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Hard Water Softening by Chronoamperometry

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Water distributed from the Hamma resource is supersaturated on carbonate of calcium, a not very soluble salt and a major component of tartar.

During their circulation in the network, these waters give rise to scaling phenomenon which involves a significant economic problem because of the low thermal conductivity of the solid layer which reduces the output of the exchangers of heat. Moreover, the increase of the thickness of tartar reduces the water flow and causes the seizing of the valves and taps.

The maintenance of the furred installations or the replacement of the drains is very expensive.

For this reason, several chemical and electrochemical processes were applied for the evaluation and the inhibition of the furring capacity of the earthy waters of Hamma which feed the town of Constantine with drinking water.

Electrocrystallization was executed on a steel electrode to study germination and growth of the calcium carbonate crystals.

The method of accelerated scaling was also considered in the presence of lime, sodium carbonate and soda.

The results indicated that water of Hamma is furring.

The use of the method of accelerated scaling and the follow-up of electrocrystallization gave satisfactory results.

1. Introduction

In the grounds of calcareous nature, the subsoil waters of Hamma become charged in significant concentrations of hydrogenocarbonate of calcium.

For a content of 60French degrees, water is known as very hard and must undergo a treatment of softening or decarbonation before use, because they deposit significant quantities of calcium carbonate during their circulation in the network of distribution.

Several methods of the evaluation of the furring capacity of a water were carried out these last years (Boulahlib-Bendaoud et Ghizellaoui, 2015, Chaussemier et al., 2015, Ghizellaoui et al., 2004, Ghizellaoui et al., 2005, Ghizellaoui et al., 2007, Ghizellaoui et Euvrard, 2008, Semineras et Ghizellaoui, 2015).

In this Study, first of all, the electrocrystallization was executed on a steel electrode to study germination and growth of the calcium carbonate crystals.

Then another electrochemical process (accelerated scaling) in the presence of lime, sodium carbonate and soda was considered for the evaluation and the inhibition of the furring capacity of waters of Hamma..

2. Material and methods

2.1 Characteristics of the water from Hamma

The physicochemical results of the analysis of Hamma water are recapitulated in Table 1.

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By considering these results, we see that water of Hamma has a significant relative content of organic matter (TOC: 3.84 -7.5 mg/L).

In addition, it is strongly mineral-bearing with a significant hardness (TH: 475-600 mg/L $CaCO_3$). Therefore it is a primarily calcium bicarbonate (Ghizellaoui, 2008).

Table 1. Hamma water analysis

Temperature °C	31-33
pH	6.95-7.94
EC mS/cm	0.9-1.30
TOC mg/L	3.84- 7.50
CO_2 mg/L	16.21-37.05
HCO_3^- mg/L	320- 432
Cl^- mg/L	128-150
SO_4^{2-} mg/L	120-212
PO_4^{3-} mg/L	0.006-0.020
NO_3^- mg/L	3.90-7,00
NO_2^- mg/L	0- 0
NH_4^+ mg/L	0- 0
Total hardness mg/L $CaCO_3$	475-600
Ca^{2+} mg/L	124-131
Mg^{2+} mg/L	30.48-43.20
Na^+ mg/L	84-115
K^+ mg/L	2.22-13

2.2 Tests of accelerated scaling

This technique was developed by Lédion et al. 1985 (Fig. 1). Its principle consists in covering with $CaCO_3$ a metal surface carried to a fixed negative potential of -1 V compared to an electrode of reference to calomel saturated with KCl. The application of this negative potential involves the reduction on the surface of metal primarily, of oxygen, according to the equation:

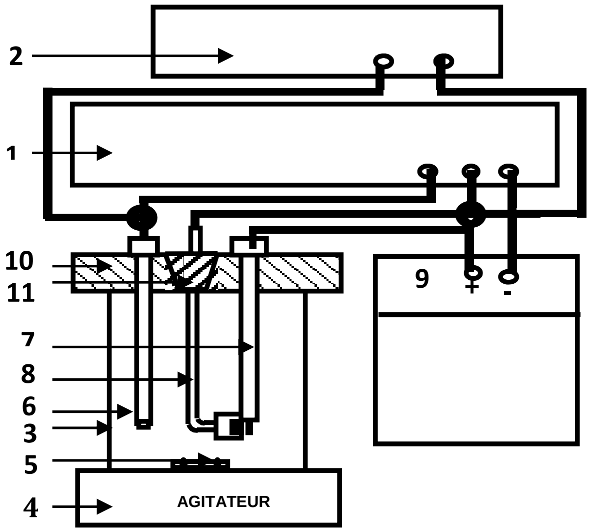
$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$$

In the vicinity of this electrode, the presence of the ions hydroxides involves an increase in the pH locally and the hydrogenocarbonate ions can be transformed into ions carbonates according the reaction:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

The increase in the content of CO_3^{2-} then involves the precipitation of calcium carbonate on the surface of the electrode according to the reaction:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\ (\text{Solid})$$



1. Potensiostat-galvanostat
2. Voltmeter to control potential.

3. Beaker of glass of 600 ml
4. Magnetic stirrer.
5. Bar magnet.
6. Electrode of reference to Calomel saturated with KCl.

