# Scale reduction and scale modification effects induced by Zn and other metal species in physical water treatment

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## Abstract

The effect of Zn and other metal ions, released by some physical water treatment devices, on the nucleation rate and crystal morphology of calcium carbonate was investigated. Zn in particular caused a substantial increase in induction time and induced the formation of calcium carbonate in the aragonite rather than the calcite form. These effects were quantified. A minimum Zn/Ca mass ratio of 0.06 x $10^{-3}$ was required for Zn to cause measurable effects. At [Ca] > 300 mg·$dm^{-3}$ addition of Zn of up to 100 μg·$dm^{-3}$ had a negligible effect on nucleation rate and crystal morphology. Cu was found to be only half as effective as Zn while Mg required to be present at concentrations 1 000 times more than Zn to produce comparable effects. Colloidal $Fe_2O_3$ caused a decrease in induction time. The direct effect of Zn on scale reduction in laboratory tests amounted to about 77±6 % and was achieved with 300 mg·$dm^{-3}$ Ca solutions to which 200 μg·$dm^{-3}$ Zn was added.

## Introduction

We have previously reported (Coetzee et al., 1996) that Zn and other metal ions released from surfaces in certain magnetic and other physical water treatment (PWT) devices used for antiscale treatment, were primarily responsible for the observed scale reduction effects. We have shown that trace amounts of Zn in particular, can slow down the nucleation rate of calcium carbonate and also promote its crystallisation in the aragonite rather than the calcite form even under conditions where calcite would be the preferred crystal form.

These findings seem to account for at least some of the more frequently encountered claims (Baker and Judd, 1996) in physical water treatment. Claims such as reduced rates of crystallisation (Dalas and Koutsoukos, 1989) and the formation of a soft scale with less adhesive strength (Ellingsen and Fjeldsend, 1982) fit into this mould. There may or may not exist effects directly related to magnetic or electric fields generated by physical water treatment devices. It is, however, beyond the scope of this paper to comment on this issue.

The fact that ionic impurities can influence crystallisation reactions, is well known. Meyer (1984), for instance studied the effect of impurities on the crystal growth rate of calcite. He reported that 2±$10^{-7}$ mol·$dm^{-3}$ of $Zn^{2+}$ ions can reduce the crystal growth rate in calcite by 80%. A number of metal and non-metal ions were tested, all showing different efficiencies in influencing crystal growth rates. No obvious correlation was found between the physical and chemical properties of the ions and their effect. A model based on the blocking effect of an impurity at a particular growth site for the inhibition mechanism was nonetheless proposed.

Other researchers reported on the role of dissolved and suspended Fe species, either released from magnetic water treatment devices or initially present in the water. Pajaro and Pandolfo (1994) reported that magnetic fields applied to flowing tap water containing more than 5 μg·$dm^{-3}$ iron ions cause the formation of $CaCO_3$ in the aragonite crystal form. They speculate that the magnetic field induced the formation of complex Fe species which may act as nucleation centres for the crystallisation of $CaCO_3$. Herzog et al. (1989) found that different forms of iron hydroxides or hydrated iron oxides did not have any effect on the rate of precipitation of $CaCO_3$. The presence of Fe as the sulphate salt, however, decreased the rate of crystallisation. The precipitation was forced by the addition of seed crystals of calcite or aragonite and was dependent on Fe concentration but independent of all other factors, including being exposed to a 3.5 T magnetic field. At an Fe concentration of 5.6 μg·$dm^{-3}$ (which is reckoned by the authors to be not untypical of groundwater), precipitation was delayed by 120 min. It was found that the formation of aragonite was promoted and that of calcite inhibited. Based on these results it was proposed that the efficiency of PWT devices depended on the amount of iron released by the device. In an investigation by Hasson (Hasson and Bramson., 1985), $FeCl_2$ was added to $Ca(HCO_3)_2$ solutions and the effect on scale reduction studied. It was found that 1.2 to 1.4 μg·$dm^{-3}$ of Fe lowers the amount of scale by 40%. Only two results were obtained however. No effects were found by Caplan and Stegmayer, 1987). In quite a number of the references (Ozaki et al., 1988; Miles et al., 1985; Tombacz et al., 1991) it was claimed and experimentally verified, that colloidal suspensions of Fe were influenced by a magnetic field orthogonal to the flow. It has, for instance, been shown that haematite coagulates under specific conditions if subjected to a magnetic field. These experiments were done with pure haematite sols and not in the presence of scale-forming salts.

The main objective of the work reported on here, was to study the effect of Zn on the nucleation rate and crystal morphology of $CaCO_3$. Nucleation rates were quantified and concentration limits for Zn and Ca established in view of the possible use in scale reduction applications.

## Experimental

### Instrumentation

For routine **elemental analysis**, a Varian Liberty 220 inductively-coupled plasma optical emission spectrometer (ICP-OES) and GBC 909 atomic absorption spectrometer were used.

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**pH measurements** were made with an Orion 940 research pH meter. **Crystal morphologies** and **crystal structures** of precipitated $CaCO_3$ were determined with an ISO-SS60 scanning electron microscope (SEM) and X-ray diffraction (XRD) using a Phillips PW1729 diffractometer. **Particle sizes** were determined by photo correlation spectroscopy using a Malvern Zetamaster.

