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MAGNETICALLY AUGMENTED WATER TREATMENT

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A test rig was constructed to investigate the effect of orthogonally applied magnetic fields on solutions of calcium carbonate and accompanying changes in scale deposits formed from solution. The rig employed recirculated calcium carbonate solutions, which were passed through magnetic fields of strengths up to 7000 Gauss. Scaling occurred on a copper heat exchanger surface at temperatures set at between 40°C and 60°C. Changes in solution chemistry, zeta potential and particle size were also investigated. Scale deposits were analysed by scanning electron microscopy.

Results showed that magnetic treatment had a significant effect on the precipitation/ deposition of calcium carbonate from solution under controlled physico-chemical conditions. Scaling was affected by the system temperature, pH and degree of supersaturation. The magnetic field was shown to influence significantly the zeta potential and particle size distribution of particles formed in solution, as well as the crystal morphology of the calcium carbonate deposits.

This paper presents a summary of laboratory results and relates them to a possible mechanism.

Keywords: magnetic water treatment; zeta potential; particle size; nucleation rate; crystal morphology.

INTRODUCTION

The build-up of scale deposits is a common and costly problem in industrial and domestic water supplies; in British industry alone the cost attributed to scale is estimated to be around £1 billion per year[1]. Traditional chemical methods used in scale control, such as water softening, are effective but significantly add to the chemical load on the water stream and can be prohibitively expensive. There is thus a need for a cost-effective reliable method for controlling scale. In recent years there has been an increased interest in physico-chemical methods for the reduction of scale formation, including magnetic water conditioning. This method, in which the water to be treated flows through a strong magnetic field produced by either permanent or electromagnets, is a cheap and attractively simple approach to treating scale. Magnet treatment devices (MTDs) have been marketed by a number of international companies for over 40 years with applications ranging from small-scale domestic to large-scale industrial. Claims made by the MTD suppliers include the reduction in the amount of scale formed, formation of a 'soft' scale and the removal of existing scale. The retention of the magnetic effect over long periods of time is also claimed by some manufacturers. Despite much anecdotal evidence supporting magnetic water treatment, it has generally failed to gain acceptance as a reliable technique for reducing scale deposits, partly due to the uncertainty surrounding its mode of action. Scientific research has done little to clarify the situation, researchers both substantiating and refuting the claims of MTD suppliers, creating widespread controversy as to the credibility of this type of water conditioning[2]. Interest in this subject area has recently been revived by a number of independent reports carried out in well-defined and controlled systems which point to a real effect.[3–6] The integrity of a number of reported results and their interpretation are compromised by a number of factors:

- Irreproducibility by subsequent research;
- Unspecified control of solution chemistry;
- Unspecified physical conditions.

Experiments carried out at Cranfield University have focused on establishing whether magnetism has an effect on calcium carbonate precipitation and, if so, identifying the parameters promoting magnetic amelioration of scaling. The research programme comprised a fundamental and systematic study of the magnetic effect on scalants such as calcium carbonate in which strict control of critical parameters were maintained.

EXPERIMENTAL

A test rig, shown in Figure 1, was designed in order to accommodate conditions generally observed to expedite antiscale magnetic treatment[7], these being:

- Orthogonal fluid flow with respect to the magnetic field orientation;
- Recirculated solution;
- Accumulative exposure to the magnetic fields of strength > 3000 Gauss.

The test rig consists of two identical flow loops, each with a 70 l reservoir supplying a recirculatory system of PVC pipework. General experimental conditions are listed in Table 1. Flow through the system is provided by means of a
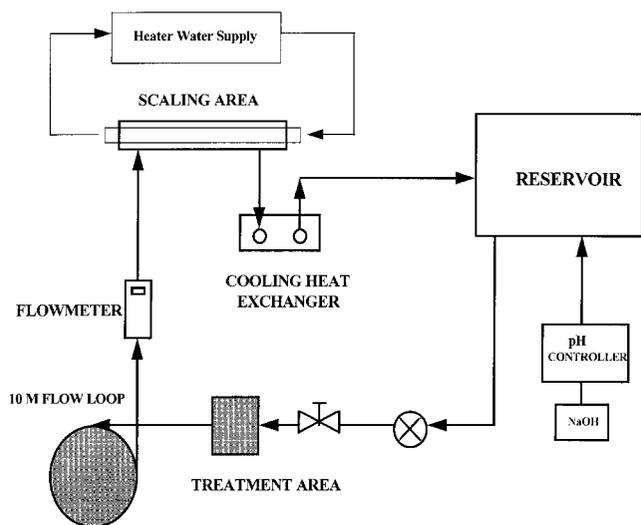
Figure 1. Flow diagram of experimental test rig.

centrifugal pump (March May) controlled by a diaphragm valve, and can be adjusted from zero to a maximum of $181 \min^{-1}$. In experiments reported here the flow rate was kept at $121 \min^{-1}$.