7. Platinium Electrode.
8. Sample : pelletizes out of steel XC10 (diameter 11.3mm) drowned In an inert resin.

9. Plotting table .
10. Lid electrode holder

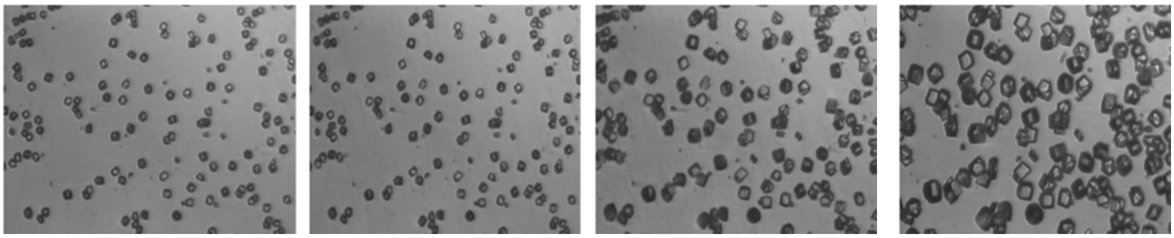
Fig.1. utilisated Assembly

3. Results

3.1. Qualitative results of electrocrytallization

The first crystals obtained from the water of Hamma appear after 2 minutes of polarization. At the end of 60 minutes, there is growth of the latter without appearance of others.

We observed a spontaneous nucleation followed by a crystals growth on all the surface of the electrode (Fig. 2).



t=2min t=5min t=20min t=60min

Fig.2. Germination and crystallization of water of Hamma

3.2. Curve of accelerated scaling for the water of Hamma

The shape of the I=f(t) curve is given by (Fig. 3).The intensity decreases as the deposit covers metal surface gradually.The intersection of the tangent of inflection of the curve of accelerated scaling centered time corresponds to t_E (time of conventional scaling). It is the time which represents the total covering of the electrode with $CaCO_3$. The water is more furring as the time of scaling is short. Therefore, we noticed that t_E for Hamma is of 3.7 minutes and its residual current is weak. What involves the formation of calcium carbonate a quite adherent precipitate.

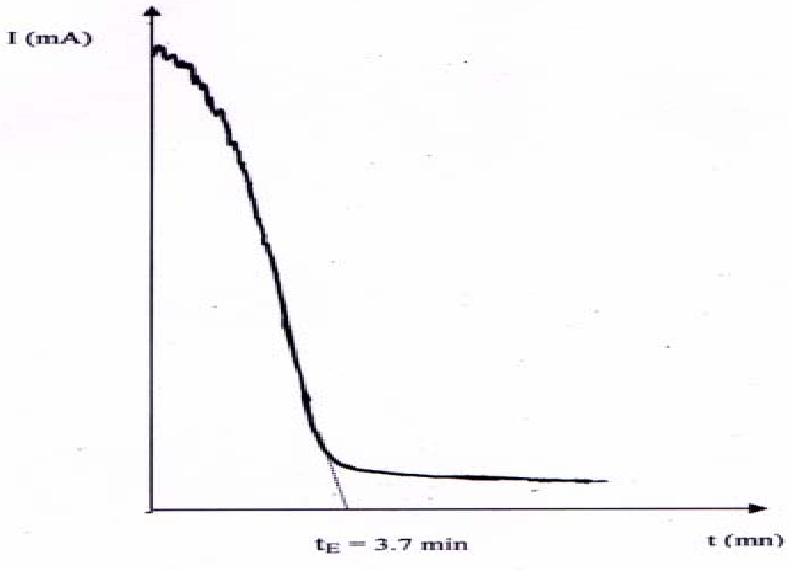


Fig.3. Curve of accelerated scaling for the water of Hamma.

3.3 Inhibition of scaling by sodium carbonate and lime

3.3.1 Use of the sodium carbonate

Increasing concentrations of Na_2CO_3 were used (200-600 mg/L) at 30 °C.The study of the curve with 400 mg/L of Na_2CO_3 revealed an increase in the time of scaling until 15.4 minutes and a weak residual current (Fig. 4). What corresponds to the formation of a quite adherent precipitate scaling. Beyond 400 mg/L there is total inhibition of scaling.

