthetically prepared in the presence of citric acid. Then they made a titration of Ca^{2+} ions remaining in solution order to follow the crystallization of calcium carbonate. The authors showed that citric acid exhibited only a moderate reduction in the growth rate of calcite crystals at concentrations as high as 10 mg L^{-1} and did not lead to a reduction in growth rate in the range of 0.01–0.1 mg L^{-1} (total calcium

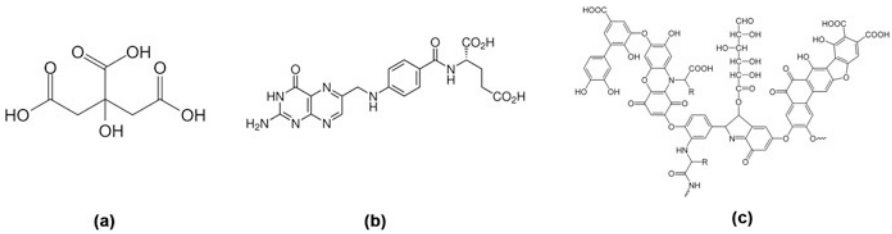

Fig. 9 Structures of some natural organic molecules: (**a**) citric acid [77], (**b**) pteroyl-L-glutamic acid [73] and (**c**) humic acid [76]

concentration 76 mg L^{-1}). This could be explained by the fact that citric acid is a linear polycarboxylic acid. The authors suggested that cyclic and rigid polycarboxylic acids, such as tetrahydrofuran-2-carboxylic acid or cyclopentane-tetracarboxylic acid, were much more effective in descaling [75].

The structures of some green antiscalant from petrochemistry are presented in Fig. 9.

4.3 Plant Extracts as Scale Inhibitors

The most promising alternatives to "natural" organic molecules are the use of plant extracts as scale inhibitors. Recently, the scale inhibition properties of plant extracts have been investigated.

Certain authors suggested that fig leaf extract may complex the cations present in the brine solution or disperse the suspended solids through adsorption. They carried out the same study concerning the olive leaf extract [76]. Indeed, olive leaves contain many phenolic molecules including oleuropein, the most abundant biophenols in olive leaves [77] and caffeic acid [78, 79] The concentration of the inhibitor was 10 mg L^{-1}. The authors assumed that these extracts were more effective than polyaspartic acid in preventing calcium carbonate formation. Indeed, the percentage of inhibition was 16.7% for both soy-based polymer and polysaccharides from sea weeds, whereas it was only 6.6% for polyaspartic acid.

A second strategy was to consider plants containing well-known compounds that can complex calcium cations. In this respect, polyphenols or polysaccharides, which have hydroxyl and/or carboxyl functional groups that interact with divalent ions such as Ca^{2+} or Mg^{2+}, are very good candidates. Abdel-Gaber et al. [80] studied the antiscaling properties of *Punica granatum* hull and leaf extract in alkaline brine at 25°C using conductivity measurements, electrochemical impedance spectroscopy, and chronoamperometry in conjunction with SEM, EDX, and optical microscopic examinations. According to chronoamperometry measurements, the current density increased from 87% when the concentration of the *Punica granatum* extracted from hull increased from 10 to 100 mg L^{-1}. This indicated that the extract is an efficient

antiscalant. It must be noticed that the aqueous extract at 50 mg L^{-1} concentration was still effective as a scaling inhibitor after 28 days of storage at 5°C.

Castillo et al. reported inhibition results of calcium carbonate scale performed with aloe vera in Venezuelan oilfields [81, 82]. The scale inhibitor was obtained by dissolving aloe vera gel in the water at a concentration in the range 5–50% wt/wt. This solution contains polysaccharides [83] that can complex with Ca^{2+} ions. Some field tests were carried out on Venezuelan oil wells with water containing high bicarbonate ions (total calcium concentration of 535.4 mg L^{-1}). Information on the inhibitory performance of aloe vera is unfortunately limited. Weekly inspections of coupons performed during field tests with inhibitors (20 or 30 days of duration) led the authors to define the recommended concentration for the inhibitor. The aloe vera solution was reported to provide very effective scale inhibition with a concentration of 15.2 mg L^{-1}. Pressure and temperature were also recorded through the entire field test and remained almost constant during the tests. This indicated the absence of precipitated solids in the system in the presence of aloe vera.

5 Research on Scale Inhibitors in Algeria

Unfortunately, the work done so far on the scale and scale inhibitors in Algeria are not many, but we cannot fail to mention some researchers who worked on ambitious projects. Figure 10 shows the location of hard waters already studied in Algeria (Bordj Bou Arreridj, Setif, Constantine, Tebbessa, Aïn M'lila, and Ouargla).

