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Prevention of $CaCO_3$ scale in ground waters by quartz crystal microbalance

Hadda Semineras, Samira Ghizellaoui
Département de chimie, Faculté des Sciences Exactes,
Université Des Frères Mentouri Constantine, Algeria

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Samira Ghizellaoui
gsamira@yahoo.com
+21331811177

Abstract

Ground water Hamma and Fourchi that supply the cities of Constantine and Ain M'lila drinking water are from calcareous soils. These waters are very hard because they are saturated by calcium hydrogencarbonate and are capable of depositing large quantities of calcium carbonate (scaling). Scale deposits often cause numerous technical and economical problems. The antiscale properties of K_2HPO_4, K_3PO_4, and sodium tripolyphosphate (STTP) applied to hard water Hamma and Fourchi were studied using electrochemical chronoelectrogravimetry method. Chronoelectrogravimetry showed that the calcium carbonate is deposited on the quartz microbalance in three stages; the electrode surface is completely blocked. In addition, in the presence of these inhibitors at very low concentration the surface coverage of deposits on a substrate was reduced.

1. Introduction

In calcareous soils, the groundwater of Hamma and Fourchi is loaded with high concentrations of calcium hydrogencarbonate. For a content of 59 ° F and 70.8 °F the water is very hard and must be treated before use because they large amounts of calcium carbonate as they circulate through the distribution system.

The precipitation of calcium carbonate as an insulating layer cause a decrease in the flow rate in pipes and reduced heat transfer in heat exchangers [1, 2]. Various methods on scaling study have been developed. These methods can be roughly divided into two categories: electrochemical methods and non-electrochemical methods [3]. The first one is made up of chronoamperometry [4, 5], chronoelectrogravimetry [6, 7] and electrochemical impedance technique [8] which are all based on the reduction of the oxygen dissolved in the test water by polarizing a metallic electrode at a sufficiently negative potential [3]. Among the non-electrochemical methods, we can enumerate the critical pH method [9], the rapid controlled precipitation method [10]. Scale formation can be effectively controlled by dosage of antiscalants [11, 12]. Low concentrations of these antiscalants influence the kinetics of nucleation and crystal growth [13-19]. In the present work, the inhibition of calcium carbonate precipitation by scale inhibitors (K_2HPO_4, K_3PO_4 and STTP) in the natural hard water of Hamma and Fourchi was studied through chronoelectrogravimetry tests.

2. Experimental details

2.1. Water studied

We present the physico-chemical analysis results obtained on the groundwater Hamma and Fourchi (Table 1). The results of physicochemical analysis of the two waters Hamma and Fourchi show very high levels of magnesium, calcium, hydrogencarbonate ions. These waters contain significant quantities of dry residue and the hydrotimetric titre (TH) is very high (for Hamma 59 ° F and Fourchi 70.8 ° F), indicating that these waters are very hard and well mineralized.

2.2. Electrochemical techniques

This method is the combination of the chronoamperometry and a quartz microbalance by which it is now possible to continuously follow extremely tiny mass changes [6]. The study of scaling electrochemical phenomenon is based on accelerated scaling tests.The scaling accelerated by electrochemical techniques 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.

Table 1: Physico - chemical analysis of Hamma and Fourchi water.

Parameter	Water of Hamma	Water of Fourchi
T, °C	30	20
pH	7.09	6.96
CE, mS/cm	1.06	1.80
O_2 dissous mg/L	7.55	8.21
HCO_3^-, mg/L	340	334
TH (°F)	59	70,8
Ca^{2+}, mg/L	158	156
Mg^{2+}, mg/L	42	81.6
Cl^-, mg/L	142	887
SO_4^{2-} mg/L	127	314
NO_3^- mg/L	7.09	30
NO_2^- mg/L	00	00
Na^+ mg/L	116	458
K^+ mg/L	2.84	4.21
PO_4^{3-} mg/L	1.62	1.02
F^- mg/L	0.35	0.72
RS mg/L	829	1023

