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Effect of temperature on the efficiency of inorganic phosphate used as antiscaling inhibitors

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Abstract

Scaling is a very widespread and inevitable problem in systems and equipments supplied with natural waters. Scale deposits are compact and adherent to the walls of water distribution piping and industrial or domestic installations causing several technical and economical problems. Hamma drillings represent an important water resource which feed most of the Constantine city with drinking water and also used for factory constructions and agronomic implantation. Nevertheless, this water is a scale forming water because of its high hardness (59°F). The present investigation is a contribution to fight against this scaling phenomenon by inhibition process using mineral phosphates (KH_2PO_4 and polyphosphates). Scaling tests were performed using the chronoamperometric method. It was shown that the scaling power increases with temperature and decreases with the addition of low concentrations of tested inhibitors. It was also concluded that the used polyphosphate is more efficient than KH_2PO_4.The electrode scaling is blocked for more than 30min at 30°C in presence of 2mg/L of monophosphate and only 0.5mg/L of polyphosphate. For high temperature (50°C), these two inhibitors seem also to be effective with 3 and 2mg/L for monophosphate and polyphosphate, respectively. So, scaling phenomenon generated by Hamma water can be prevented using phosphate inhibitors.

KEYWORDS: Scaling, electrochemical inhibition, time of scaling, residual current, inhibitors of scaling, temperature.

1. Introduction

Scaling in natural hard water is a major concern in different facets of industrial processes and domestic installations [1]. Undesirable scale deposits often cause numerous technical and economical problems such as total or partial obstruction of pipes leading to a decrease in flow rate[2]; reduced heat transfer as calcium carbonate precipitate is 15 to 30 times less conductive than steel; seizure of valves and clogging of filters, etc. In nuclear power plants, the power produced are often limited by scaling in cooling towers.

The sites of our study is natural water of Hamma, is known as major water resource that supply a large part of Constantine city with drinking water and also used for industrial and agricultural implantations. The major disadvantage of this water is that it has a very high hardness about 59°F. The high hardness of Hamma water involves consequences inevitable and undesirable by the formation of compact and adherent deposits on metallic or non-metallic surfaces, a scale inhibitor treatment to treat this hardness is obligatory.

The studies applied to the phenomenon of precipitation of calcium carbonate scaling are many, electrochemical methods [3, 4, 5], thermal or chemical methods [6].

The use of phosphate containing additives also prevents the deposition of calcium carbonate scale on pipes walls in the distribution system, in boilers and in hot water lines by sequestering calcium and inhibiting calcium carbonate (calcite) precipitation.

In this work, our study concerns the chemical treatment of hard water of Hamma by inorganic phosphates (KH_2PO_4 and Polyphosphates) which have long been recognized as inhibitors of calcite precipitation [7-14] and all of the authors shown that the inhibition of scale of calcite precipitation is due to the adsorption of the spices of inorganic phosphates onto calcite.

The objective of the present study is investigating the evaluation of the scaling power of raw Hamma water; studying the effect of chemical inhibitors (KH_2PO_4 and polyphosphates) and evaluation of the influence of temperature on the scaling power of the Hamma water raw and treated with inorganic phosphates (KH_2PO_4 and polyphosphates) using the chronoamperometric method.

2. Materials and methods

2.1. Principle of the Chronoamperometric method

The electrochemical techniques are founded on the controlled formation of calcium carbonate deposit on a working electrode through the electrochemical reduction of the dissolved oxygen [15, 16] (R1). Potential is imposed to a negatively value (-1V/ECS).

