

THE INFLUENCE OF PHOSPHATE ON CALCIUM CARBONATE FORMATION IN HARD WATER

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ABSTRACT

Calcium carbonate fouling layers form when the concentration of scaling ions in solution exceeds their solubility limit. Although small amounts of phosphate ions (0.1-3.0 mg/L) are found in tap water in some part of Europe, the effect of these species on the kinetics and characteristics of calcium carbonate scale generated from a supersaturated aqueous salt solution containing phosphate is not reliably understood. In this study, a series of experiments using model solutions containing phosphate were conducted to study the chemical characteristics of the scale formed. The results suggest that the time constant of scale formation in solution at 65°C with 2.0 mg/L phosphate ions was about 17 times longer than that in solutions without phosphate. X-ray diffraction and SEM/EDX analysis of the scale layers confirmed that deposits formed in the presence of phosphate were calcite, containing trace amount of phosphorous, while those formed in the absence of phosphate were a mixture of aragonite and calcite.

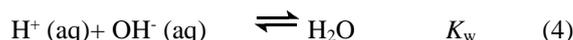
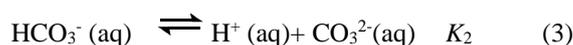
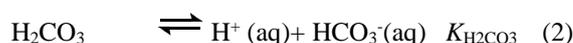
INTRODUCTION

Calcium carbonate fouling layers, *i.e.* mineral scale, are often formed on heat exchanger surfaces in a direct water heating system where hard water is heated beyond 50°C (Hasson, Avriel et al. 1968; Augustin and Bohnet 1995).

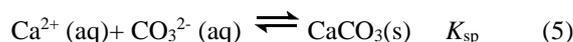
The CO₂-H₂O-CaCO₃ system exists in three phases: (a) a vapour phase characterised by the partial pressure of CO₂ in the atmosphere which is in contact with the aqueous phase (or that the liquid was exposed to before it was isolated from the vapour phase); (b) an aqueous phase in which CO₂ absorbed from the gas phase and the carbonates dissolved from the solid phase lead to ionic equilibria between HCO₃⁻, CO₃²⁻, H⁺, OH⁻, and Ca²⁺; (c) a solid phase of calcium carbonate being formed or dissolved. The distribution of the carbonate species changes markedly with the pH of solution (Pisigan and Singley 1985).

The following three sets of solution equilibria need to be considered in calcium carbonate precipitation:

(a) *Carbonic species and water equilibria*



(b) *Solid-liquid phase equilibrium*



(c) *Gas-liquid phase equilibrium*



The K values above are the thermodynamic equilibrium constants for the carbonic and calcium systems in pure water and are given by (Plummer and Busenberg 1982).

The relative solubility, S , is a measure of supersaturation, usually calculated with respect to the equilibrium solubility of calcite, as it is the most stable calcium carbonate polymorph, via

$$S = IAP / K_{\text{sp}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \cdot f_D^2 / K_{\text{sp}} \quad (7)$$

where IAP is the ionic solubility product and f_D is the activity coefficient of divalent ions.

The solution being super-saturated is not sufficient grounds for scale formation: nucleation must also occur. This is a random, kinetic process which is subject to a wide range of rate determining effects including adsorption of other species. When nucleation is a thermally activated process, the rate of formation of nuclei is expressed by the following Arrhenius-type equation (Davey and Garside 2000):

$$J = A \exp(-\Delta G_c / kT) = A \exp\left[-\frac{16\pi\gamma^3 v_c^2}{3k^3 T^3 (\ln S)^2}\right] \quad (8)$$

Here, T is the absolute temperature, k the Boltzman constant, v_c the molecular volume of critical nuclei, γ the interfacial tension and A is a kinetic pre-factor. Relationships such as (8) are often quoted in the crystallization fouling literature but the influence of trace species such as phosphate on the

kinetics is rarely considered. This is, however, critically important when applying results obtained from studies of the fundamentals of fouling mechanisms using relatively pure solutions to real systems, or when considering the fouling propensity of real (industrial and domestic) waters.