The application of this negative potential entrained to the surface of metal, they following electrochemical reaction:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad R_1$$

Thus, in the vicinity of the electrode [4, 20]. It 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:

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \qquad R_2$$

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

$$OH^- + Ca^{2+} + HCO_3^- \longrightarrow CaCO_3(s) + H_2O \qquad R_3$$

The working electrode is a gold disc which, in fact, is one of the two excitation electrodes of quartz crystal resonator inserted in an electronic oscillator. The frequency change, Δf, is proportional to the mass of scale deposited, Δm, on the electrode surface according to [3]:

$$\Delta f = -2f_o^2 \Delta m/dvS$$

Where f_o is the quartz resonance frequency, d, the quartz density, v, the speed of ultrasonic wave in the quartz and S, the active surface of the quartz (Figure 1).

3. Results and discussion

3.1. Chronoelectrogravimetry of raw water of Hamma and Fourchi

Mass changes less than ($\mu g/cm^2$), are readily detectable by the electrochemically deposited, on the surface of a quartz microbalance polarized (imposed potential of -1V/SCE).

Measuring the mass of the calcium carbonate by means of a microbalance coupled to potentiostat versus time is used to draw a curve chronoelectrogavimetric. To analyze the evolution of these curves as a function of the water scaling capacity, it is first necessary to define the parameters that characterize the scaling power. Figures (2, 3) show two chronoelectrogavimetric curves obtained during an electrochemical scaling test with a quartz microbalance of the raw waters of Hamma and Fourchi, can be retained as characteristic parameters (t_g, v_e) [21]:

- The germination time tg (min) is the point of intersection of the linear part of the curve with the abscissa axis.
- The scaling rate v_s($\mu g.cm^{-2}.min^{-1}$): this is the slope of the linear part.
- The scaling time t_S, corresponding to the end of the intermediate stage. It is defined by the intersection of the linear part and the plateau.

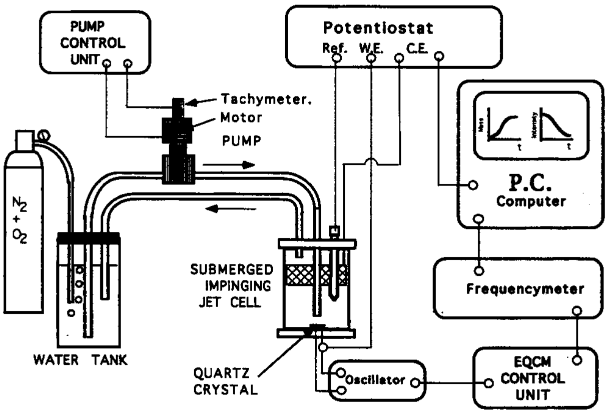

Figure 1: Scheme of the experimental set-up [3].

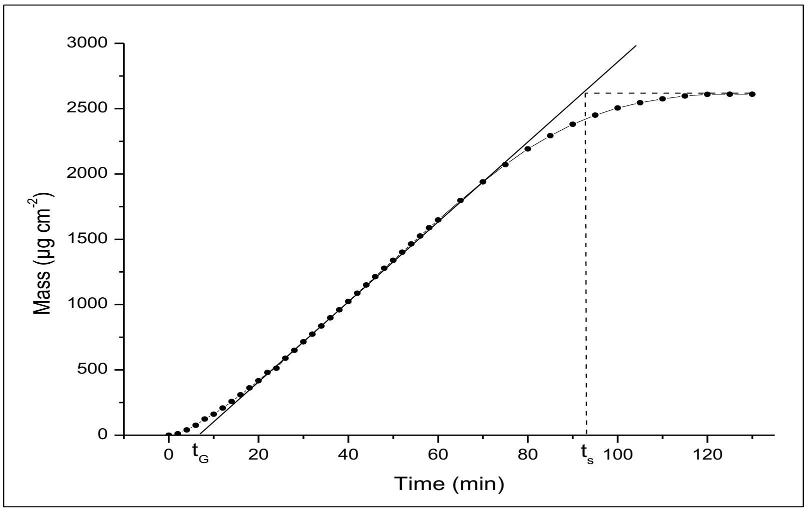

Figure 2: Chronoelectrogravimetry curve for raw water of Hamma at 30 °C.