$$1/2O_2 + H_2O + 2\acute{e} \longrightarrow 2OH^- \qquad \text{R1}$$

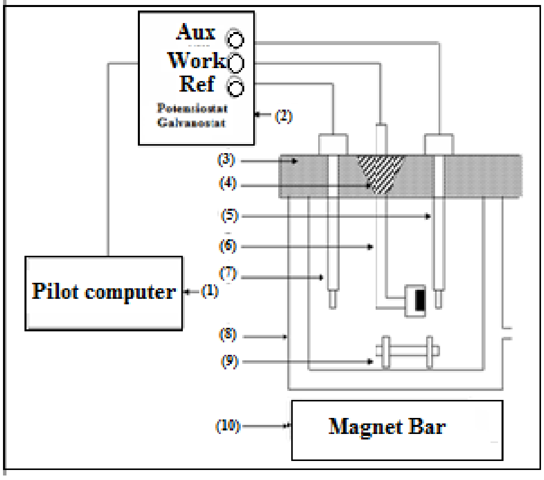
Hydroxyl groups, which are generated by this reaction, induce a strong increase of the pH in the immediate and involving the formation of CO_3^{-2} (R2) .The solubility product $(Ca^{2+})(CO_3^{2-})$ therefore increases there is precipitation of $CaCO_3$ (R3) on the electrode which becomes insulating.

$$2OH^- + 2HCO_3^- \longrightarrow 2CO_3^{2-} + 2H_2O \qquad \text{R2}$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s) \qquad \text{R3}$$

2. 2. Equipment used

Accelerated scaling is an electrochemical technical which determines the power scaling of water by controlled precipitation of calcium carbonate [17]. The chronoamperometric experiments were performed in the natural water of Hamma using a classical three-electrode cell. The working electrode is made of Steel XC10 with 1.00 cm^2 area. The electrode surface was polished with silicon carbide paper (P #400), rinsed thoroughly with pure water and carefully dried. Potential was measured versus the reference saturated calomel electrode (SCE). A platinum electrode was used as counter electrode and a potentiostat was connected to the three electrodes. Work temperature was maintained using a double glass wall recipient. Its large volume (500 ml) allowed avoiding a significant variation of species concentration during the formation of the deposit.



1-Pilot computer equipped with software
2-Potentiostat-galvanostat
3-Cover electrode holder
4-Door plug-sample
5-Platinum electrode
6- Working electrode
7- Reference electrode
8- Thermostatted cell
9- Magnet bar
10-Magnetic stirrer

Figure 1: Chronoamperometry experimental device.

3. Results and Discussion

3. 1. Water quality of Hamma

The results of the physicochemical analyze of Hamma water are given in Table 1:

Table 1: Physicochemical analysis of the water of Hamma

Parameters	Hamma water (HW)
Temperature (°C)	32
pH	6.95
Conductivity (mS/cm)	0.9
HCO_3^- (mg/L)	517
Cl^- (mg/L)	170
TH, (mg/L $CaCO_3$)	590
Ca^{2+} (mg/L)	160
Mg^{2+} (mg/L)	46

According to the results of analysis of the water of Hamma, it should be noted that this source is mineralized and present an important hardness.

3. 2. Chronoamperometric Study of raw water of Hamma at 30°C

To determine the scaling power of raw water of Hamma, we used the electrochemical method of accelerated scaling to a negative potential imposed at -1V relative to a calomel reference electrode saturated KCl. The progressive occupancy of the metal surface by the insulating layer reduces the current intensity down to zero for a fully compact layer or to a small value for a porous layer. Therefore, the time variations of the current intensity (chronoamperometric method) can be used empirically as an indicator of the scaling rate [15, 18].

Figure (2) shows the shape of the Chronoamperometric curve of raw water of Hamma. From this curve, we can determine:

* The scaling time (t_E) of raw water of Hamma which is 9.7min

* The residual current (I_R) of raw water of Hamma which is 0.044mA.