Tai and Chen (1995) studied the morphology of calcium carbonate at different values of the relative super-saturation (σ), which relates to the relative solubility(S) by $\sigma = \ln(S)$, in a semi-batch reactor. Calcite crystals of rhombic shape were produced at $\sigma < 2.91$, while rosette agglomerates of aragonite were observed at $\sigma > 3.25$ (Tai and Chen 1995). House (1987) studied the inhibition effect of inorganic phosphate on calcite crystal growth were previously studied at 25 °C. The growth rate drastically decreased by about 50% at phosphate concentrations greater than 3.2×10^{-6} mol/L due to phosphate adsorption on the steps of calcite crystals (House 1987). The adsorption isotherms and pH dependence was described by a simple two-component model of adsorption involving PO_4^{3-} or CaPO_4^- and HPO_4^{2-} or CaHPO_4^0 (House and Donaldson 1986). Dove and Hochella (1993) analysed the inhibition effect of orthophosphate under Scanning Force Microscopy during calcite precipitation at $S=1\sim 2$ at 25 °C. The results indicated that phosphate introduced resulted in the formation of amorphous shape nuclei at concentrations of 0.6 and 1.0×10^{-5} mol/L (Dove and Hochella Jr 1993). The inhibition effect of a polymorphic phosphonate (methylenephosphonic acid) on the formation and trans-formation of calcium carbonates was investigated in detail (Sawada 1997). They reported that the transformation of vaterite to calcite was prohibited at phosphonate concentrations greater than $10^{-5.5}$ mol/L, and that amorphous calcium carbonate alone was generated at concentrations above $10^{-4.0}$ mol/L.

In this study, a series of scaling experiments were conducted using model hard water solutions containing trace amounts of phosphate ion (0.1-3.0 mg/L) to study its effect on the chemical characteristics of scale formed.

EXPERIMENTAL PROCEDURE

The experimental setup used is illustrated in **Fig. 1**. The test bottle was rinsed with 0.01 mol/L H_2SO_4 aqueous solution for 1 hour at room temperature then twice with distilled water before each experiment to remove any calcium carbonate residue. The temperature in the 585 mL Pyrex-glass bottle was controlled by water bath at 65 ± 0.1 °C. The solution was mixed continuously by a poly-tetrafluoroethylene-coated stirring bar rotating at 200-300 rpm. In order to study scale formation on copper heat transfer surfaces, a plate made of phosphorous-deoxidized copper (JIS C1220, dimensions 160 mm \times 23.5 mm, thickness 1 mm) was immersed vertically in the test solution. Prior to testing the plate was sanded with #320 and #1000 sandpapers and rinsed with 10% nitric acid followed by de-ionized water.

Analytical reagent grade chemicals (Wako Pure Chemical Industries) were used for all experiments. Distilled water, with a conductivity $< 1 \mu\text{S/m}$, was used throughout. The reactants were prepared in 1 L volumetric flasks, containing CaCO_3 , H_2SO_4 , HNO_3 , MgCl_2 , HCl and NaOH . A gas mixture of N_2 (99.995%) and CO_2 (pure) was used to adjust the pH of the solution to 7.7-8.7 after pure CO_2 gas was bubbled into the solution for 3 hours through a glass gas diffuser to dissolve any CaCO_3 completely. Phosphate ions were added as K_3PO_4 solution. **Table 1** compares the compositions of the test solution and a typical European tap water.

The conductivity and pH of the solution were measured by a conductivity electrode (TOA DKK, model CT-27112B) and pH electrode (TOA DKK, model GST-2729C) to monitor its change during scale formation. Deposits formed on the copper plates were analyzed by SEM/EDX (JEOL Ltd, model JSM-6335F/JED-2200F) and X-ray diffraction (MAC Science, MXP-18P) after drying in an oven at 60°C for 12 hours.

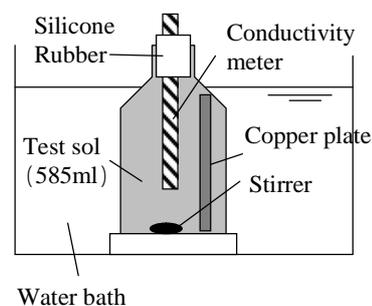


Fig. 1 Schematic drawing of apparatus

Table 1 Compositions of test solutions and tap water in Europe used in this study

	Test solution	Tap water
pH*	7.7	7.3-7.8
Ca hardness	292 mg/L	290 mg/L
M-alkalinity	220 mg/L	225 mg/L
Mg^{2+}	2.6 mg/L	3.2 mg/L
Cl^-	28.0 mg/L	23.8 mg/L
NO_3^-	43.0 mg/L	33.2 mg/L
HPO_4^{2-}	0-2.5 mg/L	2.5 mg/L
SO_4^{2-}	26.5 mg/L	22.8 mg/L