The field is provided by a non-intrusive electromagnet, which produces a magnetic field of adjustable strength orthogonal to the fluid flow. The maximum magnetic field strength provided by the magnet is 7000 Gauss at the pole gap of 35 mm used in all reported experiments.

The heat exchangers were based on a previously reported design[8]. They consist of a heated copper pipe encased in PVC tubing over which the treated solutions can flow. The copper pipe is heated by thermostated water set at the required temperatures and monitored by thermocouples placed on the heated surface. These can be readily dismantled for analysis of scale deposits. The temperature at the heat exchanger surface was held at set temperatures between $40(\pm 2)°C$ and $60(\pm 2)°C$ throughout these experiments. The solution flows from the heat exchanger through a cooling system consisting of plate heat exchangers (OCCO Coolers) which reduce the solution to a temperature of between 28°C and 30°C before returning to the reservoir.

The system had two 'Blackstone' pH controllers (Hanna Instruments) which are supplied with a 0.1 M NaOH solution (BDH). AnalaR grade calcium chloride and sodium hydrocarbonate were used as purchased (BDH), and 15 mΩ water, provided by an ELGA Optima 60 Water Purifier, was used in the preparation of solutions.

Particle size measurements were made periodically throughout an experimental run using a HIAC/ROYCO 'HIAC LV VersaCount' instrument. Samples were taken from the reservoir tank and sampled immediately. This instrument is an eight channel particle counter and is capable of sizing particles with diameters in the $2–200\,\mu m$ size range. Calcium carbonate precipitates formed on the heat exchanger and on glass slides within the reservoir were viewed by scanning electron microscopy.

Zeta potential measurements were made using a Rank 'MkII' microelectrophoresis instrument.

RESULTS AND DISCUSSION
Effect on Scaling Kinetics and Scale Formation

Effects of magnetic water treatment on calcium carbonate scaling rates have been measured under a wide range of physico-chemical conditions, system hydrodynamics and industrial applications. It has been reported that the magnetically-induced change in the scaling rate can vary with:

- Magnetic field strength[5,9,10];
- Supersaturation level[11];
- System pH[12];
- Flow rate[13,14];
- Dissolved solids concentration[13].

The formation of calcium carbonate can be represented chemically by:

$$Ca^{2+} (aq) + CO_3^{2-} (aq) \xrightarrow{k} CaCO_3(s) \qquad (1)$$
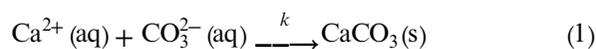
where:

$$\frac{d[CaCO_3]}{dt} = k\left[Ca^{2+}\right]\left[CO_3^{2-}\right] \qquad (2)$$

where k is the rate constant for the calcium carbonate scale formation reaction (1). Magnetic fields have been previously shown to influence kinetics of a range of reactions[15].

The effect of heat exchanger temperature on reaction (1) is illustrated in Figure 2 in which the reaction half life (the time taken for the [Ca] to fall to half its original concentration) is compared over the range of temperature 40–60°C. As expected the rate is faster at higher temperatures but there is no apparent magnetically-induced trend. Specific temperature dependency has been reported for silica scaling[16], although at higher temperatures to those employed in our study.

Figure 3 shows how the rate constant k for reaction (1) varies with calcium concentration, in ppm, depicting the percentage difference between magnetically treated and blank systems at concentrations within the range 250–400 ppm

Table 1. Operating and experimental conditions of the test rig.

Condition	Operational range	Experimental conditions
Heat exchanger temperature, °C	20–80 ± 2	Experiments at 40, 50 and 60°C
Tank temperature, °C	20–40 ± 2	28–30°C
Flow rate, $1\,min^{-1}$	0–18	12
Field strength, Gauss	0–7000	7000
[Ca], ppm	0–450	250–400
pH	1–12	8[a]

[a] The pH was set initially at pH 8
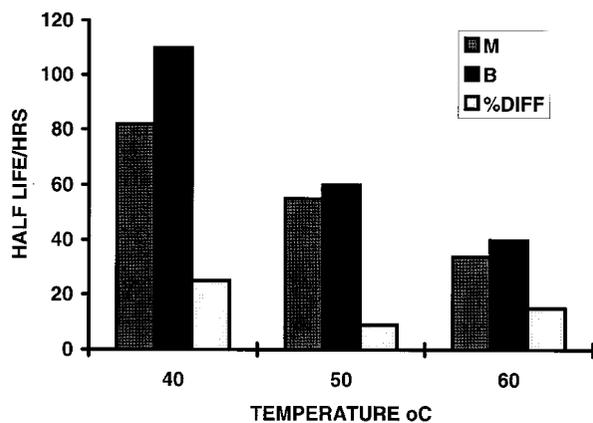
Figure 2. Effect of temperature on the reaction half life for the formation of calcium carbonate.

