

USE OF I_E WATER FOR THE MITIGATION OF CALCIUM CARBONATE SCALING

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Duplicate recirculation loops simulating a real heat exchanger flow loop were used to study the effect of I_E water on calcium carbonate scale deposition. When the total amount of scale formed was greater than 250mg I_E water at a dose of 1000 ppm was found to reduce the amount of scale formed by up to 65%. However, when the total amount of scale formed was less than 200mg no effect or a reverse effect was noted. The effect of I_E water on the rate of precipitation of calcium carbonate was also investigated.

1. Introduction

The aim of this project was to test the efficacy of using I_E water for calcium carbonate scale control. The objective, of this preliminary study, was to investigate the effects of I_E water on calcium carbonate scaling on a heat exchanger surface.

Fouling of heat transfer equipment by inverse solubility salts, known as scaling or crystallization fouling, is a common process problem in domestic, commercial, and industrial applications. The primary agents causing scaling are the carbonates and sulphates of calcium and magnesium, although barium salts, silicate and phosphate scaling are significant, in certain areas and industries. Recent estimations of the overall cost of fouling to industry in the UK was in the range £8-1400 M. Costs due to water scaling constitute an important fraction of this total, which does not include the costs of scaling in domestic and trade water systems.

Mitigation methods include chemical treatment, particularly in cooling water systems; removal of active agents by ion exchange; and use of antifouling heat exchangers (e.g. fluidised beds, HEXTRAN inserts). These methods all involve increased capital and running costs, with varying degrees of environmental impact. The use of I_E water, where fouling mitigation is achieved with minimal maintenance and chemical/environmental costs, represents a very attractive option for systems subject to crystallization fouling.

Initial experiments examined calcium carbonate scale formation using I_E water on a heat exchanger test rig. The rig has been previously used to test magnetic treatment devices and is based on a standard design¹. The rig consisted of test and control flow loops which allow direct comparison of treated and blank experiments conducted simultaneously. Objectives of this work were to establish reproducibility, develop analysis protocols and compare fouling rates in the presence of I_E with existing crystallization fouling results.

2. Experimental Program

Two experimental protocols were used (i) scaling tests and (ii) precipitation experiments. The scaling tests were carried out in a recirculating heat exchanger test rig while the precipitation experiments were conducted in quiescent solutions.

2.1 Heat Exchanger Scaling Trials

The rig consisted of two identical flow loops for direct comparison between treated and untreated systems (Figure 1). The loop was designed to simulate a real heat exchanger flow loop. The experiment was conducted under conditions that expedited scaling, including a pH range of 7.5-8.0, a heated surface temperature of 65°C, and a flow velocity of 1.5 m/s. The fouling cell had flat plate design used previously at Cranfield. Figure 2 is a schematic diagram of the device and shows the heating plate A where scale developed.