### Solutions

#### *(i) $H_2O$*

Deionised water with an electrical resistance of 18 MΩ was used to prepare stock and test solutions. All solutions were filtered through 0.45 μm membrane filters before use.

#### *(ii) Supersaturated $CaCO_3$*

Supersaturated $CaCO_3$ solutions were prepared by mixing appropriate dilutions of 0.025 $mol\cdot dm^{-3}$ $Ca(NO_3)_2.4H_2O$ and $NaHCO_3$. The pH of the $NaHCO_3$ solution was adjusted to between 7.2 and 7.6 with $HNO_3$ (AR from Merck) beforehand to prevent premature precipitation on mixing with $Ca(NO_3)_2.4H_2O$. Below pH 7.2 nucleation times were too slow for some mixtures used in this study. The initial pH was kept constant for a particular batch of experiments to ensure that results were comparable. The mixtures were kept at room temperature for a period of 15 min before starting the experiments.

#### *(iii) Spiked $NaHCO_3$*

The influence of trace amounts of metals on the induction time of the precipitation of $CaCO_3$ was studied by spiking $NaHCO_3$ solutions with different species immediately before mixing with the calcium solution. Stock solutions of the metals, Ag, Cu, Zn, Ni, Fe, and colloidal $Fe_2O_3$ were prepared from the salts: $AgNO_3$ (AR Merck); $Cu(NO_3)_2.3H_2O$ ( AR Merck); $ZnSO_4.7H_2O$ (AR BDH); $Ni(NO_3)_2.6H_2O$ (AR Merck); $FeSO_4.7H_2O$ (AR Merck). The solutions were rendered acidic to a pH of 2.2 by the addition of 66 μl of $HNO_3$ (AR, Merck) per 100 ml solution to prevent hydrolysis. After preparation these solutions were stored in polyethylene containers. The change in pH after addition of up to 100 μl of spike to $NaHCO_3$ was negligibly small (i.e. pH change of less than 0.1 unit).

The colloidal haematite suspension was prepared as follows: 25 ml of 0.72 $mol\cdot dm^{-3}$ $FeCl_3$ (final concentration 0.018 $mol\cdot dm^{-3}$) was added to 975 ml of boiling 0.004 $mol\cdot dm^{-3}$ HCl and incubated for 24 h at 100 °C. The sol was purified by flocculation with 0.15 $mol\cdot dm^{-3}$ KCl and resuspended after the supernatant was poured off. The sol was stored in 0.001 $mol\cdot dm^{-3}$ $HClO_4$.

### Procedures

#### *(i) Cleaning procedures*

We tried to prevent premature heterogeneous nucleation of $CaCO_3$ caused by the possible presence of impurity particulates, by taking extreme care with the cleaning of equipment and solutions. Only glass and polyethylene equipment was used to eliminate all uncontrolled sources of metal contamination during the experiments. Glass equipment was soaked in 10 % $HNO_3$ (AR Riedel de Haen), for at least 12 h. It was then washed profusely with de-ionised water and subjected to steam cleaning for at least 10 min to remove insoluble particles that might adhere to inner glass surfaces.

#### *(ii) Measurement of pH vs. time curves*

The crystallisation of $CaCO_3$ from supersaturated solutions was followed by measuring the pH of the solution over time until the reaction was complete. The pH vs. time or precipitation curves so recorded could then be used to obtain information regarding induction times and nucleation rates. A batch method was used in which test and control samples could be measured simultaneously in triplicate under exactly the same conditions. $Ca(HCO_3)_2$ solutions prepared by mixing appropriate volumes of $NaHCO_3$ and $Ca(NO_3)_2$ solutions were always supersaturated to varying degrees. The concentration was, however, chosen in such a way that the solution was metastable with regard to precipitation. Precipitation was therefore thermodynamically possible but did not occur immediately because kinetically the nucleation rate was too slow. Precipitation thus only started after heating at 37°C for varying periods depending on the saturation index and the presence of ionic impurities. Extreme care was taken to ensure that all experimental conditions such as, temperature, concentration, age of solution, condition of glassware, and pH were exactly the same for test and control measurements.

The same stock solutions were used to prepare samples for test and control measurements. After a predetermined waiting time, typically 15 min after mixing, glass beakers containing sample solutions were placed on a multi-point magnetic stirrer assembly (the rate of stirring was exactly the same at all stirring positions) in a waterbath at 37 °C. The pH of six solutions, three tests and three controls, was measured until completion of the reaction which was indicated by the pH remaining constant. The same pH probe was used to monitor all six solutions to ensure comparability of the measurements. The probe was rinsed between measurements to prevent cross-contamination.

#### *(iv) Crystal morphology*

Crystals were collected when the crystallisation process was completed, vacuum-dried and small amounts mounted for SEM analysis. Calcite, aragonite and vaterite crystal forms were easily identified by recognising the calcite rhombohedrons, aragonite needles and vaterite discs. It was possible to estimate the percentage composition in samples where mixtures of crystal morphologies occurred. Crystal structures were also determined by XRD. Crystal morphology is an important parameter in determining the properties of scale. Calcite is usually associated with a hard scale whereas aragonite and vaterite could give rise to a softer type of scale that is easily removed. No consensus has, however, been reached on this issue.

