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Effects of temperature and dissolved CO₂ on the scaling of water in the presence of copper and zinc

Dan Liu · Bingru Zhang · Fengting Li · Franck Hui · Jean Lédion

Abstract In this study, through the method of rapid controlled precipitation (RCP), the influence of temperature and dissolved CO₂ on the scaling capacity of mineral water in the presence of copper and zinc ions was studied in laboratory experiments. The results indicated that with a rise in temperature or concentration of dissolved CO₂, the scaling time of Salvetat water greatly decreased and the rate of precipitation considerably increased; therefore, the minimum dosage of copper or zinc ion for achieving total inhibition of scaling needed to be increased, which would provide better guidance for practical use of metal ions in inhibiting the scaling of drinking water.

Keywords Drinking water · Scaling · Calcium carbonate · Copper ion · Zinc ion

Introduction

Scaling, a frequent phenomenon in the distribution of drinking water, is characterized by the appearance on a surface, metal or not, of an adherent mineral deposit primarily made up of calcium carbonate (CaCO₃). These

deposits lead to serious technical and economic problems such as obstruction of drains, scaling of water heatings, seizing of stopping devices (taps, vannes), etc. Therefore, finding some economical and environmentally friendly inhibitors is one of the major research focuses nowadays [1–6].

In previous studies we reported that zinc and copper ions had great effectiveness in inhibiting the scaling of drinking water at a low concentration [7–10]. In order to provide better guidance for their practical use in inhibiting scaling in mineral water, it is necessary to study how various factors affect the performance of zinc and copper ions as inhibitors. In this study, using the method of rapid controlled precipitation (RCP), the effects of temperature and dissolved CO₂ on the scaling of water in the presence of copper and zinc were studied in laboratory experiments.

The rapid controlled precipitation method

The RCP method, proposed by Lédion et al. [11], consists in degassing of CO₂ from the test water by a moderated agitation using a magnetic stirrer. In this way, the nucleation and the growth of CaCO₃ are initiated in a way similar to a natural scaling phenomenon. The water scaling capacity is then characterized by taking measurements of pH and resistivity as functions of time, as seen in Fig. 1. The maximum in the pH–time curves corresponds to the precipitation threshold in the water concerned. The start of precipitation is also indicated by a change in slope of the resistivity–time curves, while the slope beyond the inflection characterizes the kinetics of the CaCO₃ precipitation.

In RCP, temperature and dissolved CO₂ are two key factors; by modifying the parameters of temperature and dissolved CO₂ concentration, the scaling of water can be

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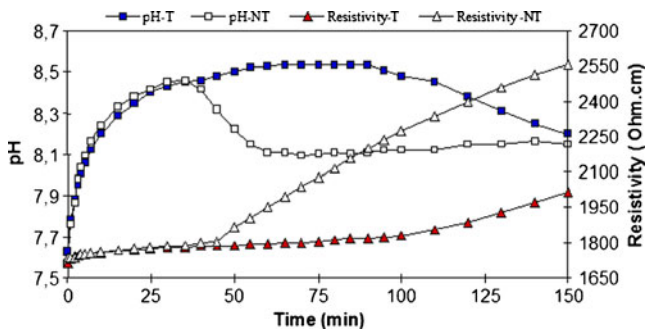


Fig. 1 RCP curves: variation of pH and resistivity versus time. (T treated water, NT nontreated water)

accelerated and CaCO_3 precipitates can be observed in a reasonable period of time.

Materials and methods

Water studied

To obtain a drinking water whose scaling potential remained rigorously constant, it was decided to work with a mineral water named Salvetat, whose physicochemical characteristics [12] are shown in Table 1. Salvetat solutions of different volume percents (25%, 30%, 40%, 50%, 75%, 100%) were prepared by diluting Salvetat with deionized water.