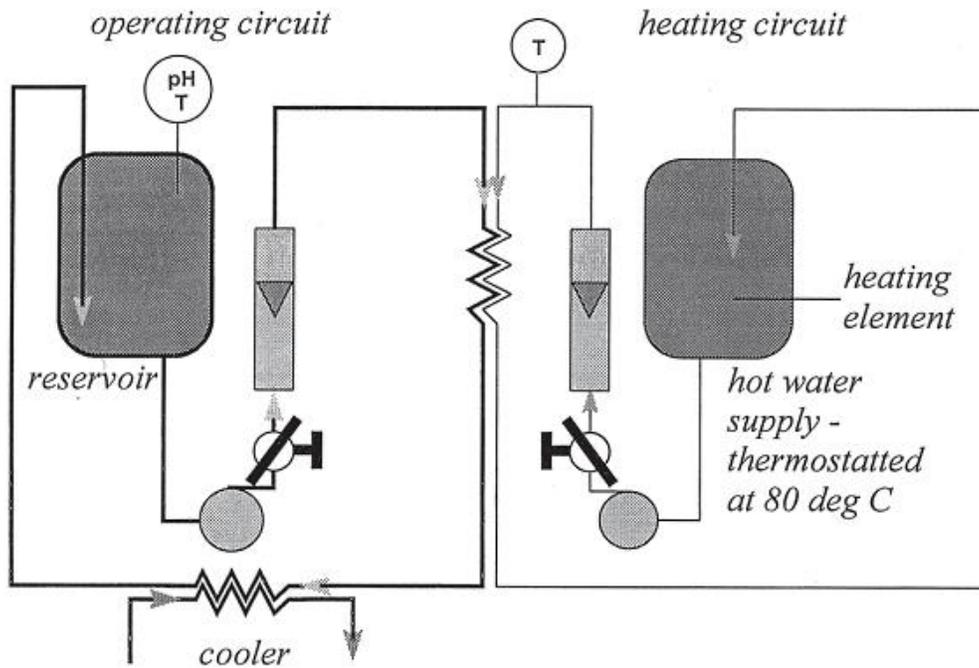


Figure 1 Recirculating heat exchanger test rig.

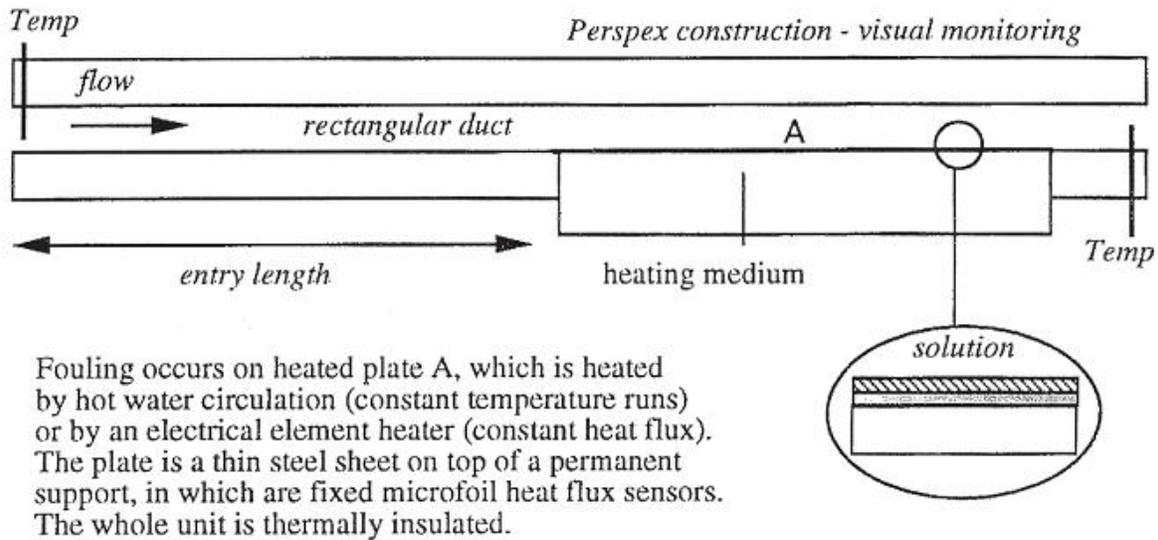


Figure 2 Schematic diagram of fouling cell.

A series of experiments were completed with I_E water concentrations of 500, 1000 and 2000 ppm, Table 1. The rig was acid washed prior to each experiment by circulating a HCl solution through the experimental loop. The rig was then thoroughly rinsed with deionized water. $CaCl_2 \cdot 2H_2O$ and $NaHCO_3$ were added to 70 liters of deionized water in the feed tanks to provide a hardness of 250 ppm and an alkalinity of 500 ppm. I_E water was added to the desired concentrations. The solution was circulated through the loop for four days.

Table 1 I_E water dose.

Run	I_E water dose ppm Loop A	I_E water dose ppm Loop B
<i>a</i>	1000	0
<i>b</i>	0	1000
<i>c</i>	0	1000
<i>d</i>	0	500
<i>e</i>	0	2000
<i>f</i>	0	2000
<i>g</i>	0	1000
<i>h</i>	0	0
<i>i</i>	0	1000

Daily samples were collected from each circulation loop and then analyzed for dissolved solids, calcium, magnesium, iron, copper and zinc concentrations, particle size distributions, and pH. Alkalinity and hardness were adjusted daily by the addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaHCO_3 . Crystal morphology, of the solids formed on the heating plate was investigated using scanning electron microscopy (SEM). The amount of scale formed on the heating plate was measured by weighing and drying the plates at the start and the end of each experiment.