We found aragonite crystals prepared from pure solutions to be brilliantly white and they appeared to be having a fluffy character whereas calcite appeared to be flaky and not as brilliant. These observations are of course somewhat subjective. Visual inspection of crystals formed during the course of experiments, however, provided an early indication of what the crystal structure of the precipitates might be.

## Results and discussion

### Interpretation of pH vs. time curves

The effect of non-lattice ions, such as $Zn^{2+}$ released from PWT devices, on the crystallisation reaction of $CaCO_3$ can conveniently be studied by following over time the pH changes in the precipitating solution containing these species in addition to $Ca^{2+}$

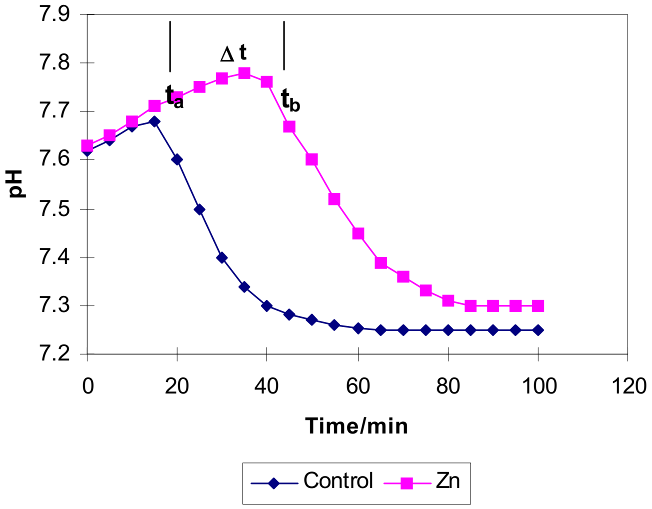

**Figure 1**
*pH vs. time curves for the precipitation of $CaCO_3$ from 150 mg·dm$^{-3}$ Ca solutions, induction time $t_a$ (control) and 150 mg·dm$^{-3}$ Ca + 50 µg·dm$^{-3}$ Zn solutions, induction time, $t_b$ (Zn)*

and $CO_3^{2-}$ species. The data from these experiments, graphically presented as pH vs. time curves or precipitation curves, can then be used to calculate induction times, i.e. time from mixing of reagents to first precipitation. Precipitation curves obtained for the precipitation of $CaCO_3$, from a pure solution of its ions (including the counter ions $NO_3^-$ and $Na^+$) and a solution containing in addition to the above also trace amounts of $Zn^{2+}$ and $SO_4^{-2}$ species, are shown in Fig 1.

The curves are characterised by a gradual rise in pH caused by the initial slow release of $CO_2$ from the solution as the temperature is increased from ambient (22°C in a temperature-controlled laboratory) to 37°C. The experimental temperature was reached within 5 min after introducing the test solutions to the water bath.

The sharp downward adjustment in the pH marks the onset of the precipitation of solid $CaCO_3$. This process is accompanied by the appearance of a slight milkiness in the solution. It also approximately marks the end of the nucleation process and the beginning of the crystal growth phase. The induction time or nucleation time, denoted as, $t_a$, for pure $CaCO_3$ and, $t_b$, for $CaCO_3$ in the presence of $Zn^{2+}$, and the delay time, Δt, where:

$$\Delta t = t_b - t_a$$

could then be determined graphically. Typically, induction times were increased in the presence of $Zn^{2+}$. This increase compared to the control was used as experimental parameter to study the effect of Zn and other metal ions on the nucleation rate of $CaCO_3$. It is also important to note that the precipitation commenced at a higher pH in the presence of $Zn^{2+}$.

All experiments were done in triplicate (3 controls and 3 tests) and repeated in case the precision was inadequate. Average induction times were calculated and the standard deviation for each set was used to calculate a Gaussian distribution for each average. The difference between the position of these curves, which coincided with $t_a$ and $t_b$, gave the delay time, Δt. The relevant Gaussian distributions for the induction times are shown in Fig. 2. Visual inspection of these curves gave a good indication of the quality of the data supporting the calculated delay time.

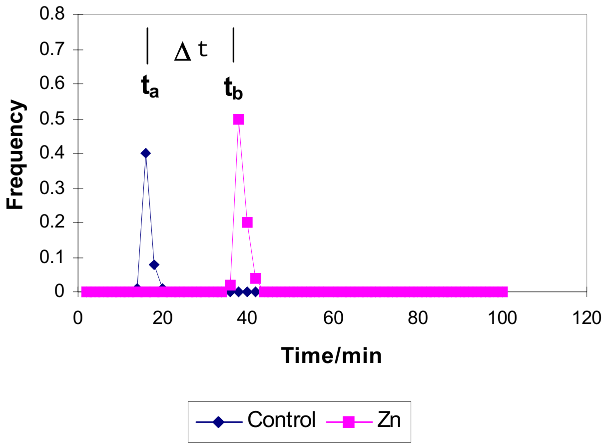

**Figure 2**
*Gaussian distributions of induction times for the precipitation of $CaCO_3$ at 37°C from a pure solution (control) and one with 50 µg·dm$^{-3}$ of Zn added (Zn)*

Narrow curves without baseline overlap indicated strong statistical support for a particular Δt value.