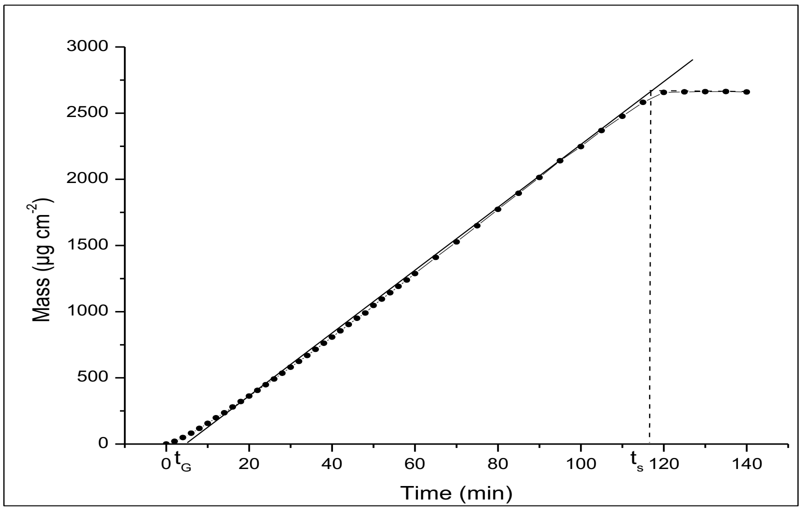

Figure 3: Chronoelectrogravimetry curve for raw water of Fourchi at 20°C.

The calcium carbonate is deposited on the quartz microbalance in three stages:
At the first stage, the scale mass increases only very slowly. This corresponds to a germination process on the surface of the quartz microbalance. The time associated with this step is noted germination time t_g. For Hamma water (t_g = 7.5 min) and for Fourchi (t_g = 6 min). During this first step, the first germs of calcium carbonate appear at the electrode surface.

In the second step, the scale mass on the surface of the quartz microbalance increases rapidly as a function of time. The first germs grow and other germs appear. The slope of the chronoelectrogavimetric curve corresponds to the scaling rate (V_e).

In the third step, the scale rate on the surface of the microbalance slows down. Indeed, the active surface is gradually covered with the deposited scale. When the electrode surface is completely blocked, the curve reaches a plateau. The time to arrive at this plateau corresponds to the scaling time t_e for the Hamma water (t_e = 94 min) and for Fourchi (t_e = 116 min).

3.2. Effect of temperature on chronoelectrogravimetric curves

We studied the influence of temperature on the chronoelectrogravimetric curves. Experiments were carried out with Hamma water and Fourchi water at different Temperatures (20, 30, 40 and 50 °C). The chronoelectrogavimetric curves are shown in Figures (4, 5).

The study of these curves shows that, when the temperature increases, the rate of scaling becomes very high.

The study of these curves shows that, when the temperature increases, the scale becomes faster and the rate of scaling becomes very high. For Hamma water, a scaling time decrease from 113 to 35 min and also germination time decrease from 5 min to 0.5 min are observed when the temperature increases from 20 °C to 50 °C.

The decrease in scaling time is greater when the temperature varies between 40 and 50 °C and the t_s drops from 87 to 35 min, see (Table 2).