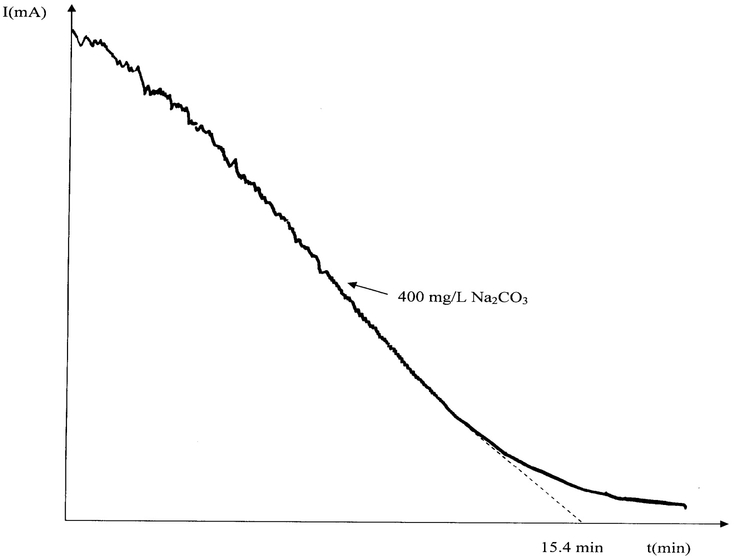


Fig.4. Curve of accelerated scaling for the water of Hamma added with 400 mg/L of Na_2CO_3.

3.3.2 Use of lime

The lime (100-500 mg/L) was added to the water of Hamma. The effect of lime is more significant than the addition of Na_2CO_3. For the same concentration (400 mg/L), the time of scaling increased until to reach 27 minutes and form of chronoamperometric curve is modified (Fig. 5).

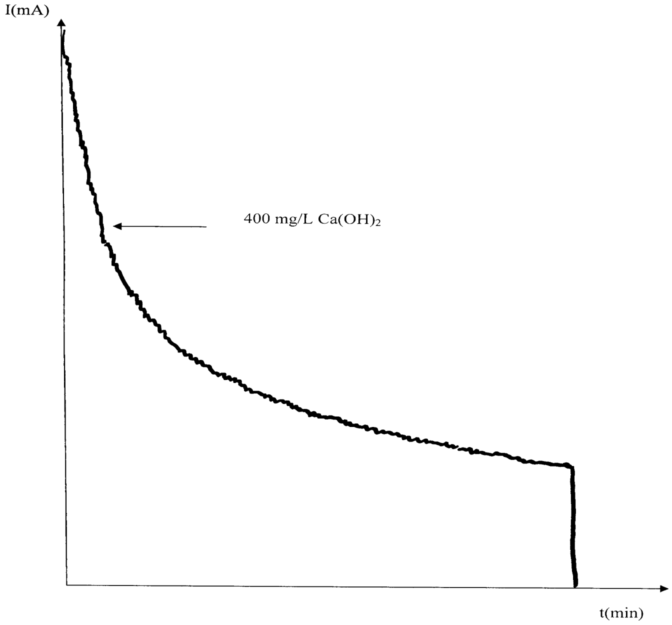


Fig.5. Curve of accelerated scaling for the water of Hamma added with 400 mg/L of lime.

3.3.3 Use of soda

The tests of accelerated scaling carried out on the water of Hamma at 30 °C for various soda concentrations (100-400 mg/L) showed that the time of scaling becomes significant as the soda concentration increases. The inhibiting effect marked is characterized by obtaining of a line for an addition of 400 mg/L of soda where the time of scaling is infinite (Fig. 6).

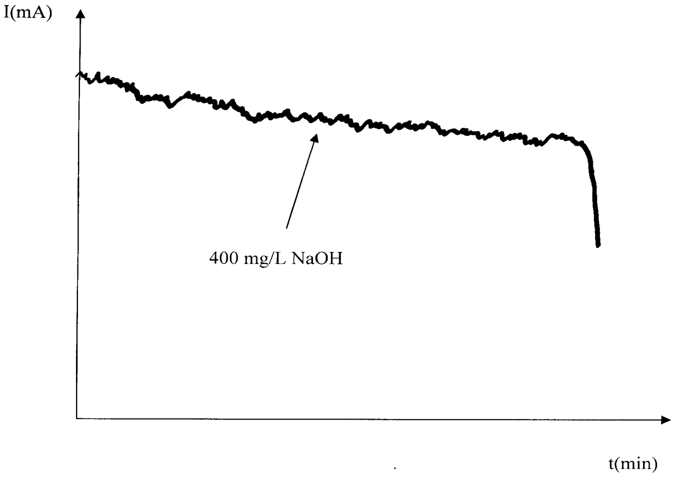


Fig.6. Curve of accelerated scaling for the water of Hamma added with 400 mg/L of soda.