Figure 3. Effect of calcium carbonate concentration on the magnetically-induced change in reaction rate constant, B = 7000 Gauss, temperature = 55°C.

of Ca^{2+}. The figure indicates that the degree of magnetically-induced change is dependent on solution concentrations reaching a maximum at 350 ppm. An indication of the reproducibility of these results is shown in Table 2 and in Figure 4. Whilst the scale suppression trend appears reproducible, relating changes in rate constant to changes in scaling is not always easy to achieve due to the nature of the system under investigation.

Slight variations in pH will lead to changes in the carbonate equilibrium where a unit pH increase has been reported in inducing scaling faster than an 80°C increase in temperature[17]. A number of experiments were previously carried out to assess the effect of changing the pH within the range pH 7–8.5[18]. Under the conditions of this study the effects of magnetic treatment on scale formation are nullified when the pH is maintained at a constant value, in this case by sodium hydroxide dosing. This observation indicates that pH plays an important role in the mechanism by which magnetic fields reduce scale formation. The changes are not solely due to pH elevation. It has also been previously noted that the magnetic effect is influenced by the solution pH, with precipitation enhanced at pH values below 9.0 and inhibited above 9.3[11].

When the pH is not controlled, a pronounced magnetic effect on solution pH has been recorded with the treated solution pH reduced by up to 0.5 pH units. Similar trends have been reported while using intrusive magnets[19].

No velocity dependency of the magnetically-induced changes on scaling rate was apparent between flow rates of $1-2\,ms^{-1}$. The small deviations noted could be attributed to increased shearing. Previous tests conducted by Crolet and Ledion[14] found that scaling was consistently dependent on flow rate through an intrusive MTD and subsequent reports h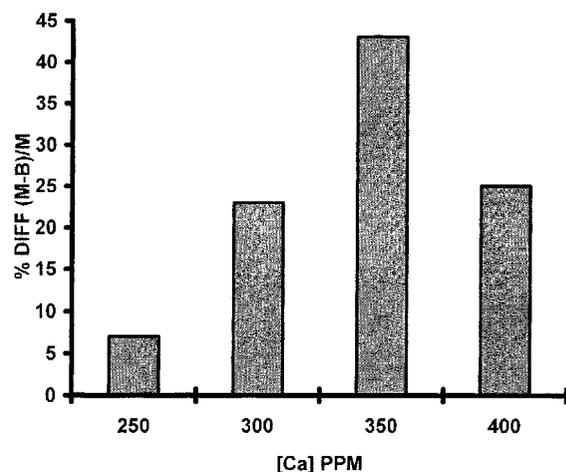ave shown that the turbulence created by the device itself contribute more to observed effects on scale formation than the magnetic field[13].

Effect on Nucleation, Crystal Growth and Morphology

A number of theoretical studies have been carried out to support proposed mechanisms for magnetically-influenced crystallization behaviour, usually with reference to nucleation site formation[10,14,20]. Contradictory reports have appeared, however, claiming that magnetic treatment can both accelerate nucleation[20–24] and suppress nucleation[5,10,23,25,26]. Reported effects of magnetic treatment on the nature and size of precipitated particles again vary widely. In the current study, information has been gathered on zeta potential, particle size and crystal morphology.

Surface charge

Experiments have shown an average reduction of 16% in the zeta potential of calcium carbonate particles in solution after magnetic treatment. The particles were taken from the bulk reservoir towards the end of each experiments, and duplicate samples were also taken. Figure 5 shows how the magnitude of this reduction in zeta potential is dependent on the levels of calcium in the solution. This observation implies that colloidal stability is influenced by the application of a magnetic field, possibly indicating a reduction in charge density within the Stern layer. This may be a direct effect or possibly a secondary effect, as surface charge is known to depend on many factors including ionic strength and solution pH.

Previous research has also reported a reduction in the zeta

Table 2. Effect of magnetic fields of 7000 Gauss on rate constants and scale reduction.