Table 1 Salvetat water analysis

Parameter	Value	Parameter	Value
T ($^{\circ}\text{C}$)	18.8	Electrical conductivity (mS/cm)	1.328
pH	6.5	Hardness (deg)	38
Alkalinity ($\times 10^{-3}$ mol/L)	13.4	Silica (mg/L)	72
Calcium (mg/L)	253	Bicarbonate (mg/L)	820
Sodium (mg/L)	7	Sulfate (mg/L)	25
Magnesium (mg/L)	11	Chloride (mg/L)	4
Potassium (mg/L)	3	Nitrate (mg/L)	< 1
Total cations (meq/L)	13.95	Total anions (meq/L)	14.09
Degree of supersaturation (α)	1.15	180 $^{\circ}\text{C}$ drying residue (mg/L)	850
pHs	6.28	I_L (Langelier index)	0.22

Fig. 2 Experimental device of RCP

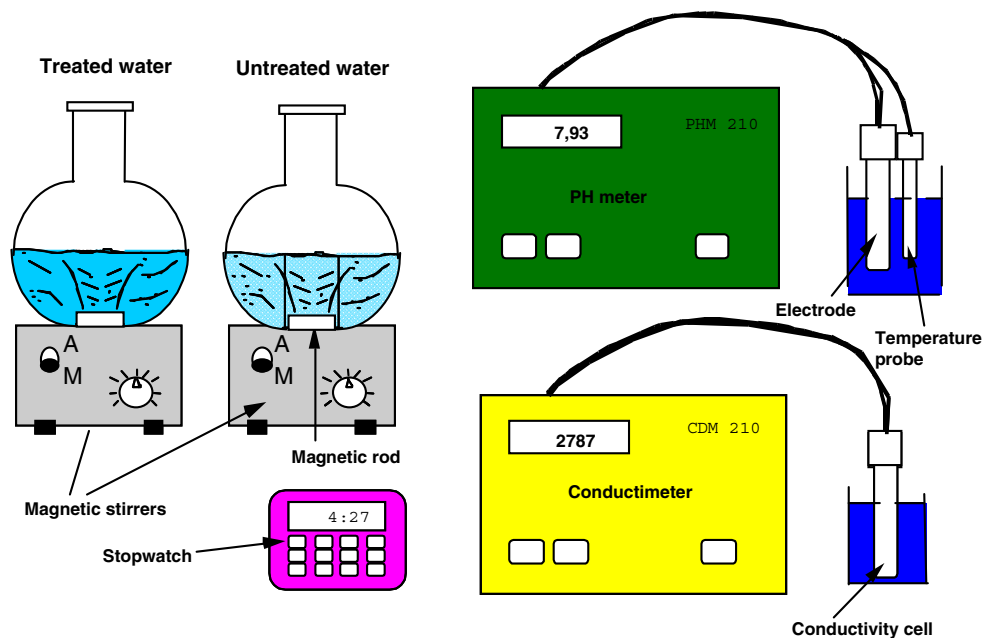
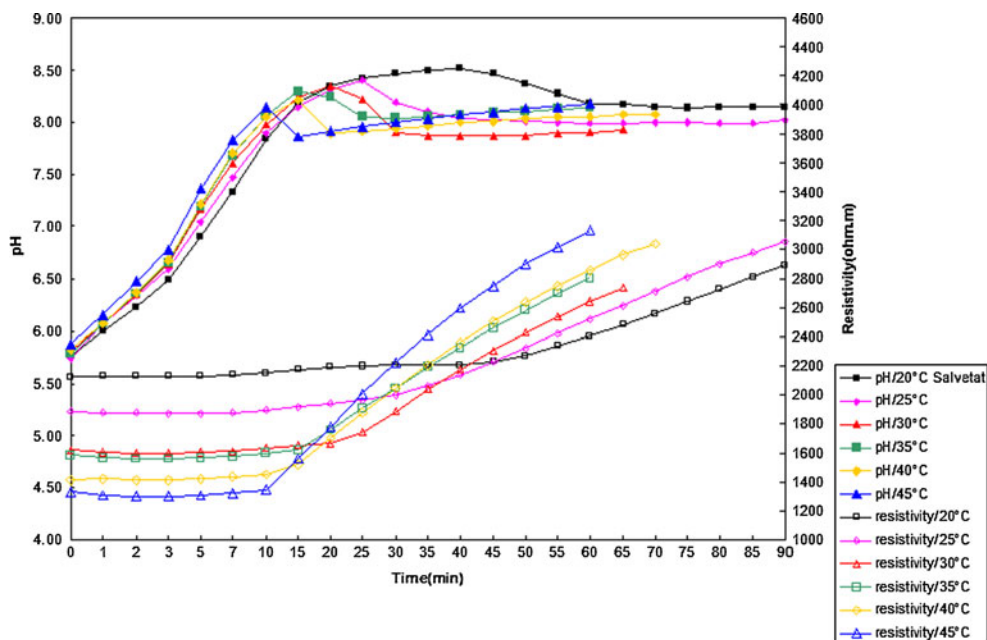