* Measured at 15°C

RESULTS AND DISCUSSION

Figure 2 shows the evolution of conductivity in solution in the presence and absence of phosphate after their pH values were adjusted to 8.7 by N_2 gas bubbling at 65 °C. The conductivity was averaged over three sets of experiment at the same condition. It was found that the conductivity dropped more slowly at higher concentration of phosphate. At 0.4 mg/L HPO_4^{2-} , the conductivity ranged between 56

and 67 mS/m for 150 hours and it reached its equilibrium after more than 400 hours. The percentage normalized conductivity, X , was defined as

$$X = (C_0 - C) / (C_0 - C_s) \times 100 \quad (9)$$

where C_0 is the initial conductivity, C is the value at a given time and C_s is the conductivity at equilibrium

The nucleation rate was estimated by comparing the time required for X to change from unity (initial value) by 20%, as shown by the arrow in **Fig. 2**. The nucleation time with 2.0 mg/L HPO_4^{2-} was about 17 times longer than that with no phosphate present. As scale formation proceeded, the conductivity of the solutions decreased, due to removal of ions by precipitation. The rate of scale formation was considered to be proportional to the change in conductivity. The results suggest that the time constant of scale formation in solution with 2.0 mg/L phosphate ions was about 17 times longer than that in solutions without phosphate.

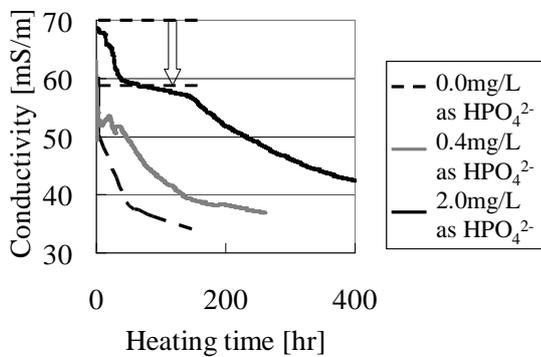


Fig. 2 Influence of initial concentration of HPO_4^{2-} ion on solution conductivity at 65°C

During the experiments, crystals were generated in solution as well as on the copper surface. SEM images for the cases of no and 2.0 mg/L HPO_4^{2-} are shown in **Fig. 3**. The images indicate that crystals with rhombic shape were produced at 2.0 mg/L HPO_4^{2-} , while acicular ones were observed in its absence. The trace amount of phosphate therefore affected the scale crystal habit.

Fig. 4 presents results from EDX analysis of the deposits in **Fig. 3**. In the case with no added phosphate, the peaks can be attributed to Ca, O, C, and Cu, whereas in the case with 2.0 mg/L HPO_4^{2-} added the spectrum shows the presence of Ca, O, C, Cu and P. This indicates the deposits consisted of CaCO_3 in both cases, and that the latter deposit contained trace amounts of phosphorus (taken to be adsorbed on growing crystal faces).

Fig. 5 shows X-ray diffraction patterns of the scale deposits. These confirmed that deposits formed in the presence of phosphate were calcite, while those formed without phosphate were a mixture of aragonite and calcite.

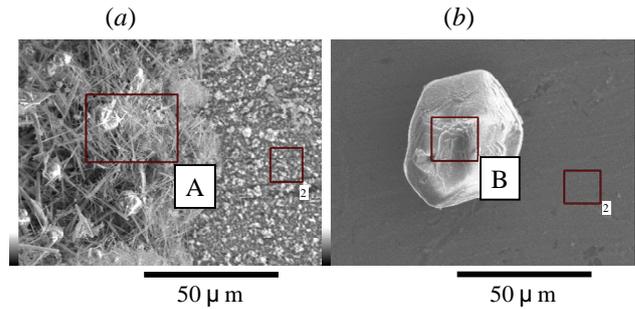


Fig. 3 SEM images of deposits or crystals. (a) no phosphate; (b) 2.0 mg/L HPO_4^{2-} .

In the presence of phosphate, the morphology of calcium carbonate was calcite regardless of the relative saturation ratio of the solution between $S=7$ ($\sigma=1.9$) and $S=72$ ($\sigma=4.3$). Therefore, the addition of phosphate may have different effects on the morphology, e.g. the adsorption of phosphate ions or the formation of phosphate salts on calcite surface, from that reported by Tai and Chen (1995), because Tai and Chen stated that the morphology of calcite formed had a correlation with the relative solubility in their system where phosphate is absent.