Ghizellaoui et al. [84] studied the effect the temperature and the concentration of NaOH and K_3PO_4 inhibitors on hard water in Constantine (Hamma), as well as the effect of CaOH, Na_2CO_3, and KH_2PO_4 concentration as inhibitors on Fourchi drilling water [85].

A new green inhibitor, based on the aqueous extract of *Paronychia argentea* (PA), for the reduction of $CaCO_3$ formation on metal surfaces, have developed by Belarbi et al. [86]. They tested the PA extract at different temperatures and with the addition of several biocides. The results concluded that 70 ppm is necessary to completely inhibit scale at 20 and 45°C. However, its efficiency decreases at 60°C [86]. Another green inhibitor has been tested by Kahoul et al. [87] scaling power of Hammam drinking water. The addition of olive leaf extract to the Hammam water even at low concentration (20 ppm) prevents scale coverage of the surface, indicating that the extract can be used as a good antiscalant.

Karar et al. [88] have published an interesting paper; this paper focuses on the study of the glutamic acid (GA) for reducing $CaCO_3$ scale formation on metallic surfaces in the water of Bir Aissa region. This study showed that at 30 and 40°C, a complete scaling inhibition was obtained at a GA concentration of 18 mg L^{-1} with 90.2% efficiency rate. However, the efficiency of GA decreased at 50 and 60°C. This team also investigated the inhibitive effect of citric acid (CA), sodium citrate (SC), and their mixture (CA–SC) on the $CaCO_3$ scale. The electrochemical study showed that CA provides a slight inhibition of $CaCO_3$ deposit at a concentration of 70 ppm

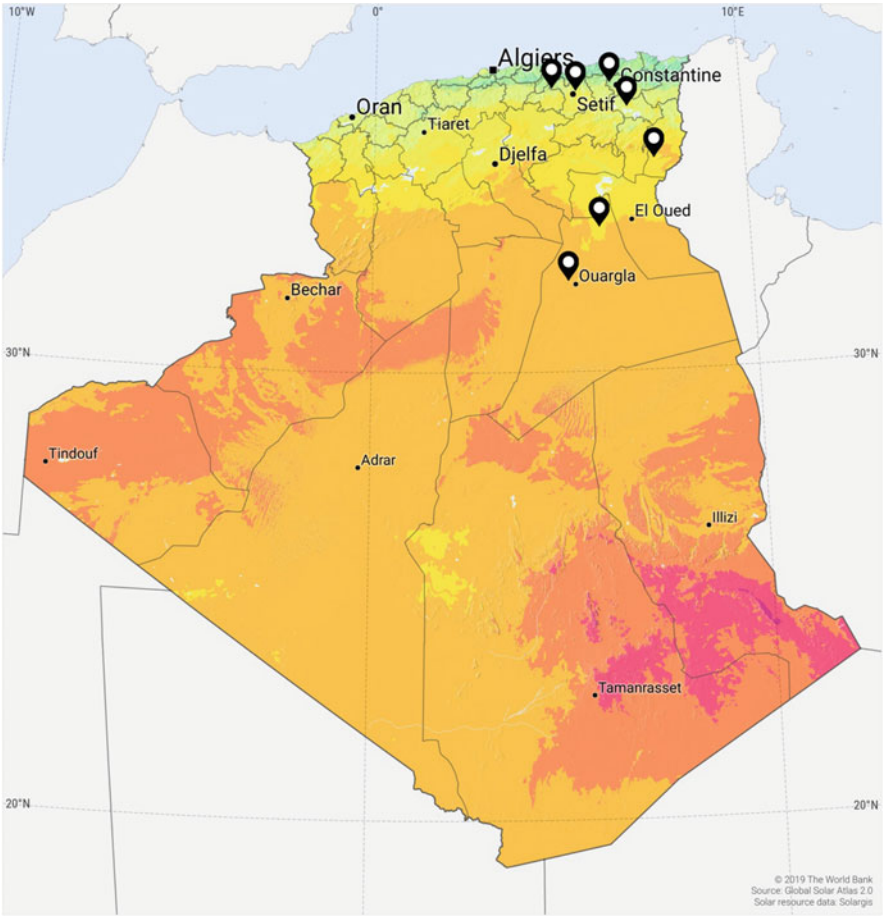

Fig. 10 Location of hard waters already studied in Algeria

on stainless steel surface. The use of SC alone inhibits very little formation of scale. The use of the mixture (50% of CA and 50% of SC) with small concentration led to a significant inhibition of the $CaCO_3$ formation [89, 90]. The works done so far on scale inhibitors in Algeria are given in Fig. 11.