## The effect of Zn/Ca concentration ratios on delay time

A series of experiments were performed to establish the minimum concentration of Zn that would still produce a measurable effect on the induction times and crystal morphology. At the same time the upper limit for [Ca] (The symbol [ ] in this paper denotes concentration as specified, e.g. mg·dm$^{-3}$ or µg·dm$^{-3}$ and not necessarily molar concentration at equilibrium as in its usual meaning) beyond which adding Zn would have a negligible effect, was to be determined. Table 1 summarises the Δt-values or delay times observed for various parameters studied.

Delay times generally increased almost linearly with [$Zn^{2+}$] and decreased with [$Ca^{2+}$]. Typical curves showing this effect are given in Fig. 3.

At higher [$Zn^{2+}$] a levelling-off in Δt occurred. This is better illustrated when Δt is plotted as a function of the [Zn]/[Ca] ratio as in Fig. 4. Despite the scatter in the points a useful trend in the dependence of Δt on [Zn]/[Ca] ratio can be recognised. Mass ratios as low as 0.06 x $10^{-3}$ (i.e. 0.06 µgZn/mgCa) can still result in a measurable delay time of ca. 9 min and represent a practical lower limit to the [Zn]/[Ca] ratio. Strong levelling-off occurs at ratios above 2 x$10^{-3}$ which can be taken as an upper limit above which the law of diminishing returns applies. Each point on the curve represents an average of 3 to 6 replicates. The data represent results from independent experiments done by different research workers over a period of one year.

Limiting [Ca] would at the lower end be determined by the minimum supersaturation level that would give rise to the precipitation of $CaCO_3$. Theoretically precipitation would occur when $[Ca^{2+}][CO_3^{2-}] > K_{sp}(CaCO_3)$. The higher the supersaturation the smaller the metastable region becomes. The concentration where precipitation occurs too soon after mixing equimolar solutions of $Ca^{2+}$ and $HCO_3^-$ for proper measurement of induction times, is at levels slightly >300 mg Ca·dm$^{-3}$ in filtered ( 0.45µ) solutions made with deionised water. This value can change depending for example on the presence and concentration of colloidal particles not efficiently removed in the cleaning procedure. To demonstrate the existence of such a limiting maximum

**TABLE 1**
**DELAY TIMES,ΔT, MEASURED FOR VARIOUS NON-LATTICE IONS ADDED TO SUPERSATURATED METASTABLE $Ca(HCO_3)_2$ SOLUTIONS AT 37°C. WAITING TIME = 15 MIN.**

| Spiked ions | | [Ca] mg·dm$^{-3}$ | [ion]/[Ca] x 10$^{-3}$ | Δt min |
|---|---|---|---|---|
| species | µg·dm$^{-3}$ | | | |
| Zn$^{2+}$ | 10 | 75 | 0.13 | 24±5 |
| | 25 | 75 | 0.33 | 47±9 |
| | 50 | 75 | 0.66 | 68±6 |
| | 75 | 75 | 1.00 | 73±8 |
| | 100 | 75 | 1.33 | 78±5 |
| Zn$^{2+}$ | 10 | 100 | 0.10 | 19±9 |
| | 25 | 100 | 0.25 | 34±7 |
| | 50 | 100 | 0.50 | 42±5 |
| | 75 | 100 | 0.75 | 53±6 |
| | 100 | 100 | 1.00 | 61±9 |
| Zn$^{2+}$ | 10 | 150 | 0.06 | 9±3 |
| | 25 | 150 | 0.16 | 19±2 |
| | 50 | 150 | 0.33 | 30±2 |
| | 75 | 150 | 0.5 | 36±1 |
| | 100 | 150 | 0.66 | 42±3 |
| | 250 | 150 | 1.67 | 43±2 |
| | 500 | 150 | 3.33 | 109±1 |
| Zn$^{2+}$ | 50 | 250 | 0.25 | 10±3 |
| Zn$^{2+}$ | 25 | 300 | 0.08 | -1±1 |
| | 50 | 300 | 0.16 | 0±1 |
| | 75 | 300 | 0.25 | 1±2 |
| | 100 | 300 | 0.33 | 2±1 |
| Ag$^{+}$ | 100 | 100 | 1.00 | 0 |
| Ni$^{2+}$ | 100 | 100 | 1.00 | 2±1 |
| Mg$^{2+}$ | 10000 | 150 | 66.7 | 14 |
| Mg$^{2+}$/Zn$^{2+}$ | 10000/50 | 150 | 667/0.33 | 21 |
| Cu$^{2+}$ | 50 | 100 | 0.50 | 14±6 |
| | 100 | 100 | 1.00 | 28±12 |
| Cu$^{2+}$/Zn$^{2+}$ | 50/50 | 100 | 0.5/0.5 | 29±4 |
| | 100/50 | 100 | 1.0/0.5 | 41±8 |
| Fe$^{2+}$ | 50 | 100 | 0.5 | 4±2 |
| | 100 | 100 | 1.0 | 0±2 |
| | 500 | 100 | 5.0 | 1±2 |
| | 1000 | 100 | 10.0 | 7±3 |
| haematite sol | 1000 | 100 | 10.0 | -13±3 |
| $Na_2HPO_4$ | 1x10$^{-5}$ mol·dm$^{-3}$ | 150 | 2.5x10$^{-3}$ | 159 |
| $Na_2HPO_4$ | 1x10$^{-6}$ mol·dm$^{-3}$ | 150 | 2.5x10$^{-4}$ | 5 |
| $Na_2P_2O_7$ | 1x10$^{-6}$ mol·dm$^{-3}$ | 150 | 2.5x10$^{-4}$ | 252 |
| $Na_2P_2O_7$ | 1x10$^{-7}$ mol·dm$^{-3}$ | 150 | 2.5x10$^{-5}$ | 30 |
| EDTA | 1x10$^{-5}$ mol·dm$^{-3}$ | 150 | .5x10$^{-3}$ | -16 |

