Effects of iron and manganese on the scaling potentiality of water

B. Pernot,*† M. Euvrard,* and P. Simon†,* Equipe Chimie des Eaux, Laboratoire de Corrosion et Traitements de Surface (EA no. 476), Faculté des Sciences et Techniques, 25030 Besançon Cedex, France; †S.A.U.R., Centre Pierre Crussard, 2 rue de la Bresle, 78312 Maurepas Cedex, France

ABSTRACT: This paper presents a study of the influence of the mineral composition of water on its scaling potentiality. The importance of two metallic cations was studied: Fe(II) and Mn(II), which are often present in water. The water was prepared as either doped or not with the cation under study. The chosen concentrations were 0.2 or 2 mg/L for Fe(II) and 0.05 or 0.38 mg/L for Mn(II). Analytical tests were applied to the water with or without the metallic cation: doped water or control water. By comparison, it was possible to determine the significance of Fe(II) or Mn(II) in the crystallisation of calcium carbonate. Scaling risks were reduced when iron was present in the water—it brought about an increase in the formation of fine particles in the liquid. Unlike Fe(II), Mn(II) did not have a significant effect on the scaling power of the water.

INTRODUCTION

For some years, our research team has been studying scaling risks. An experimental procedure has been developed to determine the scaling potentiality of water and the effects induced by physical antiscaling devices [1].

A recent study of various networks has shown that the scaling power of water varies from month to month; these differences are probably due to the mineral composition of the water [2]. Consequently, statistical procedures were used to correlate the composition of water and its scaling power. However, no overall effects was found because the natural water contained both minerals and organic compounds.

Thus, in order to determine the influence of specific elements, it was decided so prepare synthetic water which could be doped with metallic cations. The aim of this study was to investigate the influence of iron (II) and manganese (II) cations on the scaling power of water.

MATERIALS AND METHODS

Compared with previous studies [3–7] this investigation applied an experimental procedure under authentic conditions:

- aerobic conditions (the concentrations of dissolved dioxygen was approximately 8 mg/L);
- without seed nuclei.

In order to study and quantify the influence of ferrous (Fe(II)) and manganese (Mn(II)) ions, the following experimental procedure was applied:

- preparation of synthetic water (control water);
- possible addition of doping elements: Fe(II) or Mn(II);
- application for two analytical methods to quantify the scaling potentiality of water.

The iron and manganese concentrations chosen were standard and 10 times the standard for drinking water in France, i.e. 0.2 and 2 mg/L for Fe(II) and 0.05 and 0.38 mg/L for Mn(II);

- synthetic water

In France, much natural water has a Ca²⁺ concentration between 80 mg/L (i.e. 20 °F) and 160 mg/L (i.e. 40 °F). This explains why synthetic water with a concentration of 120 mg/L of Ca²⁺ (i.e. 30 °F) was prepared and used for the experiment.

The method of dissolving the ions [8] was based on the calcocarbonic equilibrium:

$$\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{Ca}^{2+} + 2 \text{HCO}_3^-$$

Direction 1 corresponds to the dissolution of the calcium carbonate. Direction 2 corresponds to the precipitation of the calcium carbonate. The experimental assembly is shown in Fig. 1.

A double wall thermostated cell was maintained at 25 °C, its...
capacity was 5 L. Permuted water and pure (99.5%) calcium carbonate were used. The quantity of calcium carbonate was strictly weighted to obtain a hydrotimetric titre of 30°F.

Temperature and pH were measured throughout the preparation period. Five litres of water were mixed with calcium carbonate and its weight strictly controlled (Fig. 2). CaCO₃ was dissolved using CO₂ (quality Alphagaz) bubbling. Then, air was introduced to bring about the supersaturation, but not precipitation, of calcium carbonate. Thus, air bubbling was stopped when there was the slight degree of supersaturation of about 2 (established by pH measurement). The control water was then taken in closed glass bottles and submitted to analytical tests to determine its scaling power.

In accordance with this experimental procedure, doped water was prepared as follows. The addition of a doping element was carried out at the end of the air bubbling. An iron (II) sulphate (99.0% min) solution and a manganese (II) chloride (99.0% min) solution were used.