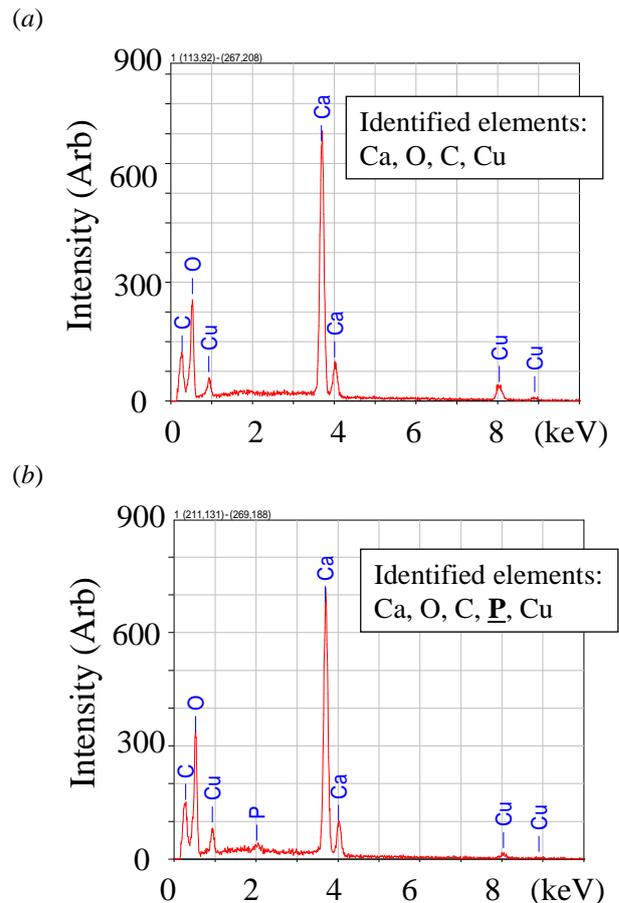


Fig. 4 EDX patterns of the deposits formed in test solutions (Acceleration voltage 15 keV). (a) HPO_4^{2-} 0.0 mg/L, location A in **Fig. 3(a)**; (b) HPO_4^{2-} 2.0 mg/L: location B in **Fig. 3(b)**.

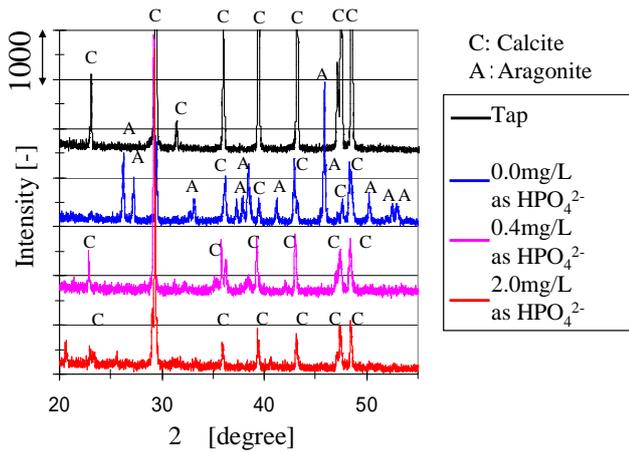


Fig. 5 X-ray diffraction patterns of the deposits (CuK α line, Voltage 40 keV, Current 200 mA). A denotes a peak from the aragonite spectrum, C one from calcite.

Fig.6 summarizes the change in ion composition in solutions containing 2.0 mg/L phosphate during heating at 65°C. More than 90% of the phosphate and 20% of the calcium were removed from the solution in forming scale. These changes suggest that the deposits formed contain both calcium and phosphate. Apart from Ca²⁺ and HPO₄²⁻, the ion composition did not change (within experimental error).

Fig.7 shows evolutions of the solution conductivity during heating at different relative solubility ratios. The conductivity was averaged over three sets of experiment at the same condition. N₂ gas bubbling was used to adjust the relative solubility ratios. In the presence of phosphate, the conductivity decreased more quickly at higher relative solubility. The induction period, the time before the nucleation starts, decreased in a similar way at higher relative solubility. It should be noted that the morphology of calcium carbonate was calcite regardless of the relative saturation ratio, here between S=7 and S=72. As shown in Fig.2, the conductivity in solution with no phosphate dropped more quickly than when phosphate was present.

According to the nucleation theory, as shown in equation (8), the induction time can be related to the relative solubility, S, and the interfacial energy between the nuclei and water. The induction time (t) was evaluated by calculating the time required for 5% decrease in conductivity in Fig.7.

Firstly, as shown in **Fig.8**, the relationship between t and S for the case with 2.0 mg/L reasonably follows this relationship reasonably well. This suggests that the interfacial energy between water and the deposits were constant, and is supported by the observation that calcite were formed in all cases. Secondly, the relationship for the case with no phosphate differed from that with phosphate. A 30% increase in the interfacial energy caused by HPO₄²⁻ may account for the difference. This suggests that the adsorbed phosphate or salts increase the interfacial energy.