Fig. 3 Effect of temperature on the scaling of Salvetat water



Instruments and materials

The experimental setup of RCP is presented in Fig. 2. Since the tests are comparative, two identical 500-mL borosilicate glass flasks are employed, equipped with PTFE-coated magnetic stirrer rods. The rods can be rotated at a certain speed with the aid of Tacussel Agimax magnetic stirrers, the velocity being adjusted using a DT-311P digital stroboscope. The pH and resistivity are measured using Tacussel PHM 210 pH meters and radiometer CDM 210

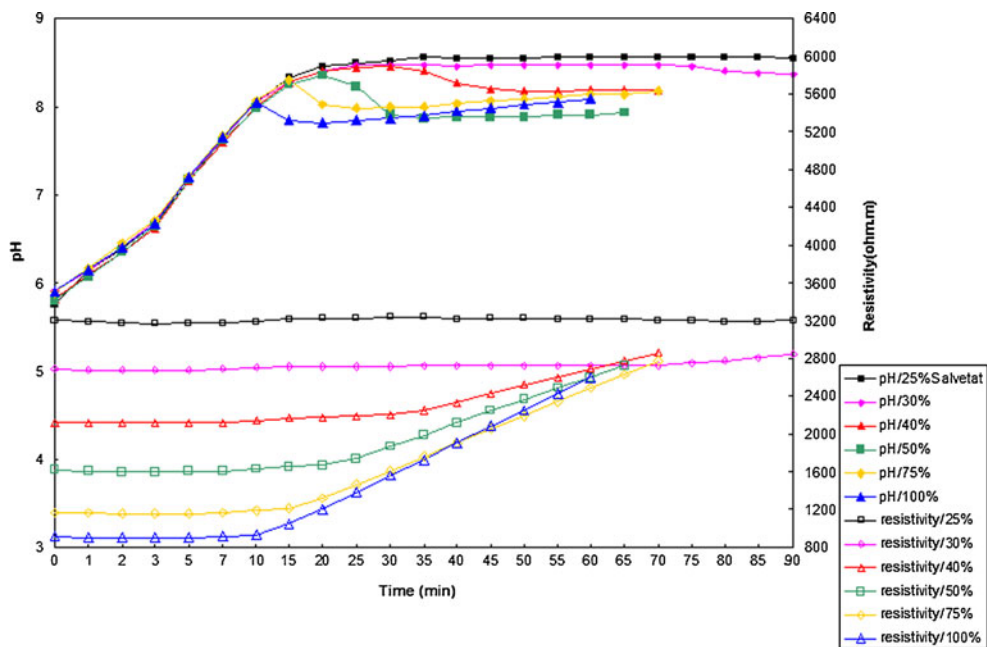
conductimeters, respectively. The resistivity is automatically corrected to 20 °C.

All the chemicals were pure grade reagents or ACS certified, such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, etc.; they were weighed with a Mettler MT5 electron balance.

Experimental procedure

One flask was filled with 300 mL Salvetat solution (untreated water); the other was filled with 300 mL Salvetat solution