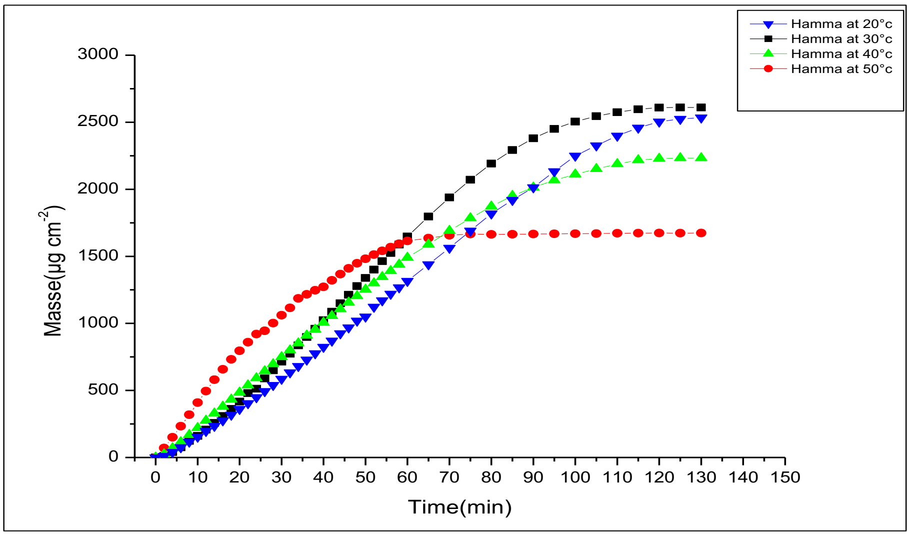

Figure 4: Chronoelectrogravimetry curves of the raw water of Hamma at different temperatures.

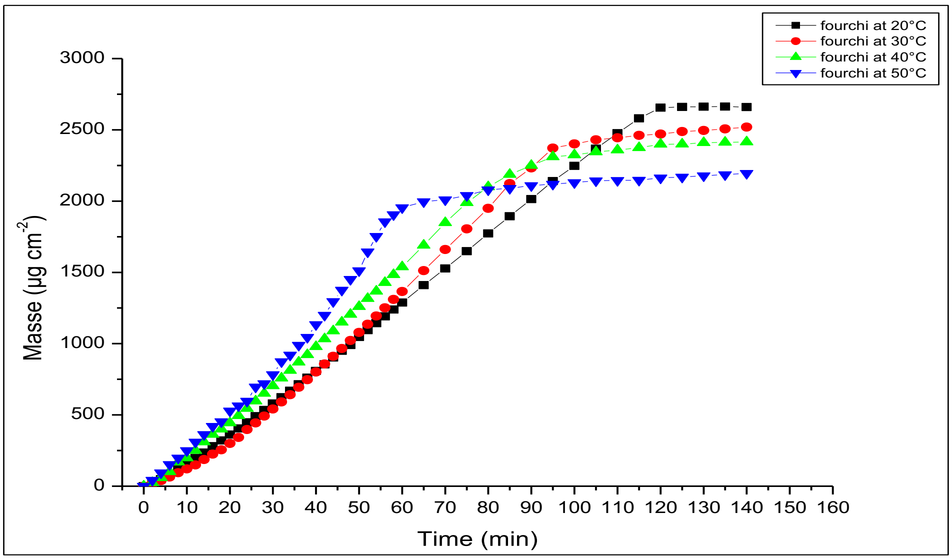

Figure 5: Chronoelectrogravimetry curves of the raw water of Fourchi at different temperatures.

Table 2: Variation of the chronoelectrogravimetric parameters of Hamma water as a function of temperature

Temperature (°C)	20	30	40	50
t_g (min)	5	7 .5	4.5	0.5
t_s (min)	113	94	87	35

For Fourchi water there is a decrease in scaling time from 116 to 71 min and germination time from 6 to 1 min when the temperature increases from 20 °C to 50 °C. See (Table 3).Germination occurs in a very small time.

