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Use of chronoamperometry for the inhibition of scaling in hard waters

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Abstract

The formation of scale on the surface of the drinking-water pipes in industrial plants or leads to clogging of pipes and causes a decrease in heat transfer .Several methods of assessing hard water scaling power exist, but the most commonly used to slow the formation of deposit of calcium carbonate is the addition of chemical inhibitors at low concentrations in water encrusting. In this work we used the electrochemical technique of chronoamperometry imposed potential that determines the evolution of the reduction current of oxygen through the electrode as a function of time in the absence and presence of inorganic phosphate (K_2HPO_4 and K_3PO_4) that an additional water Fourchi. According to the study chronoamperometric, Fourchi raw water is characterized by scaling time (t_E) of 23.5min and which is an index scaling (Ie = 42.5).Thus, we can classify the water of Fourchi is very scale-forming. In the presence of inhibitors, the risk of scaling is reduced. The time scaling and the residual current increase with the addition of inhibitors and the effective concentration for the inhibition of calcification of the water Fourchi is 3.5mg/L for K_2HPO_4 and 2mg/L for K_3PO_4.

Keywords: Scaling, Calcium Carbonate, inhibition, K_2HPO_4, K_3PO_4

Introduction

Scaling is related to the formation of deposits compacts and adherent calcium carbonate on surfaces metal or not. Scaling can contain other residues like algae, calcium sulphate, clays and the brucite $Mg(OH)_2$. But it is always the calcium carbonate which precipitates the first. Usually in the colloidal form, because its solubility is lower than that of others [1, 2].These calcium carbonate deposits which are observed on surfaces of the drains of the industrial facilities and domestic entrained of serious technical and economic consequences such that the obstruction of the drains, a thermal loss of effectiveness in boilers or them heat exchangers, the filling of the filters, etc [1, 3]. Different process (chemical, electrochemical) exists and makes it possible to deal with the problem of scaling.

The chemical treatment based on the chemical addition of compounds have the property remarkable to be adsorbed on the calcium carbonate germs and to modify their growth and their morphology for prevents like they adherent between them and on the surface of the solids they are the inhibitors of scaling, their effective concentration is very weak [4, 5, 6]. Electrochemical methods [7, 8]. Based on intensive training of a carbonate of calcium deposit to an indicating electrode by the reduction of dissolved oxygen.

In this study we determined the furring capacity of earthy water of Fourchi by chrono-amperometry and to study the effect of the temperature and the concentration of the inhibitor K_2HPO_4 and K_3PO_4 on the furring capacity of this water.

2. Materials and methods

The formation of calcium carbonate by electrochemical way was imagined by Ledion et al.,1985[9].The scaling accelerated by chrono-amperometry consists of the forced precipitation of calcium carbonate on the surface of an electrode carried to a negative potential about (-1V) compared to a reference electrode . The application of this negative potential entrained to the surface of metal, they following electrochemical reaction:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad R1$$

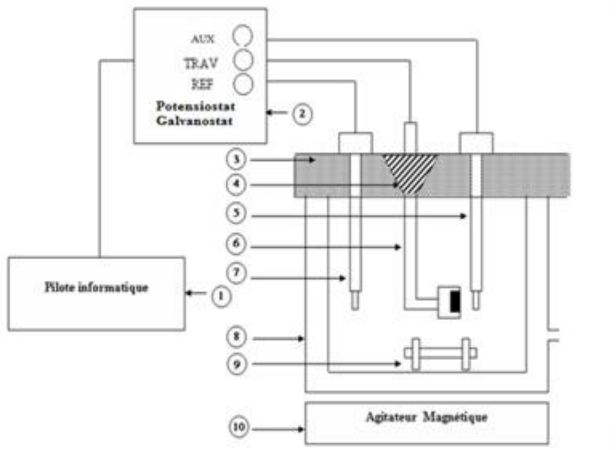
Thus, in the vicinity of the electrode [10]. it y' will have an increase in the pH due to the generation of ions OH^- and involving the CO_3^{2-} formation according to the reaction:

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

The product (Ca^{2+}) (CO_3^{2-}) increases and there is precipitation of $CaCO_3$ on the electrode.

$$OH^- + HCO_3^- + Ca^{2+} \longrightarrow CaCO_3\,(s) + H_2O \qquad R3$$

To carry out the tests of accelerated scaling the assembly of the Figure (1) is used.
Three electrodes are used: platinum electrode. The working electrodes were steel XC10with 1.003 cm2 area. The steel surfaces were polished [11] with silicon carbide paper (P400). Versus the saturated calomel electrode (SCE).The volume of water of Fourchi used is 400 ml. The solution is agitated by means of a bar magnetic. The solution under stirring (400 rpm) using a magnetic stirrer. Electrochemical experiments were driven under potentiostatic conditions using RADIOMETRE PGP 201 interface (Potentiostat/ Galvanostat (PG)) at -1 V/SCE controlled by a microcomputer.



