Prevention of CaCO₃ 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

Received 12 Aug 2017, Revised 18 Oct 2017, Accepted 25 Oct 2017

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 K₂HPO₄, K₃PO₄ and sodium tripolyphosphate (STTP) applied to hard water Hamma and Fourchi were studied using electrochemical chrono-electrogravimetry 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 (K₂HPO₄, K₃PO₄ 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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water of Hamma</th>
<th>Water of Fourchi</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, °C</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>pH</td>
<td>7.09</td>
<td>6.96</td>
</tr>
<tr>
<td>CE, mS/cm</td>
<td>1.06</td>
<td>1.80</td>
</tr>
<tr>
<td>O\textsubscript{2} dissous mg/L</td>
<td>7.55</td>
<td>8.21</td>
</tr>
<tr>
<td>HCO\textsubscript{3} -, mg/L</td>
<td>340</td>
<td>334</td>
</tr>
<tr>
<td>TH (°F)</td>
<td>59</td>
<td>70.8</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+}, mg/L</td>
<td>158</td>
<td>156</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}, mg/L</td>
<td>42</td>
<td>81.6</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}, mg/L</td>
<td>142</td>
<td>887</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}, mg/L</td>
<td>127</td>
<td>314</td>
</tr>
<tr>
<td>NO\textsubscript{3} -, mg/L</td>
<td>7.09</td>
<td>30</td>
</tr>
<tr>
<td>NO\textsubscript{2} -, mg/L</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>Na\textsuperscript{+}, mg/L</td>
<td>116</td>
<td>458</td>
</tr>
<tr>
<td>K\textsuperscript{+}, mg/L</td>
<td>2.84</td>
<td>4.21</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}, mg/L</td>
<td>1.62</td>
<td>1.02</td>
</tr>
<tr>
<td>F\textsuperscript{-}, mg/L</td>
<td>0.35</td>
<td>0.72</td>
</tr>
<tr>
<td>RS mg/L</td>
<td>829</td>
<td>1023</td>
</tr>
</tbody>
</table>

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

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad R_1 \]

Thus, in the vicinity of the electrode [4, 20]. It will have an increase in the pH due to the generation of ions \( \text{OH}^- \) and involving the \( \text{CO}_3^{2-} \) formation according to the reaction:

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad R_2 \]

The product \((\text{Ca}^{2+}) (\text{CO}_3^{2-})\) increases and there is precipitation of \( \text{CaCO}_3 \) on the electrode.

\[ \text{OH}^- + \text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O} \quad R_3 \]

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, \( \Delta f \), is proportional to the mass of scale deposited, \( \Delta m \), on the electrode surface according to [3]:

\[ \Delta f = -2f_0^2 \Delta m/dvS \]

Where \( f_0 \) 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 \((\mu\text{g/cm}^2)\), 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 chronoelectrogravimetric. 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 chronoelectrogravimetric 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 \((t_g, v_s) [21]\):

- The germination time \( t_g \) (min) is the point of intersection of the linear part of the curve with the abscissa axis.
- The scaling rate \( v_s(\mu\text{g.cm}^{-2}.\text{min}^{-1})\): this is the slope of the linear part.
- The scaling time \( t_{50} \), 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 chronoelectrogravimetric 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 chronoelectrogravimetric 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 $t_e$ drops from 87 to 35 min, see (Table 2).

![Figure 4: Chronoelectrogravimetry curves of the raw water of Hamma at different temperatures.](image)

![Figure 5: Chronoelectrogravimetry curves of the raw water of Fourchi at different temperatures.](image)
Table 2: Variation of the chronoelectrogravimetric parameters of Hamma water as a function of temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_g$ (min)</td>
<td>5</td>
<td>7.5</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$t_s$ (min)</td>
<td>113</td>
<td>94</td>
<td>87</td>
<td>35</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_g$ (min)</td>
<td>6</td>
<td>9.5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>$t_s$ (min)</td>
<td>116</td>
<td>104.5</td>
<td>87</td>
<td>71</td>
</tr>
</tbody>
</table>

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 ($V_s$) 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 5 mg/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$_3$PO$_4$

The chronoelectrogravimetric curves carried out on the water of the two waters for different concentrations of K$_3$PO$_4$ 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$_3$PO$_4$ (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$_3$PO$_4$ 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$_3$PO$_4$.

![Figure 8](image1.png)  
**Figure 8:** Chronoelectrogravimetric curves of the raw water Hamma added increasing concentrations of K$_3$PO$_4$.

![Figure 9](image2.png)  
**Figure 9:** Chronoelectrogravimetric curves of the raw water Fourchi added increasing concentrations of K$_3$PO$_4$.

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$_2$HPO$_4$, K$_3$PO$_4$ 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

(2018) ; http://www.jmaterenvironsci.com