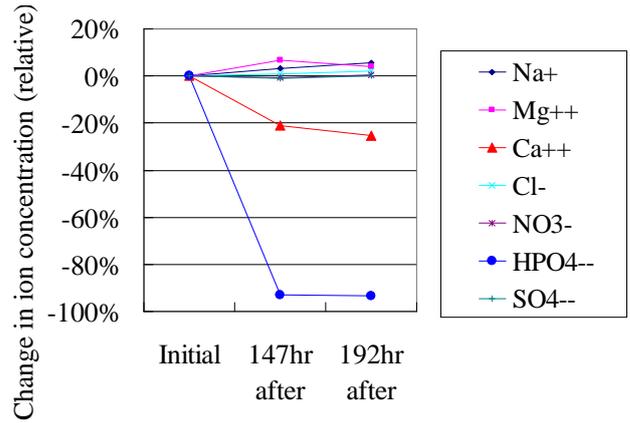


Fig.6 Change in ion composition in solution containing 2.0mg/L HPO₄²⁻

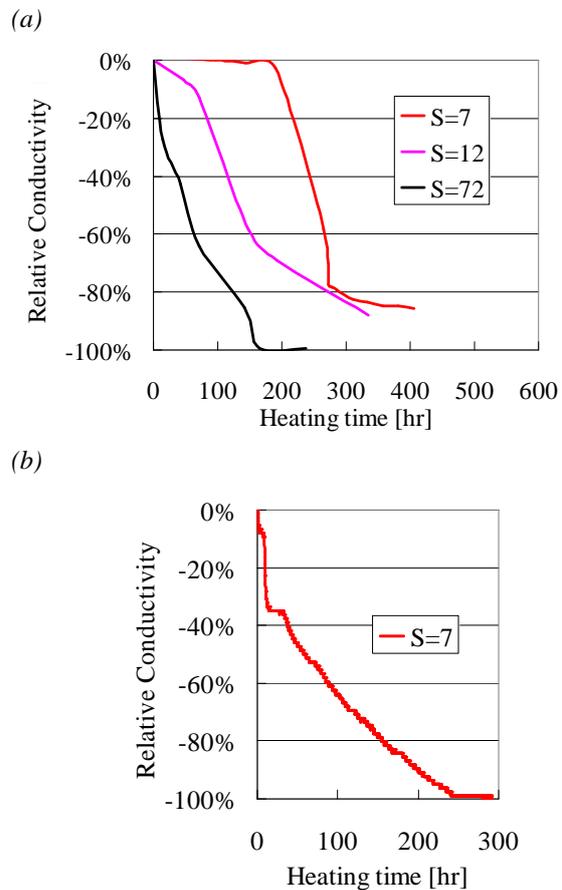


Fig.7 Evolutions of solution conductivity at different relative solubility ratios. (a) HPO₄²⁻ 2.0 mg/L (b) no HPO₄²⁻

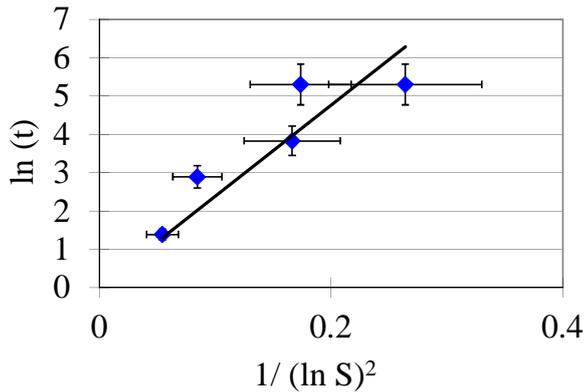


Fig.8 Relationship between the induction time and the relative solubility

CONCLUSIONS

1. A trace amount (2.0 mg/L) of phosphate slowed down the rate of formation of the deposits at 65°C significantly.
2. X-ray diffraction and SEM/EDX analysis of the scale layers confirmed that deposits formed in the presence of phosphate were calcite, while those formed without phosphate were a mixture of aragonite and calcite.
3. The relationship between the induction time and the relative solubility (S) follows nucleation theory reasonably well at 2.0 mg/L HPO_4^{2-} , and is supported by the observation that only calcite was formed between $S=7$ and $S=72$.

NOMENCLATURE

- f_D activity factor for divalent ions (-)
 ΔG_C free energy of nucleation at a critical condition (-)
 IAP ion activity product (-)
 k Boltzman constant (J/K)
 K equilibrium constant (-)
 K_{sp} solubility constant for calcite (-)
 S relative solubility (-)
 T temperature (K)
- v_C molecular volume of critical nuclei (m^3)
 γ interfacial tension (J/m^2)
 $[]$ = species concentration, in mol/L

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