1-Pilot computer equipped with software,
2- Potentiostat-galvanostat,
3-Cover electrode holder,
4-Doorplugsample,
5-Platinum electrode,
6- Electrode work: pellet steel XC10 (1.003 cm^2diameter) embedded in a resin chemically inert,
7-Electrode calomel reference electrode, saturated KCl,
8-Cell thermostatted glass 500ml capacity,
9-Bar magnet, 10- Magnetic stirrer.

Figure 1: Experimental arrangement.

3. Results and discussion

3.1. Physico-chemical characterization of water of Fourchi

We have the physicochemical results of analysis obtained on the subsoil water Fourchi, Table (1).

Table 1: Analyze water of Fourchi.

Parameter	The water of Fourchi
T, °C	20
pH	6.9
EC, mS/cm	1.80
O_2 dissolved, mg/L	8.21
HCO_3^-, mg/L	447
TH, mg/L $CaCO_3$	870
Ca^{2+}, mg/L	212
Mg^{2+}, mg/L	81.6
Cl^-, mg/L	510
SO_4^{2}-, mg/L	222

It should be noted that the water of Fourchi is quite mineral-bearing (EC = 1.8 mS/cm) and very charged in anion chlorur and the content calcium and magnesium is very high. The title hydrotimetric (TH) is 870 mg/L (TH = 87°F) what corresponds to very hard water.

3.2. Tests of accelerated scaling

3.2. 1. Waters of Fourchi

Chronoamperometric curves referring Hamma waters are presented in Figure 2 at 20°C. One plots the curve I= f (t). This curves exploited in order to define a time and an index of scaling. Time of scaling (t_E) defined by the intersection of the inflexion tangent with the time scale in abscissa (Figure 2). The index of scaling is defined by:

$Ie = 1000 / t_E$ (min)

This index makes it possible to classify water as follows:

- 100<Ie<1000: extremely scale-forming water.
- 15<Ie<100: very scale-forming water.
- 5<Ie<15: medium scale-forming water.
- 0,5<Ie<5: slightly scale-forming water.

According to (Figure, 2) we see that a waning of current to the course of time. The decrease of the current is due to the covering of the surface of the electrode by the crystals of $CaCO_3$ which make it gradually insulating. When the electrode is completely covered with calcium carbonate, the current decreases up to a value called the residual current I_R. This current measure the speed to which dissolved oxygen is tiny room to the electrode of work covered with the calcium carbonate deposit. More the deposit is compact and adherent minus oxygen can diffuse through this film insulating and more the residual current is weak [3].

One characterizes raw water of Fourchi by the time of scaling (t_E) which is of 23.5 min with an index of scaling (I_E = 42.5). Therefore, one can classify the water of Fourchi like a water very furring. The residual current (I_R) is weaker of 0.015mA indicates than the deposit is less porous thus, more compact.

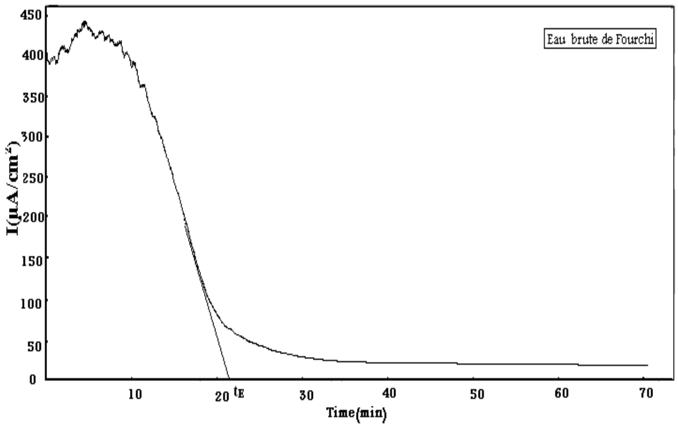


Figure 2. Chronoamperometric curve of Fourchi raw water at 20°C.