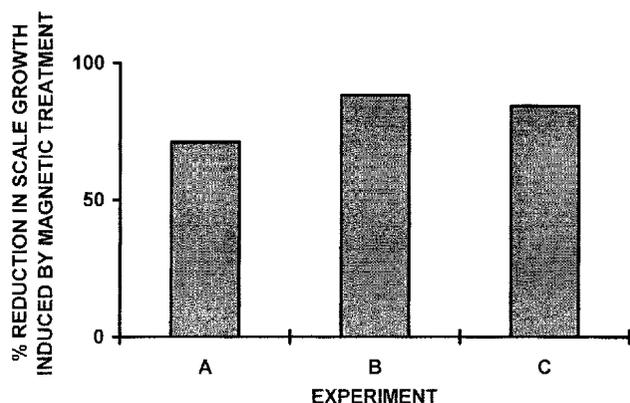| [Ca], ppm	Temp, °C	Rate constant, $k \times 10^6 \, s^{-1}$		% diff in observed rate constant	% scale reduction (mag/blank)
250	60	3.2(0.1)	2.9(0.2)	7.6	Negligible
300	60	5.1(0.2)	3.9(0.2)	24	22(15)
350	40	2.7(0.2)	1.6(0.1)	40	38(7)
350	50	3.5	3.2	8	–
350	60	5.3(0.4)	3.0(0.2)	44	81(8)
400	60	6.4(1)	4.8(0.2)	25	81(8)

Figure 4. Reproducibility of magnetically-enhanced scale amelioration, B = 7000 Gauss, temperature = 60°C, [Ca] = 350 ppm.

potential of both calcium carbonate and calcium sulphate following magnetic treatment. Recently Gehr *et al*[6] showed that suspensions of calcium sulphate placed in an NMR spectrometer generating a field strength of over 40,000 Gauss showed reductions in surface charge of approximately 25%. There were also changes in the levels of suspended and dissolved solids.

Growth on existing scale is thermodynamically favourable[27]. For magnetic treatment to prevent scale it could act so as to alter the size and surface charge of growing crystallites, thereby increasing their tendency to remain entrained within the bulk solution[14]. It has also been proposed that a reduction in zeta potential of $CaCO_3$ particles lead to the particles being unstable, resulting in aggregation, resulting in more rapid sedimentation[4,5]. The results of the current study tend to support this, as an increase in the amount and size of aggregates formed after magnetic treatment was evident.

Particle size analysis

The particle population balance depicts the ratio of particles of differing sizes within a system. Figure 6 shows how the total number of particles changes throughout the run.

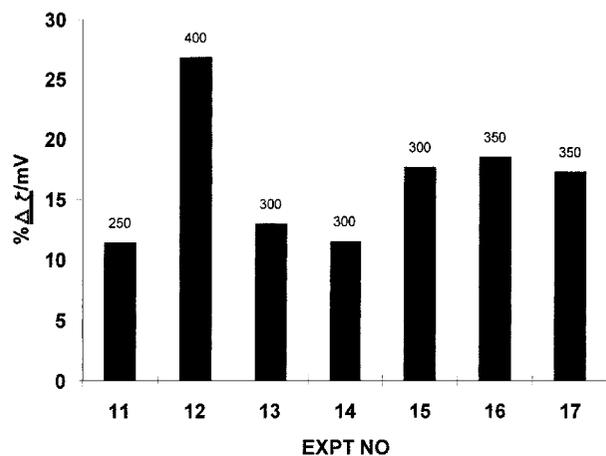Particle size distribution has been plotted in the conven-

Figure 6. Effect of magnetic treatment on particle size and particle numbers over 70 hours, B = 7000 Gauss, [Ca] = 350 ppm, temperature = 60°C.

tional semilogarithmic manner, Log $n(L)$ versus L. These plots all exhibit a steep upward curvature in the region which relates to the smallest particles (Figure 6), with the gradient decreasing at greater particle sizes. The plots show an evening out towards the larger size ranges. This differs significantly from the ideal distribution of particle sizes in the product of a mixed suspension mixed product reactor crystallizer with linear size independent growth rates, which yield linear correlations[26]. Figure 6 shows how the distribution changes throughout the run with the magnetically-treated sample showing a steeper incline at the lower ranges than the blank, but dropping off much quicker than the trends shown in the blank system.

These results show an initial magnetically-induced increase in particle size and numbers in solution, although this trend changes with time as the larger particles settle out. Donaldson has reported that this increase in particle size leads to reduced scaling as the larger particle is less likely to adhere to surfaces due to decreased surface charge[3].