Table 3: Variation of the chronoelectrogravimetric parameters of Fourchi water as a function of temperature

Temperature (°C)	20	30	40	50
t_g (min)	6	9 .5	5	1
t_s (min)	116	104.5	87	71

3.3. Chronoelectrogravimetry of Hamma and Fourchi waters treated with K_2HPO_4

We studied the action of scaling inhibitor (K_2HPO_4) on Hamma water and Fourchi water. Figures (6, 7) show the chronoelectrogravimetric curves obtained with Hamma water and Fourchi water to which increased concentrations of K_2HPO_4 have been added. It is noted that the delay scaling is even greater than the amount of added phosphate is more important. On the other hand, the scaling rate (V_e) proportional to the linear slope of the curve remains substantially constant. The presence of K_2HPO_4 in concentration of 4 mg/L for Hamma and 5mg/L for Fourchi reduced the surface coverage of deposits on the electrode and the scaling rate.

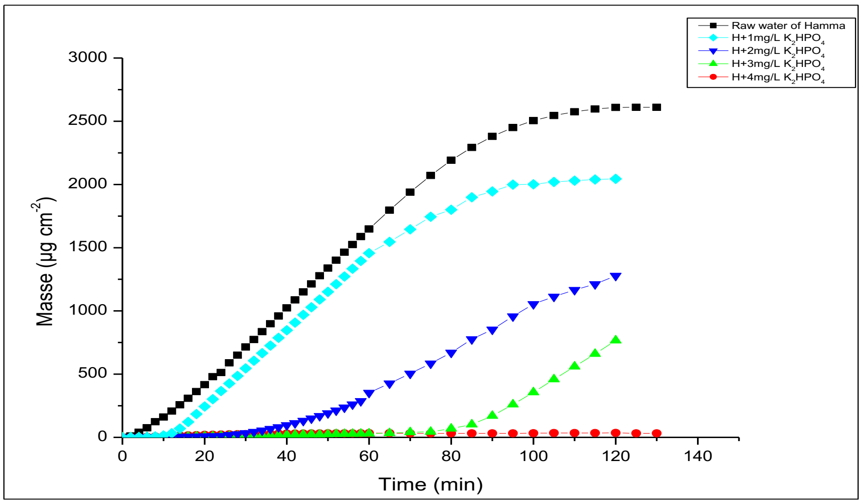

Figure 6: Chronoelectrogravimetric curves of the raw water Hamma added increasing concentrations of K_2HPO_4

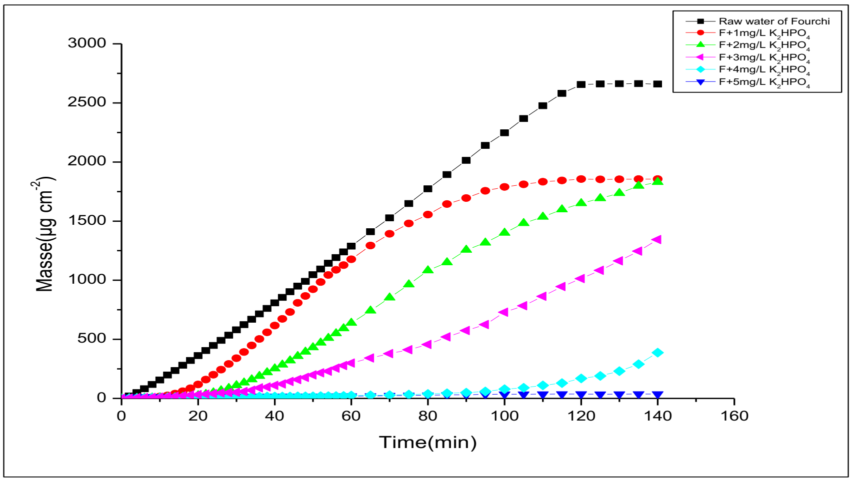

Figure 7: Chronoelectrogravimetric curves of the raw water Fourchi added increasing concentrations of K_2HPO_4