3.2. 2. Effect of the temperature on the scaling power

Scaling is much more significant hot than cold. This is in agreement with the thermodynamics of the carbonic system calco- carbonic ($CaCO_3$ - CO_2 - H_2O) [12]. Because the solubility of the carbon dioxide decreases when the temperature increases, calco-carbonic balance moves in the direction of precipitation of $CaCO_3$:

$$CaCO_{3(s)} + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^-$$

An increase in the temperature subjected tests of scaling accelerated to several influences: it increases the speed of the electrochemical reaction of the dissolved oxygen reduction (Eq 1), this increase in temperature causes an increase in ions OH^- which involves an increase in the pH to the interface of the surface of the electrode [3,13]. and the germs of $CaCO_3$ are formed with the interface of the surface of the electrode, it decreases the solubility and the coefficients of diffusion of dissolved oxygen.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (1)$$

The accelerated scaling of the water of Fourchi at various temperatures (T=20°C, 30°C, 40°C and 50°C), gave the chronoamperometric curves which are given in (Figure 3). For the water of Fourchi we see a reduction in the time of scaling of 23.5 to 7.1 min and increase in the index of scaling of 42.5 to 140.8 min^{-1} when the temperature increases 20°C to 50°C. The decrease of the time of scaling and the growth of the index of scaling are all the more significant when the temperature varies between 30 and 40°C and t_E fall of 21.4 up to 10.7 min and I_e increases by 46.7 to 93.4 min^{-1}, to see (Table, 2). It results from it that scaling becomes faster and that water becomes very furring. The residual current I_R decreases until the 9.25 µA when the temperature, increases the surface of the electrode is entirely covered with calcium carbonate. The weaker the residual current is plus the diffusion of the oxygen dissolved through the layer of precipitate is slow and more the deposit is compact and insulator.

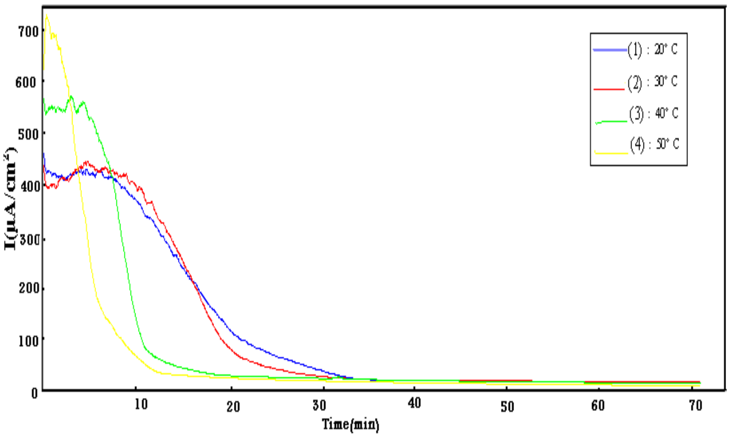


Figure 3. Chronoamperometric curves of raw water of Fourchi with differentes temperature.

Table 2: Scaling time, residual current of the chronoamperometric curves of the water of Fourchi at various temperatures.

Temperature (C°)	t_E (min)	Ir (µA)	I_e(min^{-1})
20	23.5	13.51	42.5
30	21.4	10.21	46.7
40	10.7	9.24	93.4
50	7.1	6.71	140.8

3.2. 3. Inhibition of scaling by K_3PO_4

Figure (4) represents the chronoamperometric curves of water of Fourchi at 20°C added with increasing concentrations of K_3PO_4. The time of scaling of raw water is 23.5 min and in the presence of K_3PO_4 we see an increase of time of scaling, with the introduced concentration of K_3PO_4 (Table 3). From 2 mg/L the time of scaling becomes infinite and the shape of the curve becomes a right, which represents the total inhibition of scaling. The calcium carbonate does not precipitate any more on the surface of electrode, the index of scaling decreases and water becomes fairly furring.

The residual current varies until reaching a high value of 178.42 µA starting from an addition of 2 mg/L of K_3PO_4, the deposit formed in the presence of K_3PO_4 is modified, it is more porous and less compact.