Before applying a particular test, pH and O₂ concentrations were measured. The solution pH was near neutrality. The O₂ concentration varied between 7 and 8 mg/L, providing an aerobic system corresponding to natural water and similar to conditions in a network.

### Analytical methods

**Accelerated scaling test**

This test was developed by Ledion *et al.* at Ensam-Paris [9]. A constant electrical potential (−1 V/SCE; SCE = Saturated Calomel Electrode) was applied to a steel electrode (cathode) immersed in the water (Fig. 3). There was a precipitation of calcium carbonate on the work electrode and the strength of the current decreased. The tangent of inflection of the intensity–time curve (Fig. 3) defines, by intersection with the time axis, the conventional scaling time $T_E$; the greater the $T_E$, the less the scaling power of water.

**Test of scaling potentiality**

This test was developed by Ferreux *et al.* [10] and is based on the evaluation of the number of crystals $N$ present within a sample of supersaturated water. After concentration in a rotary evaporator, the water is collected in a closed glass Erlenmeyer flask and placed in an oven at 20°C for 24 h (Fig. 4). When it has been filtered, two different analyses are carried out.

1. A chemical analysis to determine the precipitated mass of CaCO₃, and
2. A morphometric analysis to define the characteristics of the

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**Fig. 2** Preparation of carbon-free, pure water.

**Fig. 3** Accelerated scaling test.
crystals (diameter, shape and length). ESILAB software (marketed by Aries, France) was used in this analysis.

The following were determined:
- percentage of calcium carbonate precipitated (% CaCO₃);
- crystal size; and
- number of crystals \( N \) in a sample brought to an initial unit quantity of calcium present before concentration.

With \( \% \text{CaCO}_3 \):

\[
\% \text{CaCO}_3 = \frac{C_{a2}^2 - C_{a2}^2}{C_{a2}^2} \times 100
\]

where \( C_{a2}^2 \) : calcium concentration before concentration, and \( C_{a2}^2 \) : calcium concentration after filtration. The \( C_{a2}^2 \) concentration was determined by a complexometric analysis with EDTA (ethylenediaminetetraacetic acid disodium salt dihydrate: \( C_{10}H_{14}N_2Na_2O_8.2H_2O \)) and:

\[
N = \frac{M}{\frac{4}{3} \pi r^3 Q_a}
\]

where \( N \) = number of precipitated crystals per mole of initial calcium, \( M \) = precipitated mass (g), \( r \) = mean particle radius (cm) (as the distribution of the particle size was homogeneous the mean particle radius was used), \( \rho \) = mass of crystalline variety (g/cm³), and \( Q_a \) = quantity of \( C_{a2}^2 \) before concentration (mole).

When \( N \) was high the scaling potentiality was low. An antiscaling effect (or not) was determined by comparison between \( N_d \), number of crystals for doped water, and \( N_r \), number of crystals for control water:

\[
E(\%) = \frac{N_d - N_r}{N_r} \times 100
\]

The difference between duplicate determinations was 10%.

At the same time, tests of the reaction kinetics were carried out. The waiting time (between concentration and filtration) was changed to either 0, 0.33, 1, 4, 8, 16, or 24 h. If the waiting time was 24 h, the trial was termed a systematic trial.

The doping element (iron or manganese) and calcium concentrations were measured in sample form before the test and in the filtrate after concentration. An atomic absorption spectrometer (SpectraAA-640 Varian) was used for these measurements. These two tests (test of scaling potentiality and accelerated scaling test) were selected because they are correlated. Prior testing had shown that the test of scaling potentiality was complimentary to the accelerated scaling test which is based on the follow-up of heterogeneous nucleation on a surface—whereas the test of scaling potentiality is based on a determination of the number of crystals formed in the liquid. Moreover, a previous study has shown that the analytical results of such tests are in accordance with in situ observations on networks [2].

**RESULTS**

**Control water**

Table 1 shows that the precipitated percentage of calcium carbonate and crystal size increased with the concentration of \( C_{a2}^2 \). Consequently, the number of crystals was larger for water of 30 °F than for water of 20 °F. Similar observations were made when the accelerated scaling test was applied. The conventional scaling time on the steel electrode decreased with increases in the concentration of \( C_{a2}^2 \); however the reproducibility of these results was not good, compared with the results from the test of scaling potentiality.

Thus, carbonate-free pure water of 30 °F had higher scaling power than carbonate-free pure water of 20 °F.