3.4. Chronoelectrogravimetry of Hamma and Fourchi waters treated with K_3PO_4

The chronoelectrogravimetric curves carried out on the water of the two waters for different concentrations of K_3PO_4 are represented by Figures (8, 9). The raw water test of Hamma gives a deposit of 715 µg cm^{-2} and on the Fourchi water a deposit of 580 µg cm^{-2} after 30 min. On the other hand, when a small amount of K_3PO_4 (1 mg/L) is added, only 110 µg cm^{-2} for Hamma and 46 µg cm^{-2} for Fourchi are deposited for the same time. At a content of 4 mg/L de K_3PO_4 added to the water for Hamma and 4.5 mg/L Fourchi, no measurable $CaCO_3$ deposit is obtained, the curve is coincident with the time axis. The deposition of calcium carbonate ceases to oppose the reduction of dissolved oxygen from a threshold of 4 mg/L to K_3PO_4.

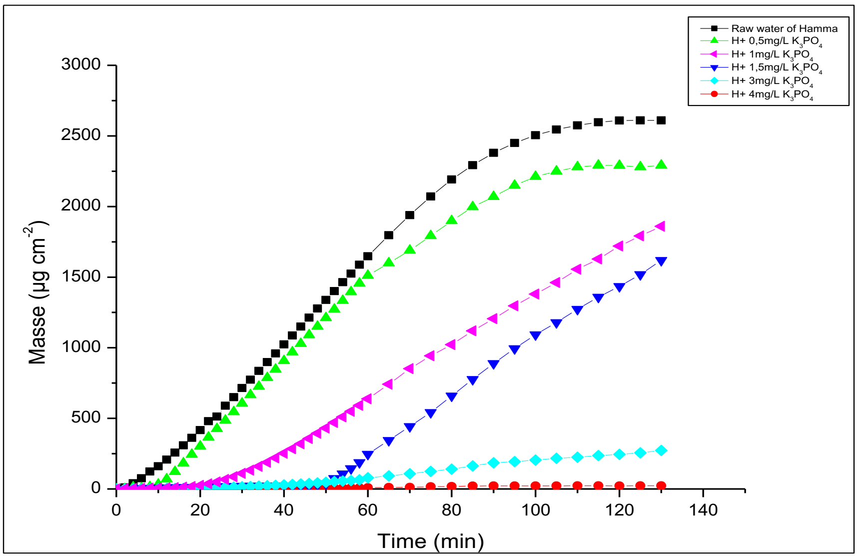

Figure 8: Chronoelectrogravimetric curves of the raw water Hamma added increasing concentrations of K_3PO_4.

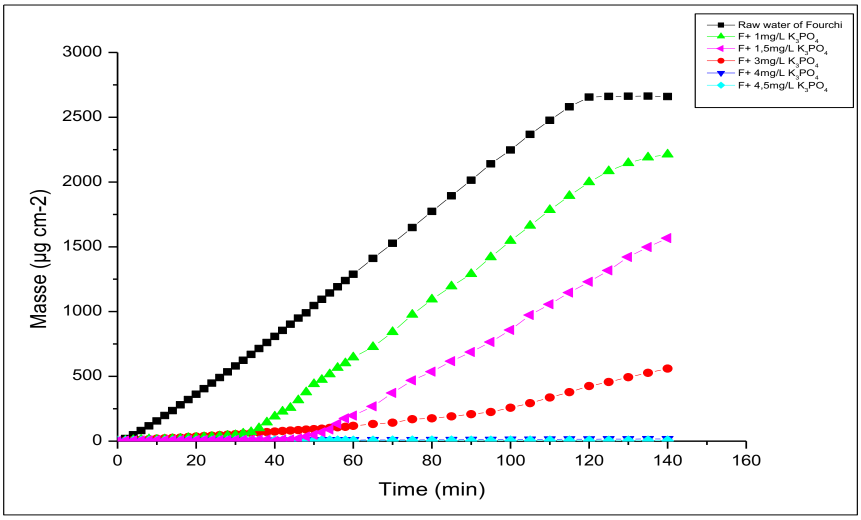

Figure 9: Chronoelectrogravimetric curves of the raw water Fourchi added increasing concentrations of K_3PO_4.