Fig. 4 Effect of dissolved CO_2 concentration on the scaling of Salvetat water



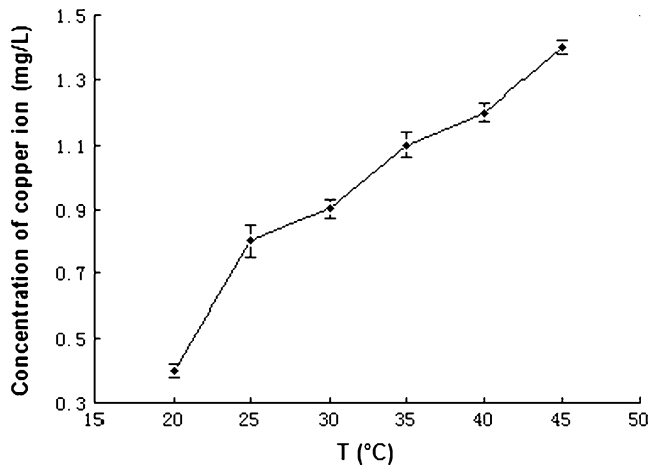


Fig. 5 Influence of temperature on the dosage of copper ion

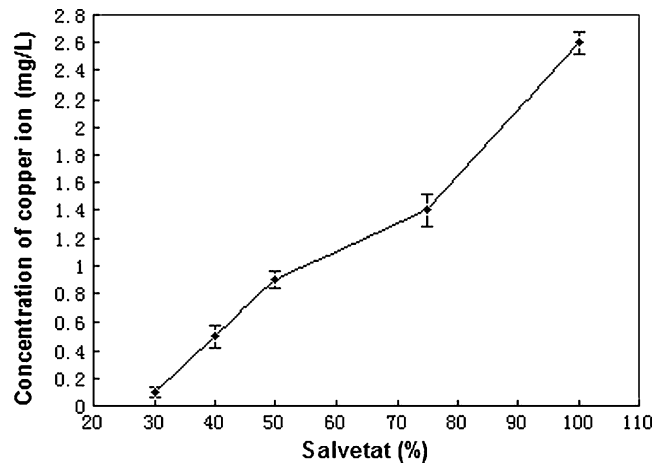


Fig. 7 Influence of dissolved CO₂ concentration on the dosage of copper ion

adding quantitative copper or zinc ion (treated water). At a given temperature, the treated water and the reference water (untreated) were stirred simultaneously at a speed of 600 rpm in sequences of 1, 2, 3, or 5 min. After each sequence, the pH and the resistivity of the two waters were measured. The whole experiment normally lasted 70 min.

Results and discussion

Tests on scaling capacity of Salvetat water

The influence of temperature

For 50% Salvetat water of different temperatures, as shown in Fig. 3, at $T=20, 25, 30, 35, 40, 45$ °C, the precipitates

appeared at 40, 25, 20, 15, 15, 10 min correspondingly. As the temperature rose, (1) the initial pH of the Salvetat water increased while the initial resistivity decreased; (2) both the maximum pH and its corresponding resistivity decreased; (3) the scaling time greatly decreased (comparing to 35 °C, pH fell more sharply at 40 °C); (4) the rate of precipitation, indicated by the slope of the resistivity curve, considerably increased.

The influence of dissolved CO₂

Salvetat water of different volume percents was chosen for the factor of dissolved CO₂. At $T=30$ °C, as seen in Fig. 4, for 25% Salvetat water, no precipitate appeared in 90 min. However, for 30%, 40%, 50%, 75%, 100% Salvetat water,

Fig. 6 Effect of temperature on the scaling of Salvetat water in the presence of copper ion