**Iron**

The precipitated percentage of calcium did not change when the water was doped with iron (Table 2). The calcium precipitation time-curve for doped water was similar to that of the control water (Fig. 5). It was seen that nearly all the iron was precipitated by the end of the concentration.

However, the crystal size in the doped water was smaller than the crystal size in the control water. Crystal size did not increase.

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after 10–15 h, when the water was doped with iron (Fig. 6). Therefore, the number of fine particles in the liquid was larger for doped water after 24 h (Table 2). The antiscaling effect was positive and increased when the concentration of Fe(II) increased.

Moreover, when the concentrations of Fe were 0.2 and 2 mg/L, the precipitate was coloured, but there were no morphometric modifications of the crystals when they were observed under a light microscope. In view of these results, another experiment was carried out with a larger concentration of Fe(II): 10 mg/L.

The precipitated percentage of calcium (37%) was similar to that of the control water. However, light microscopic observation showed two populations of crystals (Table 3 and Figs 7 and 8). The crystal composition was determined by X microanalysis.

Manganese

As for Fe(II), the precipitated percentage of calcium was similar to that of the control water and the doped water after 24 h (Table 4).

The study of kinetics showed that the precipitation of calcium was similar to both the control and doped water after 1 h. However, a delay in precipitation was observed just after the concentration (waiting time \( t = 0 \)) when the water was doped (Fig. 9). The instability of the supersaturated doped water during the first hour after concentration was less than for that of the control water (Table 5).

Whereas the iron precipitation was almost complete from the end of the concentration, the precipitation curve of manganese had the same evolution as that of calcium. The mean radius of the particles were the same as those of the control water whatever the time after concentration. The growth of crystals was similar in the control and doped water (Fig. 10). An X

| Table 2 | Results for water with iron (0.2 and 2 mg/L) (systematic trials) |
|-----------------|-----------------|-----------------|-----------------|
| Concentration (mg/L) | % precipitated | Size (\( \mu m \)) | Number (\( \times 10^{-4} \)) | Effect (%) |
| Control | 38 | 17.7 | 4.9 |
| 0.2 | 41 | 15.9 | 7.2 | 47 |
| 2 | 42 | 14.7 | 8.9 | 82 |

| Fig. 5 | Variation in the precipitation rate of calcium and iron for control water and water with iron (0.2 and 2 mg/L). |

| Fig. 6 | Variation in the size of crystals for control water and water |

| Table 3 | Observation light microscope and X microanalysis of crystals of a trial with iron concentration of 10 mg/L |
|-----------------|-----------------|-----------------|-----------------|
| Shape | Colour | Mean size | Composition |
| Type 1 | Rhombohedral | Translucide | 15 \( \mu m \) | Ca only |
| Type 2 | Not defined | Red | > 25 \( \mu m \) | Fe and Ca with Fe/Ca > 1 |

| Table 4 | Results for water with manganese (0.05 and 0.38 mg/L) (systematic trials) |
|-----------------|-----------------|-----------------|-----------------|
| Concentration (µg/L) | % precipitated | Size (\( \mu m \)) | Number (\( \times 10^{-4} \)) | Effect (%) |
| Control | 38 | 17.7 | 4.9 |
| 50 | 37 | 17.6 | 4.8 | -2 |
| 3802 | 37 | 16.6 | 5.7 | 16 |
with iron (0.2 and 2 mg/L).

Fig. 7 Control water at 30 °F.

Fig. 8 Water at 30 °F doped with iron (10 mg/L).

Fig. 9 Variation in the precipitation rate of calcium and manganese for control water and water with manganese (0.05 and
microanalysis did not detect a manganese concentration either on the specific crystals or on a specific face of the crystals.

**DISCUSSION**

Calcium carbonate crystallisation consists of two stages: nucleation and growth. The number of precipitating calcium carbonate crystals increases rapidly at the start of nucleation, and at a later stage the particles could stop increasing in number and subsequently grow [11]. Several studies were carried out on the addition of seed material. It appears that the rate of calcium carbonate crystallisation follows a parabolic curve over a large range of solid-solution ratios, and can be described by the equation [12]:

$$\frac{dN}{dt} = -ksN^2$$

where $\frac{dN}{dt}$ = rate of change of the crystal yield with respect to time (mol/L.min), $k$ = crystallisation rate constant 1/(mol/L)(mg/L) (min)), $s$ = concentration of added seed material (mg/L), $N$ = amount of calcium carbonate to be precipitated from solution to reach equilibrium (mol/L).