2.2 Precipitation Tests

In addition to scaling experiments the effect of I_E water on calcium carbonate precipitation was also investigated. A UV spectrophotometer, set at $\lambda = 302 \text{ nm}$, was used to follow the precipitation reaction. I_E water at the desired concentration was injected into the UV cell.

Solutions of CaCl_2 , CaSO_4 and Na_2CO_3 (Analar grade) were prepared using pure water provided by an Elga Optima 60 Laboratory Water Purifier ($<15 \text{ m}\Omega$). Concentrations of $8 \times 10^{-3} \text{ mol/L}$ were used for absorbance and SEM analysis. All solutions were kept in air-tight bottles at $20^\circ\text{C} \pm 1^\circ\text{C}$ prior to mixing.

The effects of I_E water on the formation of CaCO_3 crystals were determined quantitatively by absorbance measurement. Simultaneously, 1.5 ml of each reagent ($\text{CaCl}_2/\text{Na}_2\text{CO}_3$ and $\text{CaSO}_4/\text{Na}_2\text{CO}_3$) were injected into a spectrophotometer cell to ensure complete mixing. The cell was then placed in the spectrophotometer and absorbance was measured at wavelength of 302 nm ^{2,3}. An increase in absorbance values was attributed to the number and size of CaCO_3 particulates, and a decrease in sedimentation.

3. Results

3.1 Heat Exchanger Scaling

Initial experiments (*a*, *b*, and *c*) showed that I_E water reduced the total amount of scale formed on the heating plate (Figure 3). An I_E water dose of 1000 ppm produced a reduction in scale of up to 65%. However, subsequent to these results, dosing I_E water had no effect on the amount of scale formed, and in some cases, the amount of scale was increased. The explanation for this anomaly is thought to be related to the absolute amount of scale formed. In the latter experiments (*d* to *i*) the total amount of scale formed was less than $\sim 250 \text{ mg}$ (Figure 4). This reduction in the amount of scale formed in the circulation loops reduced the accuracy of % inhibition calculations. Blank experiments were run to confirm that the two loops were equivalent. The average error found was approximately 10%.

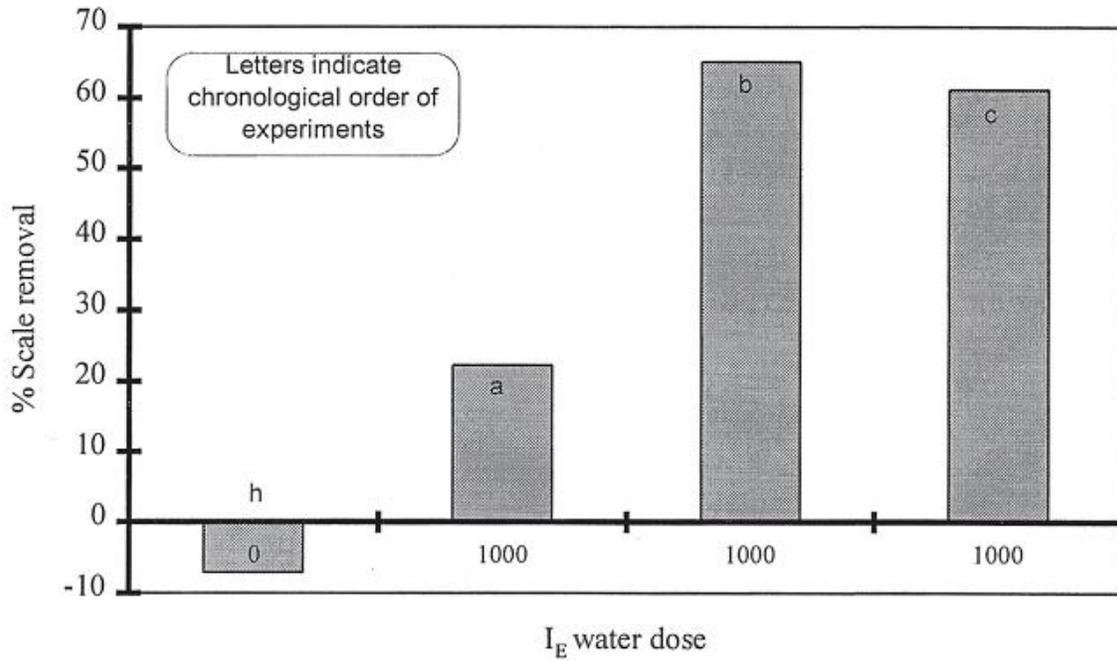


Figure 3 Summary of the scaling results a-c.