[Ca], a series of experiments was done in which Δt was determined for mixtures with different [Zn] and [Ca]. The results are shown in Fig. 5.

The curves for the different [Zn] seem to converge at [Ca] around 300 mg·dm$^{-3}$. This value would be partially dependent on experimental variables which are difficult to control, such as particulate contamination from the air and solutions.

## Mass balance checks

To establish whether Zn was actually coprecipitating with the $CaCO_3$ and whether the rate at which $CaCO_3$ was formed was changed in any way by the addition of Zn, mass balance checks were done during the course of the reaction. Samples were taken at regular intervals, one half of each sample was filtered through a 0.45 µm filter and the other half dissolved in acid, and the [Ca] and [Zn] determined by ICP-OES. The results based on 8 experiments, each done in triplicate with 150 mg·dm$^{-3}$ Ca solution to which 50 µg·dm$^{-3}$ Zn was added, are graphically depicted in Fig. 6 for Ca and in Fig. 7 for Zn.

The concentration of dissolved Ca, shows a steady decrease over time for both the pure Ca solutions and those to which Zn was added. The amount of Ca in solution is, however, consistently higher in the case of the latter. This means that the rate at which $CaCO_3$ was precipitating was lower in the solutions containing Zn. The total [Ca], as determined in the dissolved samples, remained constant at the initial level throughout the reaction proving that all Ca$^{2+}$ ions have been accounted for.

The soluble [Zn] also decreased over time as the precipitation proceeded indicating that Zn coprecipitated with the $CaCO_3$. The total [Zn] as determined after filtration in the dissolved precipitate, however, remained constant at the initial value throughout the process. This proved that no losses of Zn due to adsorption had occurred.

## Time efficiency of Zn$^{2+}$ treatment

The fact that Zn$^{2+}$ ions were introduced into a solution containing $HCO_3^-$ ions, at a concentration of up to 50 000 times more than the initial free [Zn$^{2+}$], means that the speciation of the solution will change over time. The free [Zn$^{2+}$] will decrease and its equilibrium concentration will eventually be determined by the $K_{sp}$ for $Zn(OH)_2$ and the formation constants for complexation of Zn$^{2+}$ by $CO_3^{2-}$ and $OH^-$ to form $ZnCO_3$(aq), $Zn(CO_3)_2^{2-}$(aq), $Zn(OH)^+$(aq) and $Zn(OH)_2$(aq) species. We therefore studied the effect which these changes would have