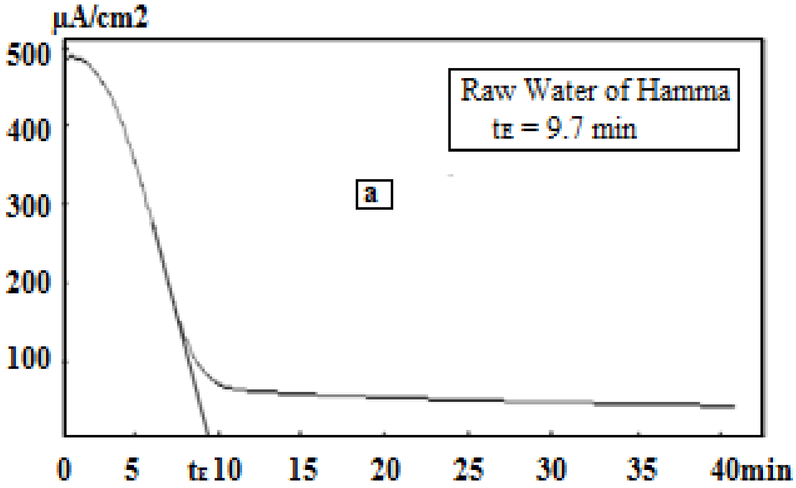


Figure 2: Chronoamperometric curve of Hamma raw waters at 30°C

According Ledion [15], Recognizing that the hardness of the Hamma water is 59°F. We can classify the scaling power of water of Hamma by scaling time and the scaling index of raw water of this source. The index of scaling is defined by:

$$I_E(min^{-1}) = \frac{1000}{t_E(\text{min})}$$

- 100 < I_E < 1000: extremely scale-forming water.
- 15 < I_E < 100: very scale-forming water.
- 5 < I_E < 15: medium scale-forming water.
- 0.5 < I_E < 5: slightly scale-forming water.

As water of Hamma present time scaling t_E of 9.7min, calculating of the scaling index gave a value of 103 min^{-1}. So we can classify water of Hamma as extremely scale-forming water.

3. 3. Treatment of Water of Hamma at 30°C

In order to treat water Hamma to reduce their power scaling, and at the source temperature, water of Hamma was treated with two types of inorganic phosphates: KH_2PO_4 and polyphosphates at increasing concentrations and we operate a chronoamperometric study to evaluate the inhibitory effect of treatment (Figure 3 and 4).

The study of these chronoamperometric curves shows that the addition of 0.1mg/L of KH_2PO_4 in water of Hamma, the scaling time increases to the value of 17min with respect to time scaling of the raw water (t_E = 9.7min). As against, adding of polyphosphates to water of Hamma shows that this inhibitor begins to retard scale formation by increasing the time scaling from an addition of 0.04mg/L of polyphosphate to Hamma water. The values of the time scaling, the residual current and scaling index of each scaling accelerated test of the water of Hamma treated by inhibitors KH_2PO_4 and polyphosphates are summarized in Table 2.

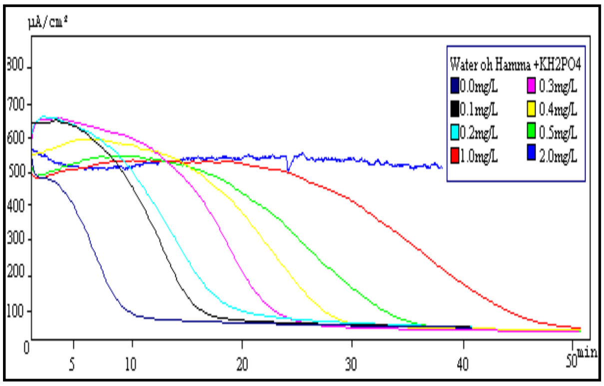


Figure 3: Chronoamperometric curves of water of Hamma treated with different concentrations of KH_2PO_4 at 30°C

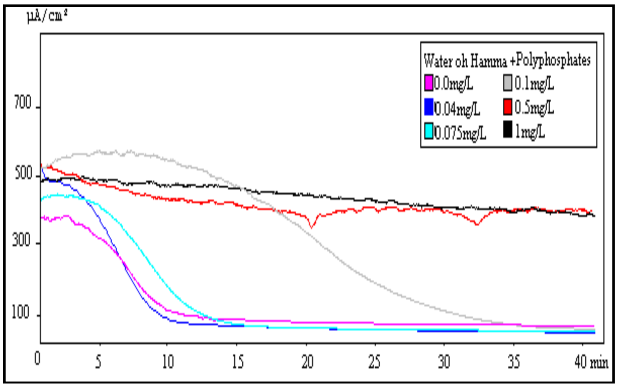


Figure 4: Chronoamperometric curves of water of Hamma treated with different concentrations of Polyphosphates at 30°C

Table 2: Time scaling, the residual current and index scaling of chronoamperometric curves of water of Hamma treated with different concentrations of the KH_2PO_4 and polyphosphates at the source temperatures 30°C.