Moreover, it appears that nucleation is likely to occur on particles from impurities which offer sites for crystal growth. Increases in the mass of seed material did not produce directly proportional changes in the number of heteronucleated particles. However, increasing the mass of the seed would produce increases in the number of particles [13].

It should be noted that calcite growth follows a second order rate equation with respect to concentration suggesting that it is a surface controlled process [14, 15]. Moreover, the initial surge in the growth curves results from additional nucleation at the surface of the added crystals and in the bulk of the supersaturated solution [16].

The effects of Fe(II) and Mn(II) on the crystallisation of CaCO3 were different.

The addition of an Fe(II) cation brought about a modification in the crystallisation of calcium carbonate, despite the fact that the masses of precipitate were similar in both the control and doped water over time, and that the number of crystals in the liquid was larger compared with the iron. Moreover, the larger the concentration of Fe, the larger the number of fine particles. Otherwise, the addition of ferrous ions induces the formation of a determined number of crystals; so a higher scaling power i.e. the number of crystals in the bulk of the solution, is lower the higher the effect of Fe(II) i.e. the increase of the number of crystals is proportionally more important. Consequently, iron had no effect on the thermodynamic equilibrium, but instead acted on the interface of the liquid-solution by increasing the germination on the liquid instead of on the surface (in the experimental situation this was the inside surface of the glass beaker, in *in situ* conditions, the surfaces are pipes or the inside surfaces of heater tanks...). Thus, *in situ*, the presence of Fe may lead to a decrease in scaling risks, not by a modification of the mass of the precipitate, but by a larger number of smaller crystals in the liquid. These observations supplement the conclusions of Kavanagh et al. [5], Meyer [6], Peters & Stevens [7], and Dromgoole & Lynn [19]: the presence of iron considerably reduced the amount of scale.

The possible explanations for this are thermodynamic and kinetic. Firstly, the graphic representation of the E-pH diagram of Fe gives us information. Figure 11 shows that Fe(II) is oxyzidised to Fe(III). The three representative points show water at three different pH values:

- point no. 1: pH = 7, characteristic of the water before concentration;
- point no. 2: pH = 8, characteristic of the water during concentration in the rotary evaporator;
- point no. 3: pH = 9, characteristic of the water during concentration in the rotary evaporator in a specific site.

<table>
<thead>
<tr>
<th>Waiting time (h)</th>
<th>0</th>
<th>0.33</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control water</td>
<td>31.3</td>
<td>27.9</td>
<td>20.0</td>
</tr>
<tr>
<td>Iron: 0.2 mg/L</td>
<td>21.8</td>
<td>17.0</td>
<td>18.7</td>
</tr>
<tr>
<td>Iron: 2 mg/L</td>
<td>16.7</td>
<td>33.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Manganese: 0.05 mg/L</td>
<td>22.4</td>
<td>9.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Manganese: 0.38 mg/L</td>
<td>16.2</td>
<td>8.8</td>
<td>5.3</td>
</tr>
</tbody>
</table>

In the aerobic conditions represented in the trials, potential values were determined as follows:

\[ E = 0.0295 \times rH - 0.059 \text{ pH}, \text{ with } rH = 27 \]

The most dominant form was Fe(OH)\(_3\), which was insoluble in accordance with the colouration during experiments and with the fact that almost all of the iron was precipitated by the end of the concentration.