The effect of mineral inhibitor on the precipitation of $CaCO_3$ in two Algerian groundwaters has been examined by Bendaoud et al. [91]. Chronoamperometry tests show that the antiscale treatment with mineral phosphates (KH_2PO_4) is more efficient for the Hamma (Constantine) than Negrine water (Tebbessa) with 2 mg/L. Tested inhibitors affect strongly the nucleation growth kinetics in the case of Hamma water and only the scale compactness in Negrine water. This was attributed to the difference in the chemical composition of the studied waters.

Djallal et al. [92] studied the electrochemical behavior of a carbon steel electrode against scale of barium sulfate. Tests conducted on water in the absence of scale

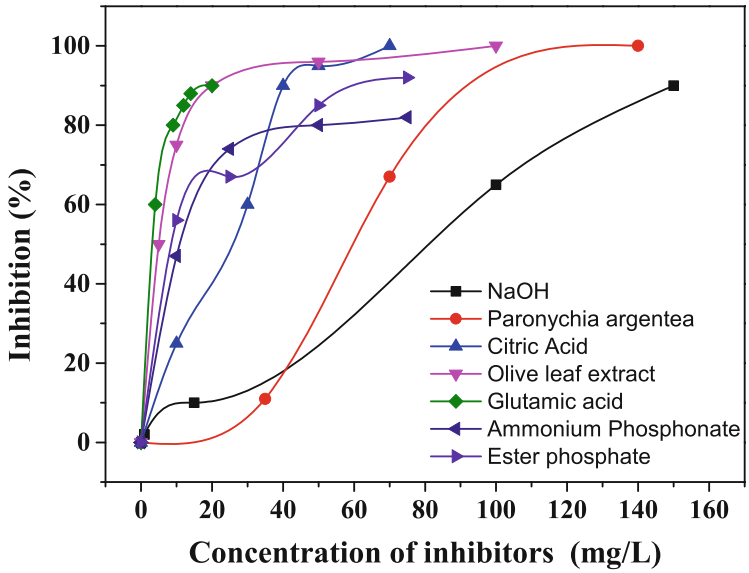

Fig. 11 The works done so far on scale inhibitors in Algeria [84–89]

inhibitors revealed the formation of a thick layer on the surface composed mainly of barium sulfate $BaSO_4$. Scale of barium sulfate naturally forms and evolves with immersion time. In the presence of inhibitors, the electrochemical impedance spectroscopy spectra show a decrease in the resistances and reveal that this inhibiting effect is a tendency to the formation of small quantities of precipitated barite solid on the surface of the electrode and that their effectiveness of inhibition increases with increasing concentration. This study shows that the inhibitor (phosphonate) is much effective at a low dose and at a high concentration. Its efficiency is limited because of the apparition of the micelles. However, the polyacrylate combined with phosphate ester has a satisfying inhibiting effect which increases with increasing of inhibitor concentration. Figure 10 shows the location of hard waters already studied in Algeria.

6 Conclusion

In recent years, many efforts have been made to generate green inhibitors, either from plant extraction or by using natural organic molecules. Green inhibitors obtained from natural products, especially by exploring the international pharmacopoeia, are clearly a growing field. Such green inhibitors could be advantageously used in situations where the use of organic materials would be limited by environmental regulations and/or application difficulties (i.e., toxicity). The Algerian

researchers are not sparing themselves to find new inhibitors of nature and health, knowing that the country is full of inexhaustible resources and new discoveries are in prospect.

7 Recommendations

Scale in hard water is a major concern for industrial processes and domestic installations. Undesirable scale deposits cause many technical problems with serious safety and economic consequences, such as:

- Total or partial obstruction of pipes leading to a decrease in the flow velocity
- The reduction of heat transfer due to the precipitate of calcium carbonate whose conductivity is 15–30 times less than steel
- The clogging of the filters

Energy production in nuclear power plants is often limited by scale in cooling towers. In Great Britain, non-productive expenses related to scaling have been estimated at 600 £ million a year. These same expenses are about 1.5 billion euros per year in France. Therefore, it is important to establish appropriate methods to study this phenomenon and find effective ways to combat it.

This study aims to shed light on the phenomenon of scaling and inhibitors that can fight or reduce the formation of scale on industrial and domestic facilities, among the recommendations necessary to minimize this phenomenon:

- Make a complete study on the phenomenon of scaling in the entire territory of Algeria, and educate industry and the government on the risk of scaling and the use of harmful scaling inhibitors.
- Focus research on more economical and environmentally friendly green inhibitors based on toxicity, bioaccumulation, and biodegradation.
- Improve the approach to the study of scaling in Algeria, look for new hard water sites to test inhibitors, and reduce the risk of scaling.

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