Inhibitors	Concentrations Of inhibitors (mg/L)	t_E (min)	$I_R .10^{-6}$(A)	$i=1000/t_E$(min)
KH_2PO_4	00	09.70	50.00	103.09
	0.1	17.00	38.50	58.82
	0.2	19.40	38.50	51.54
	0.3	23.33	23.07	42.86
	0.4	29.33	33.33	34.09
	0.5	35.00	30.70	28.57
	1	45.00	-	22.22
	2	∞	-	-
Polyphosphates	00	09.70	50.00	103.09
	0.04	11.40	60.00	87.71
	0.075	12.00	36.00	83.33
	0.1	30.00	53.00	33.33
	0.5	∞	-	-
	1	∞	-	-

From the values of the scaling time and the residual current deducted from accelerated scaling curves performed on the treated water of Hamma with KH_2PO_4 and polyphosphates we find that:

The scaling time increases with increasing concentration of each inhibitor up to complete inhibition (calcium carbonate does not adhere to the electrode steel); The residual current varies with the increase time scaling and this variation depends on the quantity of scale deposited on the working electrode.

We can say that the addition of inhibitors KH_2PO_4 and polyphosphates reduced the scaling power of water of Hamma at very low concentrations of additions.

The application of treatment of water of Hamma with the inhibitor KH_2PO_4 increases the scaling time from the addition of concentration of 0.1mg/L. As against, polyphosphates treatment influences the scaling power by increasing the time scaling of water of Hamma from the addition of concentration of 0.04mg/L.

The mode of action of inorganic phosphates on the inhibition of $CaCO_3$ is: inorganic phosphates are selectively adsorbed on the growth sites of calcium carbonate crystals therefore; they slow down or block the precipitation of calcium carbonate [19].

In the case of KH_2PO_4 inhibitor, Lin and singer (2006)[14] have expected that negatively charged $H_2PO_4^-$ species should have less affinity toward the negatively charged calcite surface and should be extensively adsorbed. In fact, the convergence of the plot using $H_2PO_4^-$ might simply result from the linear correlation between ($H_2PO_4^-$) and ($CaHPO_{4(aq)}^0$). So the adsorption of $H_2PO_4^-$ on active crystal-growth sites and blocks them. The adsorbed phosphate sites have been widely accepted to be responsible for the reduced rate of calcite precipitation.

In the case of polyphosphate inhibitor, Lin and Singer (2005) [13] have confirmed the mechanism suggested for the inhibition effect of Polyphosphates. The adsorption of the polyphosphates on the calcite surface, blocks the active crystal growth sites. This adsorption is found by the complexation of dissolved calcium with anionic species of polyphosphates and this complex is the responsible spices which block the active crystal growth sites. Polyphosphates have a remarkably high affinity to be adsorbed on calcium carbonate nuclei and change their morphology and increase thus preventing property to adhere them to the surface and solid [20].That's way the effect of polyphosphate is more important than KH_2PO_4 in the treatment of hard water of Hamma.

3. 4. Effect of temperature on the raw water of Hamma

The accelerated scaling tests using the water of Hamma at various temperatures (20°C, 30°C, 40°C and 50°C), gave the chronoamperometric curves of the (Figure 5). From the slope of the linear part of the curves, it can be concluded that the scaling rate increases with temperature; it results of both the increase of the oxygen reduction rate [18] and the decrease of the $CaCO_3$ solubility. For this, the scaling time decreases from 26.2 to 6.3 min when the work temperature increases from 20 to 50°C (Table 3).