3.4 Evolution of the time of scaling and the residual current according to the addition of the lime, sodium carbonate and soda

The study of the curves obtained, shows that the effect of the reagents (lime, sodium carbonate and soda) involves at the same time an increase in the time of scaling and an increase in the intensity of the residual current. These compounds which are adsorbed on the surface of the calcium carbonate particles which can be formed, may involve the precipitation of the calcium carbonate. It is noted that the time of scaling increases with the sodium carbonate concentration, lime and soda (Fig.7). One can consider, that starting from 500 mg/L of Na_2CO_3, 500 mg/L of $Ca(OH)_2$ and 400 mg/L of NaOH, the time of scaling becomes practically infinite, the calcium carbonate stops to adhere to the electrode.

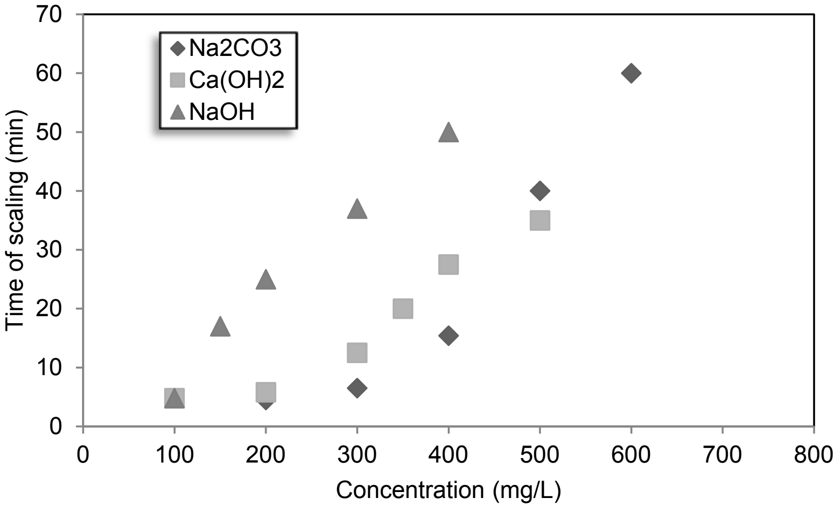


Fig.7. Evolution of the time of scaling according to the concentration

The measurement of the residual current is carried according to the concentration of (lime, sodium carbonate and soda) (Fig. 8). This residual current measures the speed to which dissolved oxygen is reduced to the electrode covered with the calcium carbonate deposit. The increase of the compactness and adherence of the deposit reduces the oxygen diffusion through this insulating film. What thus will involve a reduction in the residual current.

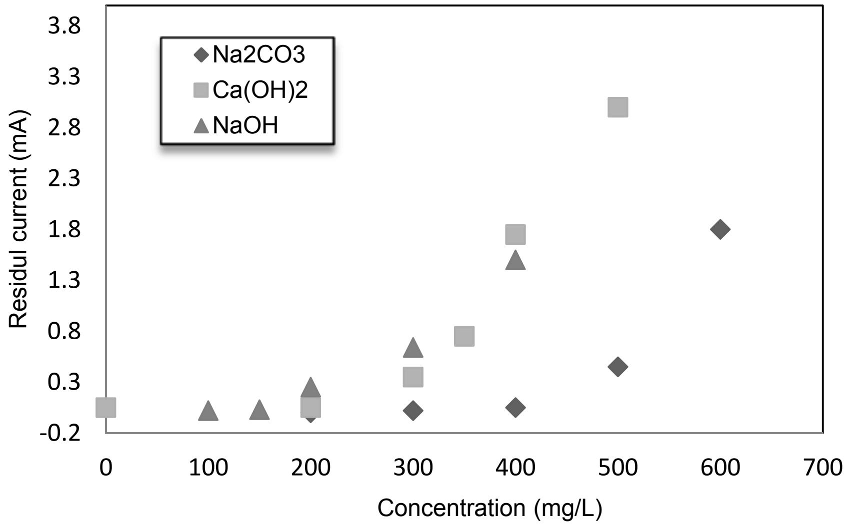


Fig.8. Evolution of the residual current according to the concentration

4. Conclusion

To characterize water of Hamma which feed the town of Constantine with drinking water, the chemical analysis which presents hardness of 60 °F reveals a furring character of the water. The compact and adherent deposits formed, crystallize in the form of calcite.

The use of the electrocrystallization revealed also a spontaneous nucleation followed by a crystal growth.

The tests of electrodeposition, carried out on furring water of Hamma, showed that $CaCO_3$ overlaps steel at a very short time of scaling (t_E=3.7 minutes). However after treatment, this time becomes high (> 3.7 minutes).The role of the chemical treatments (lime, sodium carbonate and soda) is clearly highlighted and it is possible to determine the adequate concentration of these reagents to soften the water of Hamma.

The residual current for the whole of the curves of electrodeposition is weak and thus involves the formation of compact and adherent layers of sediment.

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