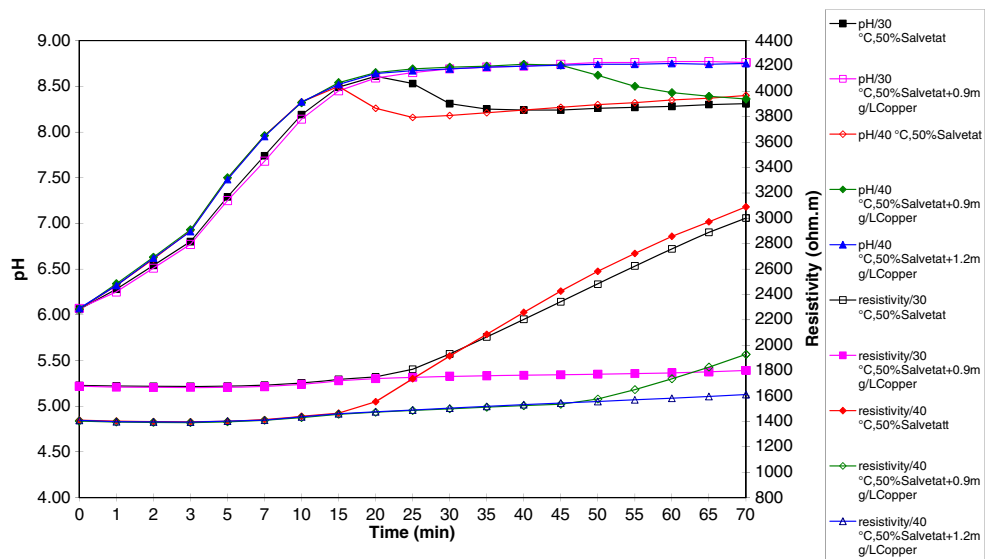
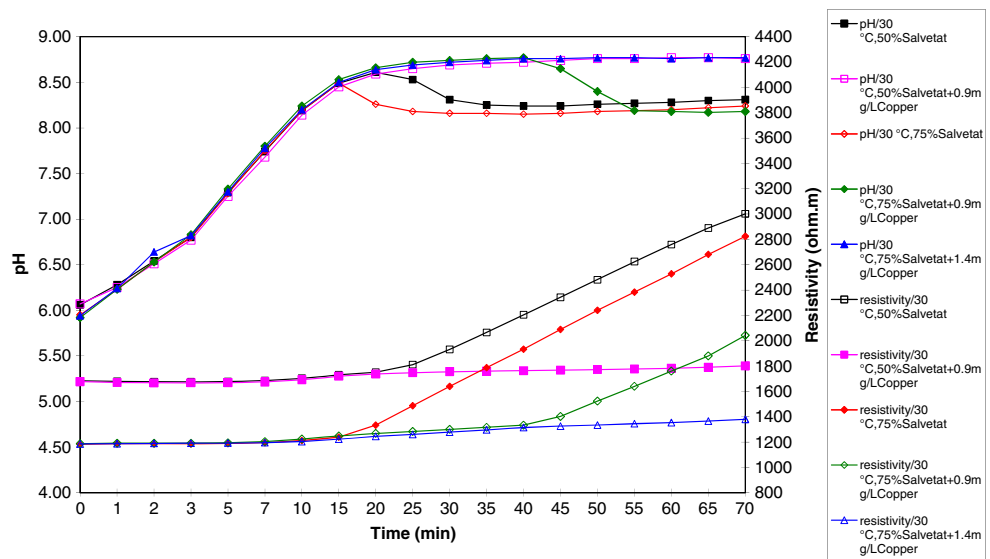


Fig. 8 Effect of dissolved CO₂ on the scaling of Salvetat water in the presence of copper ion



the precipitation started at 70, 30, 20, 15, 10 min, respectively. The results indicated that with the rise in concentration of dissolved CO₂, the scaling time of Salvetat water greatly decreased, and the rate of precipitation obviously increased.

Inhibition of scaling in the presence of copper

The influence of temperature

For 50% Salvetat water, at different temperatures, the minimum concentration of copper ion required to achieve total inhibition of CaCO₃ scaling is shown in Fig. 5. In order for the inhibition of scaling to attain an efficiency of 100% for 70 min, the dosage of copper needed to be increased as the temperature rose. For example, as seen in Fig. 6, at $T=30$ °C, for the untreated water, the scaling time was 20 min; for the treated water adding 0.9 mg/L copper, no precipitate had yet appeared in 70 min. However, when the temperature rose to 40 °C, for the untreated and treated water, the scaling time was 15 and 45 min respectively, that is, the precipitation of CaCO₃ was merely delayed for 30 min by 0.9 mg/L copper; only when the concentration of copper was higher than 1.2 mg/L could the scaling be totally inhibited for 70 min.