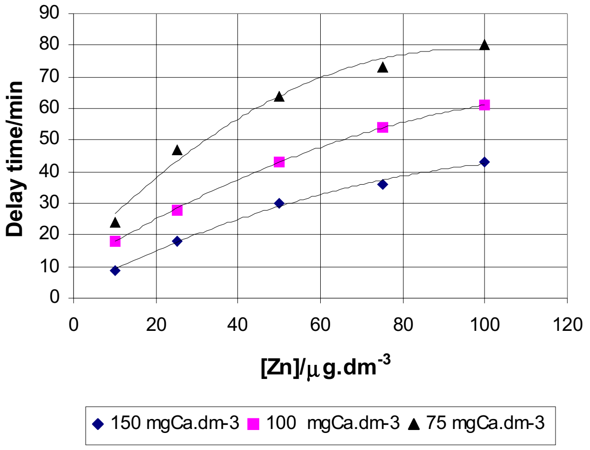

**Figure 3**
*Dependence of delay time, Δt, on [Zn] at constant [Ca]*

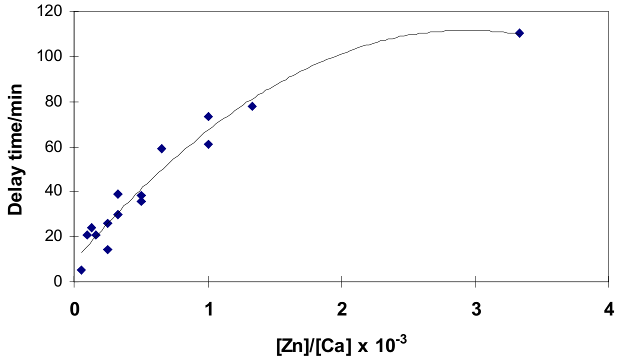

**Figure 4**
*Delay time, Δt, as a function of Zn/Ca ratio*

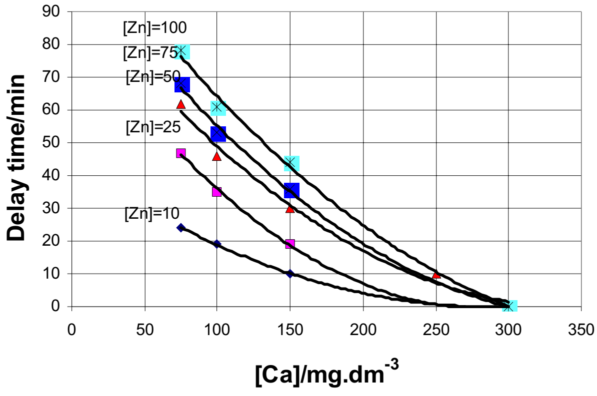

**Figure 5**
*Delay time, Δt, as a function of [Ca] for different [Zn] ([Zn] in $\mu g \cdot dm^{-3}$)*

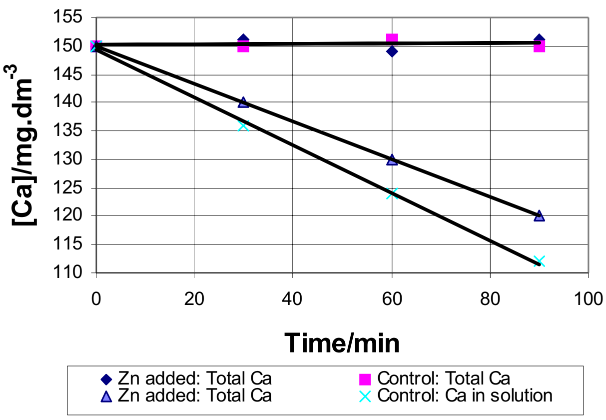

**Figure 6**
*Effect of 50 $\mu g \cdot dm^{-3}$ Zn on [Ca] during the precipitation of $CaCO_3$ from 150 $mg \cdot dm^{-3}$ Ca solution compared with a control solution without Zn*

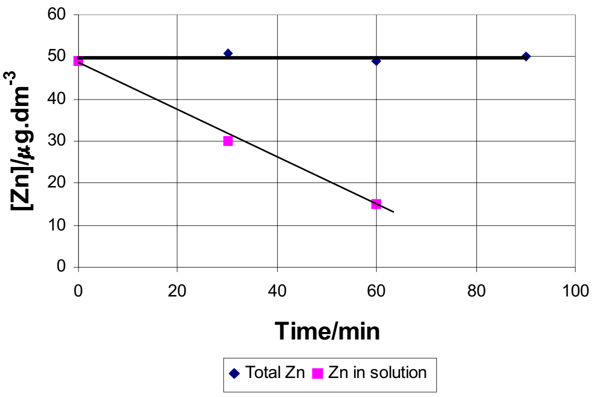

**Figure 7**
*Change in [Zn] over time during the precipitation of $CaCO_3$ from 150 $mg \cdot dm^{-3}$ Ca solution containing 50 $\mu g \cdot dm^{-3}$ of Zn*

on the effectiveness of Zn species to produce delays in precipitation.

Equimolar solutions of $NaHCO_3$ containing 50 $\mu g \cdot dm^{-3}$ of $ZnSO_4$ and $Ca(NO_3)_2.4H_2O$ (150 $mg \cdot dm^{-3}$ of $Ca^{2+}$) were mixed and left standing at room temperature for up to 24 h before the precipitation reaction was induced by heating and the delay times determined by pH measurement. A very slow decrease in Δt was observed over 24 h. This result would indicate that active species are slowly changed into inactive species over time. This was also confirmed by polarographic studies in previous work (Coetzee et al., 1996). A distribution diagram showing the change in species concentration as a function of pH in a $Zn/Ca/HCO_3^-$ system and calculated using Minteqa2 (Allison et al., 1991), is given in Fig. 8. It is evident that about 40 % of the $Zn^{2+}$ ions will be converted into $ZnCO_3(aq)$ species at a pH of between 7.7 and 8.2 which are typical pH values for the $HCO_3^-$ systems used in this study and of drinking water.

### Effect on crystal morphology of $CaCO_3$

Scanning electron microscopy of the precipitated crystals confirmed the formation of $CaCO_3$ in the aragonite form when precipitating solutions were treated with trace amounts of $Zn^{2+}$

ions. $CaCO_3$ solutions with no $Zn^{2+}$ added consistently produced calcite crystals. Calcite/aragonite percentages found for different Zn/Ca mass ratios are summarised in Table 2.