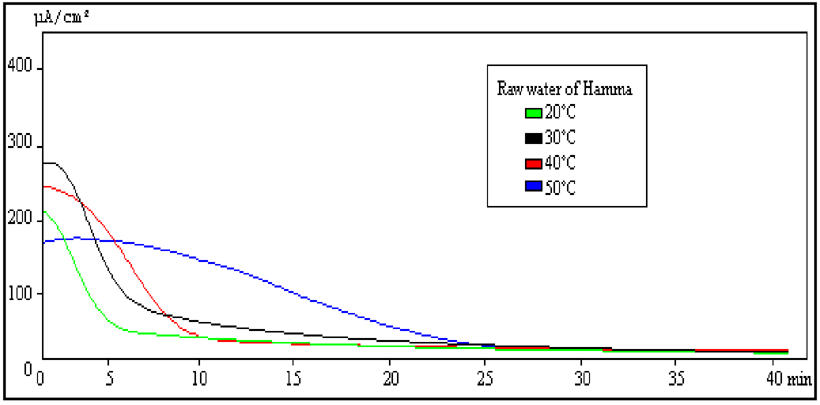


Figure 5: Chronoamperometric curves of raw water of Hamma at different temperatures 20°C, 30°C, 40°C, 50°C.

According to the pace of accelerated scaling curves registered at different temperatures of the raw water of Hamma, time scaling decreased by increasing of the temperature (Table 3).Here, it could be noted that the more significant effect of temperature was registered between 20°C and 30°C. Indeed, a sharply decrease of the scaling time from 26.2 to 9.7 min and increase of the scaling index from 38 to 103 min^{-1} were founded (Table 3). Raising the temperature increases the speed of oxygen reduction reaction and the chemical precipitation of tartar.

Table 3: Time scaling, residual current and the index scaling of the chronoamperometric curves of Hamma water at different temperatures.

Water of Hamma	Temperatures test (°C	t_E (min)	$I_R.10^{-6}$(A)	i=1000/t_E(min)
	20	26.20	40.30	38.16
	30	9.70	44.00	103.09
	40	7.40	46.00	135.13
	50	6.30	49.50	158.73

At the source temperature 30°C, water Hamma is classified as a highly scale forming water, and a lower temperature to 20°C, water of Hamma become medium scale forming. By against, at temperatures higher than the temperature of the source, the water is extremely scale forming.

3.5. Treatment of water of Hamma at 50°C

The effect of temperature on the chemical treatment of antiscalant water of Hamma by inorganic phosphate was followed by the method of accelerated scaling. This method was applied to the Hamma water treated by the KH_2PO_4 and Polyphosphtes at the same concentrations used in Table (3) but at a higher temperature of 50°C than the temperature of the source (30°C) in order to study the effect of temperature on the efficiency of antiscaling inorganic phosphate. Figure 6 include chronoamperometric curves of Hamma water treated with KH_2PO_4 at 50°C.

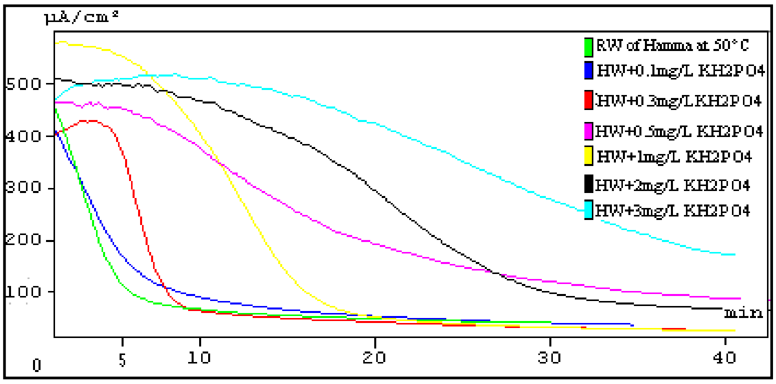


Figure 6: Chronoamperometric curves of water of Hamma treated with different concentrations of KH_2PO_4 at the temperature of 50°C.