The influence of dissolved CO₂

At $T=30$ °C, for Salvetat water of different volume percents, the lowest concentration of copper needed to totally inhibit the precipitation of CaCO₃ is shown in Fig. 7. The results indicated that the higher the concen-

tration of dissolved CO₂, the greater the minimum dosage of copper required to attain an inhibitory effectiveness of 100% in 70 min. For instance, as seen in Fig. 8, at $T=30$ °C, for 50% Salvetat water, the scaling time of untreated water was 20 min, after introducing 0.9 mg/L copper, no precipitate appeared in 70 min, but for 75% Salvetat water, the scaling time of untreated and treated water was 15 and 40 min, respectively, that is, precipitation was merely delayed for 25 min by 0.9 mg/L copper. However, if the copper concentration increased to 1.4 mg/L, the scaling could be totally inhibited for 70 min.

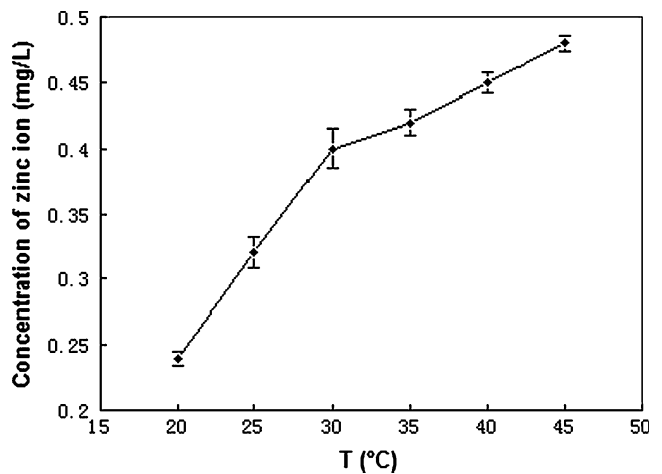
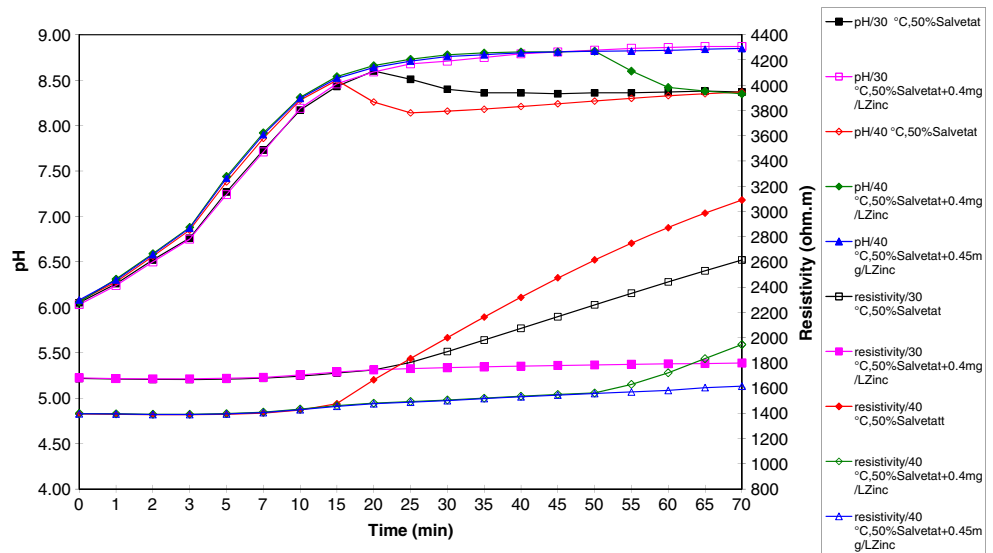


Fig. 9 Influence of temperature on the dosage of zinc ion

Fig. 10 Effect of temperature on the scaling of Salvetat water in the presence of zinc ion



Inhibition of scaling in the presence of zinc

The influence of temperature

As shown in Fig. 9, for 50% Salvetat water, the minimum concentration of zinc ion for achieving total inhibition of CaCO₃ scaling increased as the temperature rose. For example, as seen in Fig. 10, at T=30 °C, in 70 min no precipitation occurred in the treated water with 0.4 mg/L zinc. However, if the temperature rose to 40 °C, 0.4 mg/L zinc could only delay the precipitation of CaCO₃ for 35 min, but when the zinc concentration was up to 0.45 mg/L, the efficiency of inhibition attained 100% for 70 min.