**TABLE 2**
**A SUMMARY OF THE % CALCITE:ARAGONITE FOUND IN THE $CaCO_3$ PRECIPITATE, WHEN Ca SOLUTIONS WERE SPIKED WITH DIFFERENT IONS AND SOLS**

| Spike species | [Ca] mg·dm$^{-3}$ | [Spike species] µg·dm$^{-3}$ | % Calcite: aragonite | Zn/Ca x10$^{-3}$ |
|---|---|---|---|---|
| Zn | 150 | 10 | 100:0 | 0.06 |
| Zn | 150 | 25 | 75:25 | 0.16 |
| Zn | 150 | 50 | 20:80 | 0.33 |
| Zn | 150 | 75 | 0:100 | 0.5 |
| Zn | 150 | 100 | 0:100 | 0.66 |
| Zn | 150 | 250 | 0:100 | 1.67 |
| Zn | 150 | 500 | 0:100 | 3.33 |
| Zn | 100 | 10 | 40:60 | 0.10 |
| Zn | 100 | 25 | 50:50 | 0.25 |
| Zn | 100 | 50 | 5:95 | 0.5 |
| Zn | 100 | 75 | 0:100 | 0.75 |
| Zn | 100 | 100 | 0:100 | 1.00 |
| Zn | 75 | 10 | 30:70 | 0.13 |
| Zn | 75 | 25 | 15:85 | 0.33 |
| Zn | 75 | 50 | 0:100 | 0.66 |
| Zn | 75 | 75 | 0:100 | 1.00 |
| Zn | 75 | 100 | 0:100 | 1.33 |
| Ni | 100 | 100 | 100:0 | 1.00 |
| Ag | 100 | 100 | 100:0 | 1.00 |
| Cu | 100 | 50 | 90:10 | 0.05 |
| Cu | 100 | 100 | 5:95 | 1.00 |
| Cu + Zn | 100 | 50:50 | 0:100 | 0.5/0.5 |
| $Fe^{2+}$ | 100 | 100 | 75:25 | 1.00 |
| $Fe^{2+}$ | 100 | 1000 | 90:10 | 10.0 |
| haematite | 100 | 1000<br>2000 | 65:35<br>75:25 | 10.0<br>20.0 |
| $Na_2HPO_4$ | 1x10$^{-6}$ mol·dm$^{-3}$ | 150 | 100:0 | 2.5x10$^{-3}$ |
| $NaP_2O_7$ | 1x10$^{-6}$ mol·dm$^{-3}$ | 150 | 100:0 | 2.5x10$^{-3}$ |

From Table 2 it is clear that aragonite was the preferred crystallographic form for $CaCO_3$ when precipitation took place in the presence of small amounts of Zn. At Zn/Ca mass ratios larger than 0.5 x $10^{-3}$, 100% aragonite was produced with no traces of calcite. For smaller ratios down to 0.06 x $10^{-3}$, increasing amounts of calcite were found precipitating with the aragonite. Below 0.06 x $10^{-3}$, calcite was formed predominantly.

### Effect of organic and inorganic impurities

Various organic and inorganic complexing agents were tested for their effect on the efficiency of Zn to increase nucleation times of $CaCO_3$ and by implication the rate of scale formation. Chloride was tested because it forms relatively strong $ZnCl_3^-$ complexes and is always present in water. In test solutions containing 150 mg·dm$^{-3}$ Ca and 100 µg·dm$^{-3}$ Zn it was found that up to 400 mg·dm$^{-3}$ $Cl^-$ could be tolerated before a decrease in $\Delta t$ became noticeable. At 1 600 mg·dm$^{-3}$ $Cl^-$, $\Delta t$ was decreased by 40%. At a concentration of 1 mg·dm$^{-3}$, organic acid anions such as acetate caused a 70% reduction in $\Delta t$ while strong chelation agents such as EDTA caused a 100 % reduction. Acetate and EDTA form complexes with both Ca and Zn. The overall effect of Zn on the precipitation of $CaCO_3$ is therefore reduced in such systems.

### Effect of other metal and anionic species

In preliminary work we had found that other metal ions such as $Cu^{2+}$, $Ni^{2+}$, and $Fe^{2+}$ released by some PWT devices (Coetzee et al., 1996) and non-metal ionic species that might occur in industrial water, seem to affect the nucleation rate of $CaCO_3$ to varying degrees ranging from large increases in induction times (even larger than those recorded for Zn) induced by certain phosphates, to almost no effect at all by metals such as Ni and negative effects by chelating agents like EDTA. $Cu^{2+}$ gave rise to $\Delta t$ values about half of those for $Zn^{2+}$ while $Mg^{2+}$ was much less effective, requiring concentrations 1 000 times more than for Zn to produce comparable effects. Effects on crystal morphology also seem to vary. Metal ions generally induced the formation of aragonite while in solutions containing small amounts of phosphates calcite was produced. $Ni^{2+}$ and $Ag^+$, however, produced calcite. Tables 1 and 2 summarise the results for delay times and crystal morphology changes for some species tested. Results obtained for mixtures of Zn with either $Mg^{2+}$ or $Cu^{2+}$ indicate that the effects were not synergistic nor entirely cumulative, that is, the observed delay times for the mixture were smaller than delay times for the metals measured separately at the same concentration ratios.