The Chronoamperometric study of water of Hamma treated with polyphosphates is given in Figure (7) and the results of scaling time, residual currents and indexes scaling are shown in Table (4).

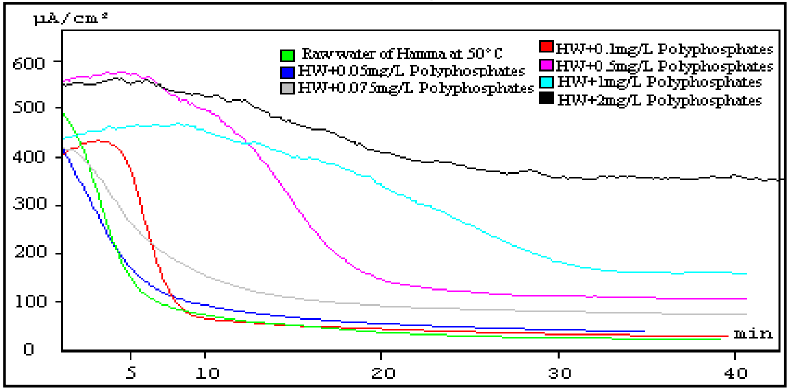


Figure 7: Chronoamperometric curves of water of Hamma treated with different concentrations of polyphosphates at the temperature of 50°C.

According to the results (Table 4), values of the time scaling of Hamma water treated with KH_2PO_4 and polyphosphate processing at 50°C for two inhibitors are less than those obtained at 30°C;
For a concentration of 2mg/L, the inhibition is total at 30°C for two inhibitors. As against the temperature of 50°C and at the same concentration, the scaling time t_E is 34.30min for KH_2PO_4 and more then for 55min for polyphosphates. So the scaling time and index scaling are reduced in higher temperature, this is due to the increasing of the solubility of all of the spaces.
However, some differences can be evoking:
• Firstly, the treatment of Hamma water with polyphosphate is more important than the treatment with KH_2PO_4; for same concentration of the tow inhibitors (0.1mg/L) t_E and i_E are more important in case of polyphosphate than their values in case of KH_2PO_4 for the tow temperatures.
• Secondly, the temperature does not affect the compactness of the formed scale layer on the metallic surface when precipitation tests were done using HW (I_R = 44 ± 4 µA) (Table 3). This was not the case for NW where the I_R (Table 3) increases from 32 (50°C) to 55 µA (50°C) for HW treated with KH_2PO_4 and 32 (50°C) to 152 µA (50°C) for HW treated polyphosphate with showing that the formed layer is more porous than the temperature increases and in case of treatment with polyphosphate is more pronounced because the values of I_R is more higher. We have observed from the values of the scaling time and index scaling of Table 05 that:
The effect of temperature is less important on the scaling time and index for the HW treated with polyphosphate; t_E and I_E varied by about 36 and 55% for HW treated with KH_2PO_4 and 36 and 70% in the case of HW treated with polyphosphate when temperature varied from 30 to 50°C (Table 5). The increase in temperature accelerates the reduction of oxygen dissolved in the hydroxide which results in the formation of calcium carbonate scale. Hard water is sensitive to changes in temperature as Hamma (30°C) and they become more scaling at a higher temperature (50°C) and their treatments require much higher concentrations than those used in the treatment at the temperature source.

Table 4: Time scaling, residual current and index scaling corresponding to the treated water of Hamma by KH_2PO_4 and polyphosphates at different concentrations at 50°C.