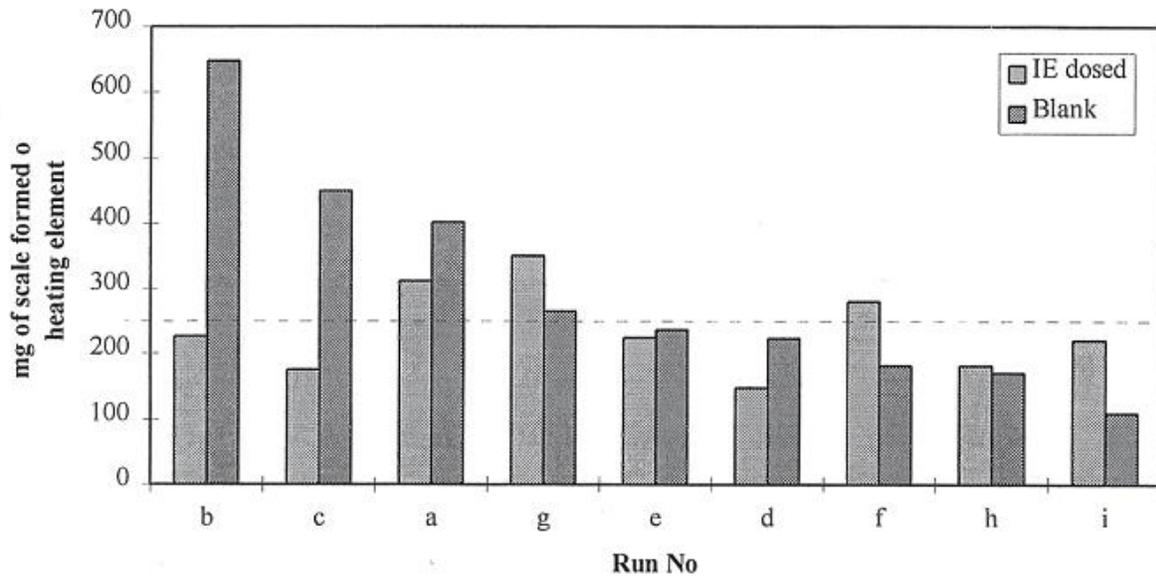


Figure 4 Summary of all the scaling experiments.

3.2 Crystallization Results

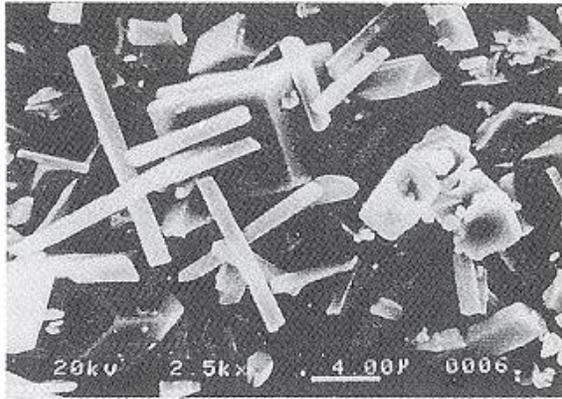
Calcium carbonate exists in at least five crystalline forms. The two polymorphs commonly found in nature are calcite and aragonite. Vaterite is a rarer metastable form which crystallizes at ordinary temperatures and pressure.

Calcite belongs to the trigonal crystal system and is commonly found exhibiting a rhombohedral shape in hand specimens and micro-crystalline deposits. The crystalline structure of calcite may be described as a cubic close packing with alternative Ca^{2+} and CO_3^{2-} . Aragonite belongs to the orthorhombic crystal system and is commonly found in acicular or needle like form. The crystallization of aragonite is favored by temperatures between 50°C and 80°C, pressure and the presence of zinc.