The effect of Fe, both dissolved Fe and colloidal iron oxides, was studied in some detail because of

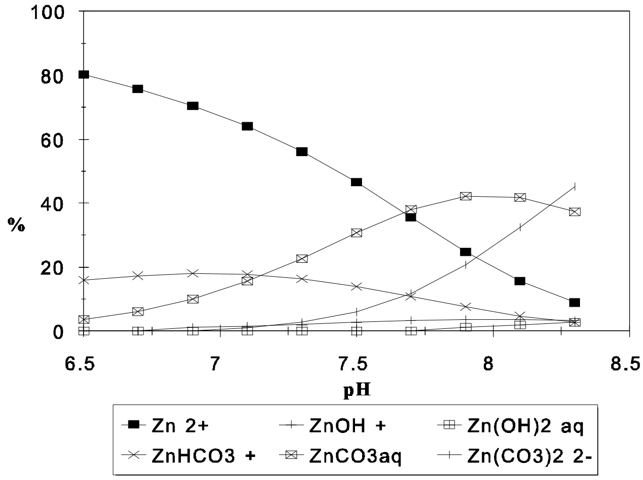

**Figure 8**
*Distribution diagramme of Zn species in a 150 mg·dm$^{-3}$ $CaCO_3$ solution containing 100 µg·dm$^{-3}$ Zn*

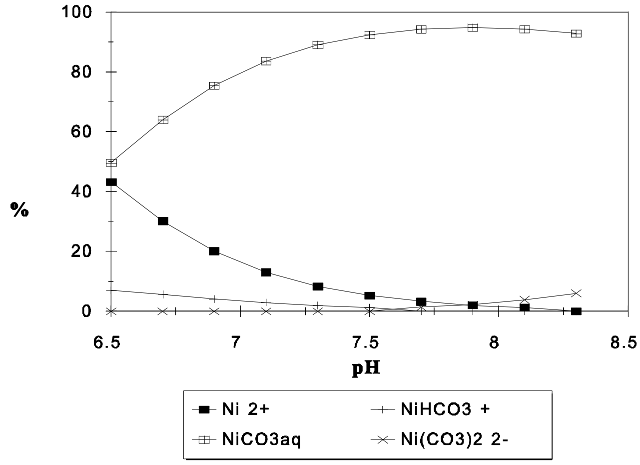

**Figure 9**
*Distribution diagramme of Ni species in a 150 mg·dm$^{-3}$ $CaCO_3$ solution containing 100 µg·dm$^{-3}$ Ni*

frequent reference in the literature to the possible role of Fe species in magnetic water treatment. Since none of the devices tested in the previous study (Coetzee et al, 1996), released more than 100 µg·dm$^{-3}$ Fe, it was decided to test a $Ca(HCO)_2$ solution with 50, 100 and 1 000 µg·dm$^{-3}$ of Fe. A minimum amount of acid was added to the Fe solutions to prevent hydrolysis and to ensure that the iron was in the $Fe^{2+}$ form when added to the $Ca(HCO)_2$ solution. Tables 1 and 2 show that the effects on nucleation rate and crystal morphology were minimal.

Tests done on the haematite sol produced results which indicate reduced induction times, i.e. increased nucleation rates and also a small effect on crystal morphology. Increased nucleation rates make sense because the haematite colloids could act as seed crystals which would then enhance the heterogeneous nucleation process.

Work is underway to study the effects induced by species other than Zn with the aim of developing a theoretical model to explain why certain metals produce effects and others do not.

### Possible mechanism

The question as to why Zn seems to be more efficient than other metal ions to induce increases in nucleation times and to promote the formation of aragonite rather than calcite is beyond the scope of this paper to answer rigorously. It can, however, be pointed out that the actual speciation of the metal in carbonate media almost certainly plays an important role. If the distribution diagram for Ni in carbonate media shown in Fig. 9 is compared to the distribution for Zn shown in Fig. 8, it is evident that the free metal fraction at pH 8 is substantially smaller in the case of Ni. This might point to a mechanism involving free metal ions. It is known that metal ions can slow down the growth rate of calcite crystals (Meyer, 1984) to varying degrees. Incidentally Zn is also very effective in this regard but has no effect on the growth rate of aragonite crystals. Our results therefore indicate the involvement of impurity ions during the nucleation process whereas results reported by Meyer applied to the crystal growth phase.

### Possible applications: Reduction in scale formation

The potential use of these phenomena in scale reduction applications was investigated in trial experiments by pumping (14 dm$^{-3}$ h$^{-1}$ ) supersaturated $Ca(HCO_3)_2$ solutions spiked with Zn through glass coils (1 m x 6 mm) immersed in a water bath at 70°C. The amount of scale formed was then determined by pumping 6% nitric acetic acid through the coils to dissolve the scale and then determining the [Ca] using ICP-OES. Scale reduction of 77±6 % in 10 repeats was achieved using 300 mg·dm$^{-3}$ Ca solutions to which 200 µg·dm$^{-3}$ Zn was added. Further work is underway to assess the viability of Zn treatment for scale reduction.

## Conclusion

It is evident from the results that trace amounts of Zn can substantially inhibit the nucleation rate of $CaCO_3$ . This effect has been quantified in terms of delay time. Limits to Zn/Ca concentration ratios necessary to produce measurable effects have been established. The formation of aragonite rather than calcite is demonstrated to occur when the Zn/Ca concentration ratio is greater than 0.06 x $10^{-3}$. We have also demonstrated that these effects can cause reduction in scaling in a simple laboratory application. Effects produced by other metal ions released from PWT devices were found to be much less than for $Zn^{2+}$.

## Acknowledgements

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