3.5. Chronoelectrogravimetry of Hamma and Fourchi Waters treated by STTP

Germination time increases with the concentration of inhibitor while the speed of precipitation decreases towards zero values. At an inhibitor concentration of 2mg/L for Hamma and 2.5mg/L for Fourchi, no deposition of calcium carbonate was observed, indicating the inhibition of $CaCO_3$ for these concentrations Figures (10, 11).

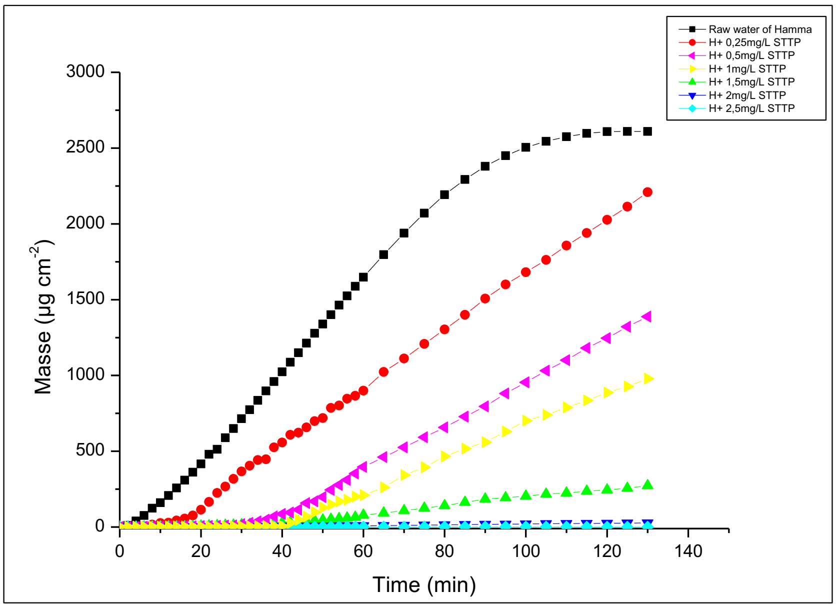

Figure 10: Chronoelectrogravimetric curves of the raw water Hamma added increasing concentrations of STTP.

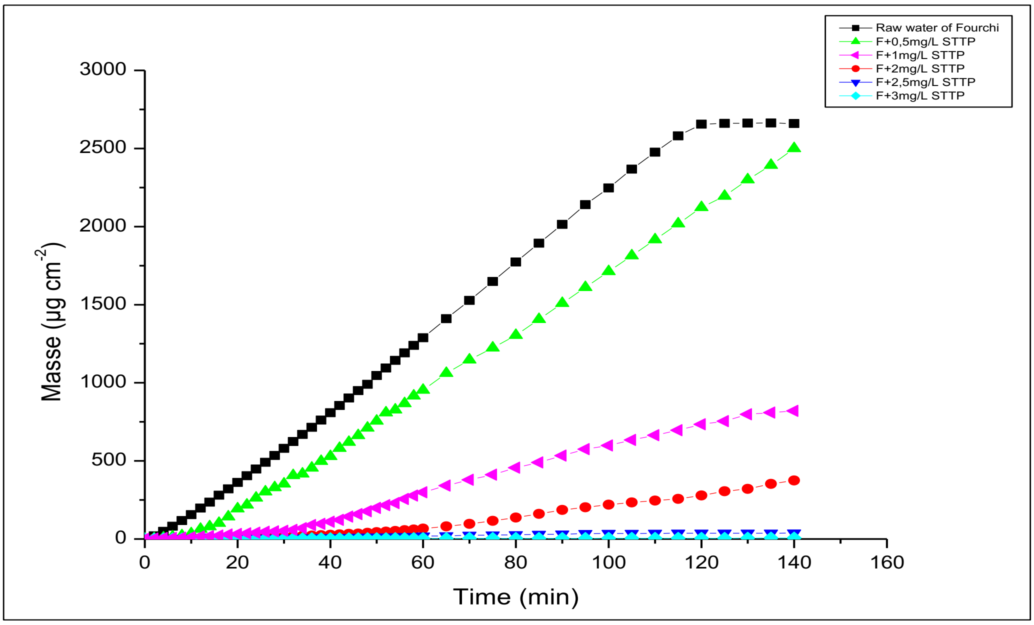

Figure 11: Chronoelectrogravimetric curves of the raw water Fourchi added increasing concentrations of STTP.