Changes, in both the crystal habit and the proportion of each form, were observed. We found no quantitative change in crystal habit in the course of our work. Qualitative observations revealed that I_E water produces deformations in the calcite form of calcium carbonate scale on the heat exchanger surface. Samples of scale were collected and analysed by SEM, and aragonite was found only in the untreated system. The results of the SEM trials are found in Table 2. Although microscopy gives good visual evidence of the effect of I_E water, the results are purely qualitative and can only be viewed as providing complimentary evidence to quantitative measurements.

Table 2 Crystalline structure of scale formed on heating elements.

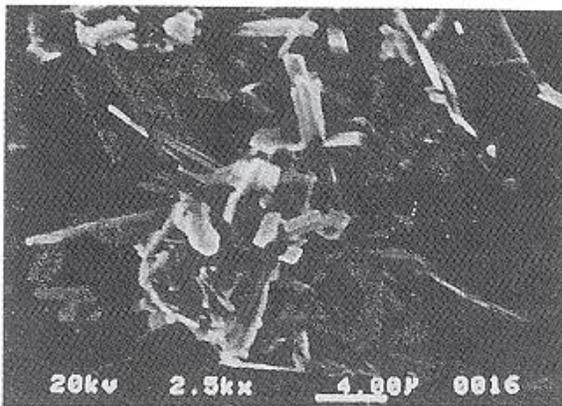
I_E Dose and position on heating element		Blank		I_E Treated	
		% Calcite	% Aragonite	% Calcite	% Aragonite
500	Top	90	10	95	5
	Bottom	70	30	100	
1000	Top	100		100	
	Bottom	60	40	100	
2000	Top	100		100	
	Bottom	90	10	100	



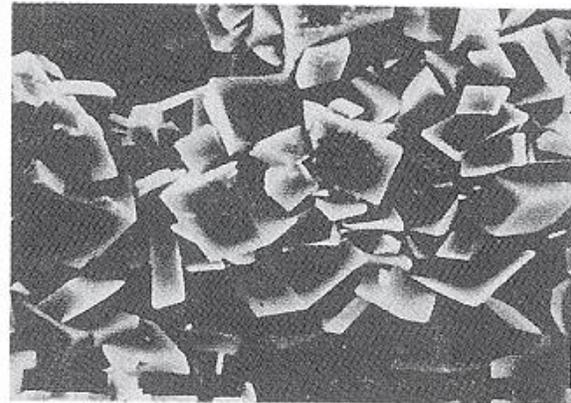
Blank



Treated



Blank



Treated

Figure 5 Examples of SEM photos of the scale found on the heat exchanger surface. The top images are at a dose of 500 ppm I_E water, the lower images are at a dose of 1000 ppm.

3.3 Precipitation Experiments

The sparse precipitation of soluble salts from solutions has been found to occur in three successive steps.

1. Nucleation
2. Crystal growth
3. Agglomeration and ripening

Experiments were carried out, to evaluate the influence of varying I_E water dose (500 - 1500 ppm), on calcium carbonate nucleation and precipitation.

Figure 6 compares the precipitation of calcium carbonate with calcium carbonate treated with 1250 ppm of I_E water. The curves show the formation and precipitation of calcium carbonate crystals.

Table 3 Summary of precipitation experiments.

Run Number	I_E Water dose (ppm)	T_{ind} (secs)	Absorbance value
1	0	350	0.07
2	500	300	0.06
3	750	200	0.06
4	1000	200	0.05
5	1250	100	0.05
6	1500	200	0.06