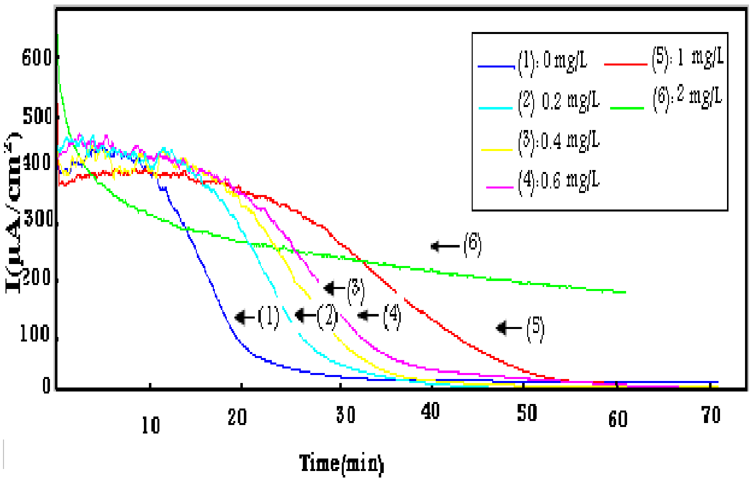


Figure.4. Chronoamperometric curves of Fourchi for an addition the different concentrations of K_3PO_4at 20°C.

Table 3: Time of scaling and residual current of the chronoamperometric curves of the water of Fourchi treated with K_3PO_4 with various concentrations with 30°C.

Concentration of K_3PO_4 (mg/L)	t_E (min)	Ir (µA)	I_E(min^{-1})
0	23.5	13.71	43
0.2	28.2	11.5	35
0.4	32.4	12.85	30
0.6	36.6	12.54	27
1	48.8	15.52	20
2	∞	178.42	-

3.2. 4. Inhibition of scaling by K_2HPO_4

Increasing concentrations of K_2HPO_4 were introduced with the water of Fourchi (0.5, 0.8, 1, 2, 3, 3.5) mg/L at 20°C. While following the intensity of the current function of time one obtained curves chronoamperometric of the water of Fourchi treated with K_2HPO_4.See (Figure 5). The growth of the time of scaling is weak between 0.5 and 1mg/L of K_2HPO_4, 26.3 to the 31.2 min, the inhibiting effect on the other hand appears starting from 2mg/L (t_E =46.3min) for K_3PO_4 the inhibiting effect is observed starting from 0.6mg/L. For an addition of 3.5 mg/L of K_2HPO_4 times of scaling become infinite, inhibition is total. The results obtained show that the inhibiting effect of K_3PO_4 more effective than K_2HPO_4. The residual current varies with the addition of K_2HPO_4 but starting from 3.5mg/L the current reaches a high value (179.26 µA) the deposit is porous and less compact. (Table, 4).

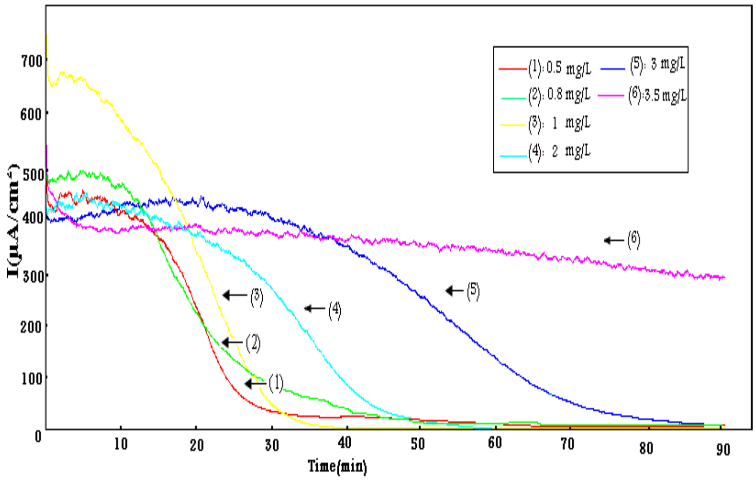


Figure 5. Chronoamperometric curves of Fourchi for an addition the different concentrations of K_2HPO_4 at 20°C.

Table 4: Time of scaling and residual current of the chronoamperometric curves of the water of Fourchi treated with K_2HPO_4 with various concentrations at20°C.

Concentration of K_2HPO_4 (mg/L)	t_E (min)	Ir (µA)	I_E(min^{-1})
0	23.5	13.71	43.1
0.5	26.3	12.42	38
0.8	29.4	11.32	34
1	31.2	11.84	32
2	46.3	12.42	21
3	73.9	12.62	13
3.5	∞	179.26	-

The mechanism of inhibit ion can be explained by the adsorption of the phosphate ions (PO_4^{3-}) on the calcite surface which blocks the site of growth and delays the precipitation of $CaCO_3$.The deposits formed in the presence of the phosphate ions are modified, they are more porous and less compact. There is a change of the morphology of the crystals [15]. The PO_4^{3-} form very soluble complexes with the ions Ca^{2+} and Mg^{2+} and slow down homogeneous and heterogeneous nucleation by sequestration [16]. But they act mainly on the growth of the germs of $CaCO_3$.