Conclusion

Chronoelectrogravimetry is used to characterize the water scaling capacity and to determine the effectiveness of an inhibitor as a function of its concentration in a given water.

The K_2HPO_4, K_3PO_4 and tripolyphosphates (STTP) appear as inhibitors particularly suitable for hard water. The presence of phosphate anion (PO_4^{3-}) even at low concentrations in hard water retarded germination and reduces the rate of precipitation of calcium carbonate.

The polyphosphates are generally more effective than the orthophosphate ion with respect to the kinetics of germination and crystal growth. They are effective at low concentrations, thus for 2 mg/L of STTP for Hamma and 2.5 mg/L of STPP for Fourchi, germination was not detected after more than 120 min.

References

1. K. Zeppenfeld, *Desalination*. 252 (2010) 60–65.
2. C. Duffau, C. Gabrielli, A. Sandra, *L'Eau, l'Industrie, les Nuisances.* 186 (1995) 50–55.
3. F. Hui, J. Ledion, *Eur. J. Water. Qual.* 33 (2002).
4. J. Ledion, P. Leroy, J.P. Labbe, *TSM L'eau.* (1985) 323-328.
5. W. Lin, C. Colin, R. Rosset, *TSM L'eau 85,* N^0 12 (1990) 613-620.
6. A. Khalil, P. Sassiat, C. Colin, C. Meignen, C. Garnier, C. Gabrielli, M. Keddam, R. Rosset, *C. R. Acad. Sci. Paris.* 314 (1992) 145-149.
7. C. Gabrielli, M. Keddam, A. Khalil, G. Maurin, H. Perrot, R. Rosset, M. Zidoune, *J. Electrochem. Soc*. 145 (1998) 2386-2396.
8. C. Gabrielli, M. Keddam, A. Khalil, R. Rosset, M. Zidoune, *Electrochimica Acta.* 42 (1997) 1207.
9. H. Feitler, *Mater. Prot. Proform*. 11 (1972) 31-35.
10. J. Ledion, B. François, J. Vienne*, J. Euro. d'hydrologie,* 28 (1997) 15-35.
11. S. Ghizellaoui, S. Ghizellaoui, H. Semineras, *J. Mater. Environ. Sci*., 6 (2017) 2105-2111.
12. Y. Bendaoud-Boulahlib, S. Ghizellaoui, *J. Mater. Environ. Sci*., 3 (2017) 1076-1081.
13. L. Yi-Pin, C. Philip, *Water. Res.* 39 (2005) 4835–4843.
14. Z. Liu, Y. Sun, X. Zhou, T. Wu, Y. Tian, Y. Wang, *J. Environ. Sci.* 23 (2011) 153–155.
15. D.E. Abd-El-Khalek, B. Abd-El-Nabey, *Desalination.* 311(2013) 227–233.
16. R. Menzri, S. Ghizellaoui, M. Tlili, *Desalination*. 404 (2017) 147–154.
17. Y. Boulahlib-Bendaoud, S. Ghizellaoui, *J. Mater. Environ. Sci*. 6 (2015) 307.
18. H. Semine Ras, S. Ghizellaoui, *J. Mater. Environ. Sci*. 6 (2015) 377-382.
19. S. Ghizellaoui, M. Euvrard, J. Lédion, A. Chibani, *Desalination*. 206 (2007)185-197.
20. P. Leroy, J. Lédion, A. Khalil, *Aqua.* 42(1991) 23-29.
21. R. Rosset, *TSM L'eau*. 11 (1993) 563-569.

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