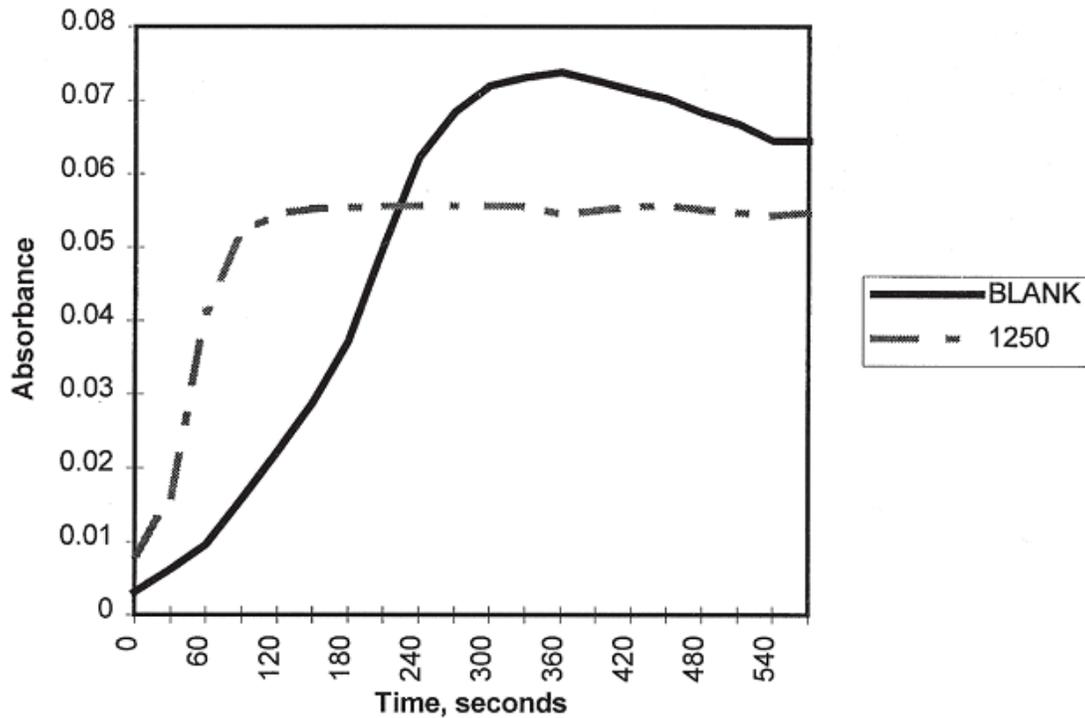


Figure 6 Change in absorbance with time curves for calcium carbonate precipitation blank and with I_E water at 1250 ppm.

A comparison of the absorbance values between treated and untreated solutions indicates that I_E water added to the reagents alone can reduce absorbance (CaCO₃ crystal formation) values. The influence on CaCO₃ precipitation is greatest at a dose of 1250 ppm. There is a clear difference between mean absorbance values for the treated and blank reagents with the growth in absorbance for the treated solutions always less than for the untreated. This reduction is attributed to the influence on CaCO₃ nucleation. Nucleation is increased in the presence of high concentrations of I_E water.

In an ideal experiment, the plot would show that the sample would precipitate until the sample becomes clear. The crystals would settle according to Stokes Law. The particles in the blank settle completely over time, but the treated system showed no evidence of settling even after a period of hours. This could be due to a decrease in the particle diameter, or a change in the relative density of the particle compared to the solution.

4. Conclusions

It is concluded from this study that I_E water influences CaCO₃ formation *under quiescent conditions* and that the mechanism possibly involves an interfacial effect. In addition, within certain experimental parameters, the influence of I_E water on CaCO₃ scaling was demonstrated.

4.1 Mechanism

Although there is insufficient, reproducible evidence to support the effect on scale formation, the results indicate that the principal action of I_E water is through formation of hydrophilic crystallites with modified surface charge instead of attached scales⁴. The implication is that colloidal stability is influenced by the application of the sample water. Growth on existing scale is thermodynamically favorable⁵. Therefore, to prevent scale or produce descaling, I_E water could act so as to alter the size and surface charge of growing crystallites, thereby increasing their tendency to remain entrained within the bulk of the solution⁴. However, this phenomenon is difficult to confirm for particles as small as crystallization nuclei.

5. References

1. D. Hasson and D. Bramson, *Ind. Eng. Chem. Process Des. Dev.* **24**, 588 (1985).
2. K. Higashitani *et al*, *J. Coll. Interface Sci.* **152**, 125 (1992).
3. K. Higashitani *et al*, *Coll. Interface Sci* **156**, 90 (1993).
4. J.L. Crolet and J. Ledion, *Techniques, Sciences, Methods - L'Eau* **83**, 435 (1988).
5. A.E. Nielsen, *Kinetics of Precipitation* (Pergamon Press, Oxford, UK, 1964).