Conclusion

The results obtained show that:

- the scaling accelerated by the method of chronoamperometry made it possible to characterize the furring capacity of water. For the water of Fourchi (t_E = 23.5min) with an index of scaling (I_E = 42.5) at 20°C is classified like a water very furring. The harder water is plus the time of scaling is short and more the residual current is weak bus the deposits will be less porous thus more compact. The increase in the temperature supports the precipitation of calcium carbonate, the time of scaling becomes shorter and water becomes harder.
- to fight against the scaling of earthy waters we showed that it is enough to add 0.5 mg/L K_2HPO_4 or 0.1 mg/L of K_3PO_4. The effective concentration for obtaining a total inhibition of calcium carbonate deposit is 3.5 mg/L K_2HPO_4 and 2mg/L of K_3PO_4.

References

1. Rosset R., *Les procédés physiques antitartre: mythe ou réalité?* L'actualité chimique. 1-2: (1992) 125-148.
2. Dan Liu. *Research on performance evaluation and anti-scaling mechanism of green scale inhibitors by static and dynamic methods.* Thèse de doctorat école nationale supérieure d'Arts et métiers (2011).
3. Zidoune M., Khalil A., Sakya P., Colin C., Rosset R., *Mise en évidence de l'effet anti-incrustant de l'acid aminotris-(méthylènephosphonique) par chronoampérométrie et chronoélectrogravimétrie.* Electrochimie. C. R. Acad. Sci. Paris, t. 315, Série II (1992) 795-799.
4. Ghizellaoui S., Euvrard M., Lédion J., Chibani A., *Inhibition of scaling in the presence of copper and zinc by various chemical processes.* Desalination. 206 (2007) 185-197.
5. Lin Y. P., Singer P. C., *Inhibition of calcite crystal growth by polyphosphates*. Water Research 39 (2005) 4835–4843.
6. Chaussemier M., Pourmohtasham E., Gelus D., Pécoul N., Perrot H., Lédion J., Cheap-Charpentier H., Horner O., *State of art of natural inhibitors of calcium carbonate scaling.* Desalination, 356 (2015)47-55.
7. Khalil A., Colin C., Gabrielli C., Kheddam M., Rosset R., *Caractérisation du pouvoir incrustant d'une eau et évaluation de l'efficacité d'un traitement antitartre chimique par impédancemetrie et microscopie électronique à balayage. C. R. Acad. Sci. Paris* t. 316. serie II (1993) 19-24.
8. Rosset R., Douville S., Ben Amor M., Walha K., *Inhibition of scale formation by southern Tunisia geothermal water field experiments.* Revue des sciences de l'eau Rev. Sci. Eau 12/4 (1999) 753-764.
9. Ledion J., Leroy P., Labbe J.P., *Détermination du pouvoir incrustant d'une eau par un essai d'entartrage accéléré.* TSM l'eau, juillet – août 1985, pp 323-328.
10. Gabrielli C., Keddam M., Perrot H., Khalil A., Rosset R., Zidoune., *Characterization of the efficiency of antiscale treatments of water.* Part I. Chemical processes. J. Appl. Electrochem. 26 (1996) 1125-1132.
11. Perais J., Martin C., Ledion J., *Influence du brossage sur la réactivité des surfaces métalliques.* Matériaux et Techniques. Sept-Oct (1991) 19-26.
12. Roques H., *Fondements théoriques du traitement chimique des eaux*. volume 1. technique et documentation, paris (1990).
13. Ketrane R., Saidani B., Gil O., Leleyter L., Baraud F., *Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: effect of temperature and concentration.* Desalination 249 (2009) 1397–1404.
14. Lin Y. P., Singer P. C., *Inhibition of calcite crystal growth by polyphosphates*. Water Research 39 (2005) 4835–4843.
14. Lin Y.P., Singer P.C., *Inhibition of calcite precipitation by orthophosphate: speciation and thermodynamic considerations.* Geochim. Cosmochim. Acta 70 (2006) 2530–2539.
15. Tlili M., *Etude des mécanismes de précipitation du carbonate de calcium.* Application à l'entartrage. Thèse de doctorat de l'université Paris VI (2002).

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