The kinetic data provides supplementary information about the oxidisation of Fe(\(\text{II}\)) in Fe(\(\text{III}\)) by O\(_2\); it is fast [17] (Fig. 12). The rate equation for oxidisation of ferrous ions is first order:

\[-d[\text{Fe(II)}]/dt = k_0[\text{Fe(II)}] \]

with \( k_0 = \) rate constant (1/min)

It should be noted that the oxidisation of ferrous ions decreased in the presence of calcium ions, hydrogenocarbonate ions and organic compounds [18] (Fig. 13). Therefore, the oxidisation of Fe(\(\text{II}\)) is dominant and has two consequences:

- the presence of germs of Fe(OH)\(_3\) act as sites of nucleation which would increase the precipitation of calcium carbonate in the bulk of the solution. Thus, it may initiate a heterogeneous nucleation of calcium carbonate and steady fine particles may appear and increase in size. Although this hypothesis is not in accordance with the results obtained by Herzog et al., it would appear to be a possibility.
- the oxidisation of Fe(\(\text{II}\)) in Fe(\(\text{III}\)) would induce the formation of \( \text{O}_2^- \) and \( \text{OH}^- \); these species could increase the precipitation of calcium carbonate [18]. The reactions are:

\[
\begin{align*}
\text{FeOH}^+ + \text{O}_2\text{OH}^- & \rightarrow \text{Fe(III)} + \text{O}_2^- + 2\text{OH}^- \\
\text{CaHCO}_3^+ + \text{O}_2^- & \rightarrow \text{CaHCO}_3\text{O}_2^- \\
\text{CaHCO}_3\text{O}_2^- + \text{OH}^- & \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]
Moreover, a small proportion of iron could precipitate in the form of ferrous carbonate, which has a solubility product smaller than the solubility constant \( k_{s} \) of CaCO\(_{3}\); consequently this salt precipitates before CaCO\(_{3}\) whatever the pH [21]. In this case, Fe may act as before, i.e. it behaves as a support for the precipitation of CaCO\(_{3}\) in the liquid.

On the other hand, manganese seems to have less importance: it only slowed down the precipitation kinetics of calcium carbonate during the first hour after concentration in the rotary evaporator. During this time, as the sizes were similar in both the control and doped water, this would suggest that Mn\(_{2}^{+}\) slightly reduced the crystallisation of CaCO\(_{3}\) in the liquid.

Diagram E–pH shows that, among the ions or oxidised forms, Mn\(_{2}^{+}\) is the steady species in the experimental procedure (Fig. 14). Looking at the E–pH diagram for iron, three representative points (1, 2 and 3) characterise the water at different pH values (7, 8 and 9 respectively). Only a small amount of manganese may be needed to precipitate in the Mn\(_{2}O_{3}\) form at pH 9. When the pH is lower, the Mn\(_{2}O_{3}\) is reduced in Mn\(_{2}^{2+}\).

Moreover, the oxidation is very slow. This is why water utilities do not use air in the treatment or elimination of Mn\(_{2}^{2+}\) [22]. Consequently, this phenomenon has no influence on the precipitation of calcium carbonate. Moreover, manganese may precipitate in the form of manganese carbonate, which has a lower solubility constant \( k_{s} = 10^{-16} \) than calcium carbonate. It is possible that manganese may slightly delay the rate of incorporation of Ca\(_{2}^{+}\) into the crystal lattice by being adsorbed onto the growing surface of the crystal, as was observed by Söhnel & Mullin [20]. However, after one hour, no significant effect was induced by this ion. Consequently, it did not modify the scaling risks of calcium carbonate.

It must be noted that the major anions (of concentration higher than 1 mg/L) are carbonates, hydrogenocarbonates, sulphates, nitrates and chlorides. Thermodynamic data, especially solubility products, show that the more insoluble of these salts is calcium carbonate. If the concentrations of these ions are low, they would not influence the scaling potential. Data are now needed concerning the effect of higher concentrations of these ions. In addition, our aim is to obtain further data concerning the influence of organic compounds.

**CONCLUSION**

During these experiments to determine the influence of metallic cations, it was found that iron reduced risks of scaling. In comparison with previous studies, our experiments have shown that iron acts on the crystallisation of calcium carbonate: it brought about an increase in the formation of fine particles in the liquid. The precise mechanism of this is not known, but iron probably precipitates in the form of ferric hydroxides which may trigger the steady formation of germination sites.

Manganese had less importance. It only slowed down the precipitation kinetics of calcium carbonate during the first hour after concentration in a rotary evaporator. However, after this initial period, manganese did not induce any significant effect. Thus, it did not modify the scaling risks of calcium carbonate. These experiments showed that some metallic cations may bring about the crystallisation of calcium carbonate. Further data are now needed concerning the importance of other cations such as zinc or aluminium, and trials need to be carried out with natural water containing organic matter.

**BIBLIOGRAPHY**