Inhibitors	Concentrations inhibitors (mg/L)	t_E (min)	$I_R .10^{-6}$(A)	i=1000/t_E(min)
KH_2PO_4	00	06.40	32.00	147.05
	0.1	07.70	33.40	129.87
	0.3	08.50	55.00	117.64
	0.5	17.00	33.80	58.82
	1.00	25.00	38.00	40.00
	2.00	34.30	54.00	29.15
	3.00	∞	-	-
Polyphosphates	00	06.40	32.00	147.05
	0.05	07.30	21.00	136.98
	0.075	08.50	42.00	117.64
	0.1	11.80	73.00	84.17
	0.50	21.10	101.60	47.39
	1	40.00	152.00	25
	2	∞	-	-

Table 5: Time scaling, residual current and index scaling corresponding to the treated water of Hamma by KH_2PO_4 and polyphosphates at different concentrations at 30°C and 50°C.

Inhibitors	Concentrations Of inhibitors (mg/L)	t_E (min) 30°C	t_E (min) 50°C	i=1000/t_E (min^{-1}) 30°C	i=1000/t_E (min^{-1}) 50°C
KH_2PO_4	00	09.70	06.40	103.09	147.05
	0.1	17.00	07.70	58.82	129.87
	0.3	23.33	08.50	42.86	117.64
	0.5	35.00	17.00	28.57	58.82
	1	45.00	25.00	22.22	40.00
	2	∞	34.30	-	29.15
	3	∞	∞	-	-
Polyphosphates	00	09.70	06.40	103.09	147.05
	0.05	11.40	07.30	87.71	136.98
	0.075	12.00	08.50	83.33	117.64
	0.1	30.00	11.80	33.33	84.17
	0.5	∞	21.10	-	47.39
	1	∞	40.00	-	25.00
	2	∞	∞	-	-

Conclusion

From the results obtained in this study:

-The use of the chronoamperometric method may characterize the scaling power of Hamma water raw or treated with inorganic phosphates at different temperatures by implementing the controlled formation of the calcium carbonate by the reduction of dissolved oxygen in water at potential negative imposed.

-The chronoamperometric study of the raw water of Hamma at the source temperature 30°C shows that this water has a scaling time t_E of 9.7min and a index scaling *i* of 103min^{-1} and by consequent Hamma water is classified as extremely scale-forming water.

The treatment of scaling of Hamma water by chemical inhibitors KH_2PO_4 and polyphosphates at the source temperature 30°C increases considerably the time scaling relative to the time scaling of the raw water.

This is the delay of the formation of scaling by the effect of inhibitors. The concentrations of KH_2PO_4 and polyphosphates increase in water of Hamma, the scaling power is reduced to total inhibition.

-The inhibitory effect of KH_2PO_4 on water of Hamma at a temperature of 30°C starting from the concentration of 0.1 mg/L, and total inhibition is reached at a concentration of 2 mg/L.

-The treatment of water of Hamma by polyphosphates shows that increasing the scaling time is obtained from an addition of 0.05 mg/L, and total inhibition is reached for addition of 0.5mg/L.

So, inorganic phosphotes (KH_2PO_4 and polyphosphates) are effective inhibitors for the sweetening of extremely scaling Hamma water. The inhibitory effect of polyphosphates is more pronounced on water Hamma because it reacts at lower concentrations.

-By increasing of the temperature of the raw water of Hamma, chronoamperometry shows that: the temperature of the raw water increase, the time scaling decreases to 6.4 minutes at 50°C by activation of the formation of calcium carbonate. As against, the temperature of the water of Hamma decrease and causes a decrease in scaling power of this water.

-The treatment of water of Hamma at a temperature of 50°C by the same inhibitors KH_2PO_4 and polyphosphates shows that the use of concentrations of 2mg/L of KH_2PO_4 and 0.5mg/L of polyphosphates cannot completely inhibit the formation of calcium carbonate, scaling inhibition can be achieved at an addition of 3mg/L of KH_2PO_4 and 2mg/L of polyphosphates.

So the treatment of the scale of hard water of Hamma with inorganic phosphates is especially effective for polyphosphates as they act at very low concentrations.

The application of chemical treatment of the water of Hamma by the KH_2PO_4 and polyphosphates is more effective at low temperatures with a low concentration, against at higher temperatures, the scale inhibition of hard water is applicable that 'at very high concentrations of inhibitors.

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