The influence of dissolved CO₂

As shown in Fig. 11, at T=30 °C, the lowest dosage of zinc ion for attaining total inhibition effectiveness of scaling needed to be increased with the rise in the concentration of dissolved CO₂. For instance, as seen in Fig. 12, at T=30 °C, for 50% Salvetat water, in 70 min no precipitate had yet appeared in the treated water including 0.4 mg/L zinc, but for 75% Salvetat water, 0.4 mg/L zinc could merely retard the scaling of CaCO₃ for 30 min; however, if the zinc concentration reached to 0.6 mg/L, an inhibitory effectiveness of 100% could be attained for 70 min.

Conclusions

Through the method of RCP, the effects of temperature and dissolved CO₂ on the scaling of mineral water in the

presence of copper and zinc ions were investigated; the results indicated:

- (1) As the temperature rose, the scaling time of Salvetat water considerably decreased, and the rate of precipitation obviously increased, so the minimum dosage of copper or zinc ion needed to totally inhibit the scaling of CaCO₃ should be increased.
- (2) The higher the concentration of dissolved CO₂, the shorter the scaling time of the Salvetat water, and the greater the lowest dosage of copper or zinc ion was needed to achieve the total inhibition of scaling.

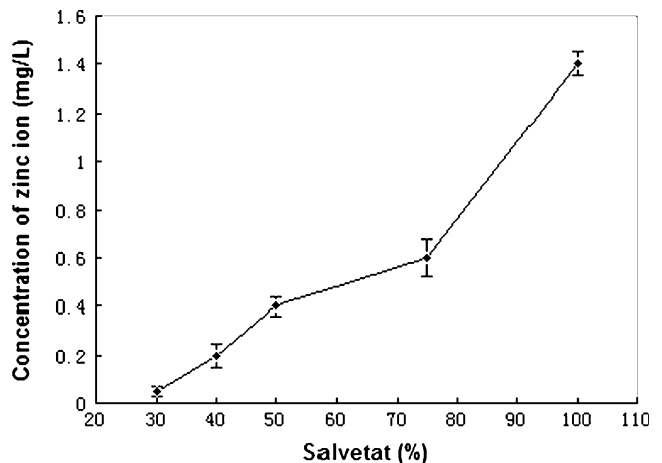
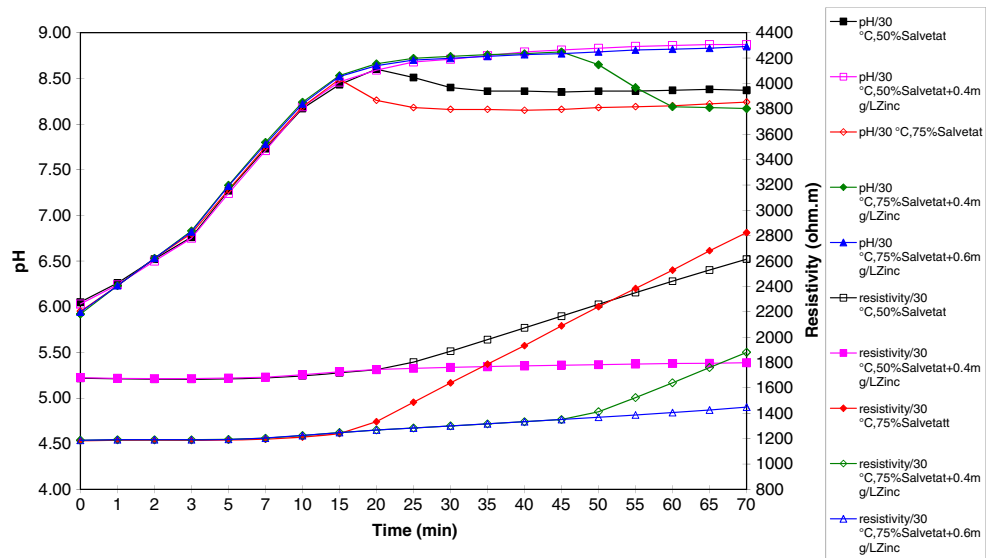


Fig. 11 Influence of dissolved CO₂ concentration on the dosage of zinc ion

Fig. 12 Effect of dissolved CO₂ on the scaling of Salvetat water in the presence of zinc ion



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