Nucleation rates, calculated using a method previously described by Neilsen[27], are reduced significantly after magnetic treatment to an extent which is time dependent (Figure 7). The generalized equation links nucleation rate with particle count and time, where it is possible to

Figure 5. Percentage reduction in zeta potential after magnetic treatment for a range of calcium concentrations. B = 7000 Gauss, temperature = 60°C. Concentrations shown are all in ppm.
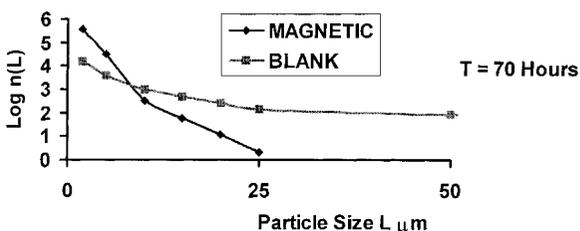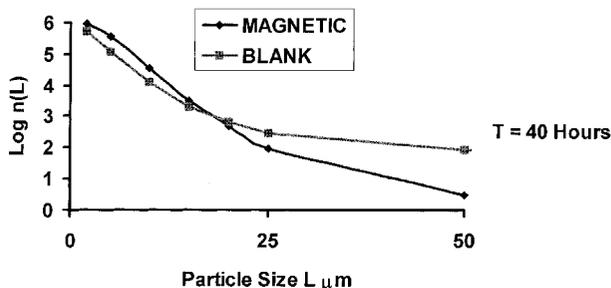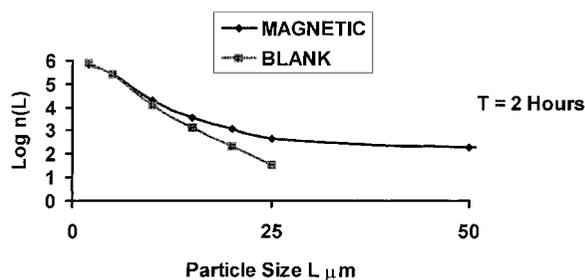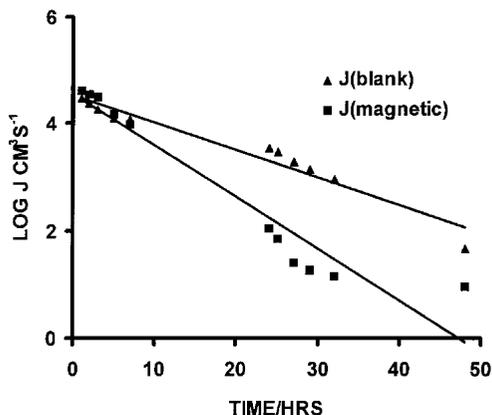
Figure 7. Change in nucleation rate bought about by magnetic treatment. B = 7000 Gauss, [Ca] = 350 ppm, temperature = 60°C.

determine the velocity of nucleation experimentally by:

$$J = N/t \tag{3}$$

Nucleation rate and total particle numbers are linked by the equation:

$$\log N = 2 + (3/5) \log J \tag{4}$$

The units are J = nuclei per cm^3 per second, N = particles per cm^3 and t = seconds.

There are limitations to the validity of the assumptions inherent in the formulae for the kinetics of nucleation and crystal growth; these are discussed in depth elsewhere[25].

The observed magnetically-induced reduction in nucleation has been reported in both flowing[10], stirred[26] and static[5] systems. All workers have produced photographic evidence indicating suppression of nucleation of CaCO$_3$ following magnetic treatment. It has been demonstrated that the homogeneous nucleation rate would be relatively unaffected by a 5000 Gauss field[2]. The authors concluded that, on the basis of current crystallization theory, magnetic treatment could produce no effect on nucleation and growth of crystals. A recent part-theoretical report, however, has shown that weak electromagnetic fields (300 Gauss) can reduce nucleation rate. This in turn leads to the formation of larger crystals[26].

Structural morphology

A number of workers have reported changes in crystallization by applying magnetic fields[10,23,28,29]. Changes in both the crystal habit and the proportion of each form have been observed. We have found no quantitative change in crystal habit in the course of our work. Qualitative observations have revealed that magnetic treatment produces deformations in the calcite form of calcium carbonate scale generated in solution and on the heat exchanger surface—see Figure 8. There is also an apparent increase in the number of agglomerates found. Although microscopy gives good visual evidence of the effect of magnetic treatment, the results are purely qualitative and can only be viewed as providing complimentary evidence to quantitative measurements.

Under the reported experimental regime it was found that agglomeration of individual crystals was the dominant mechanism for the observed increase in particle size. The agglomerate appearance and individual crystal morphology
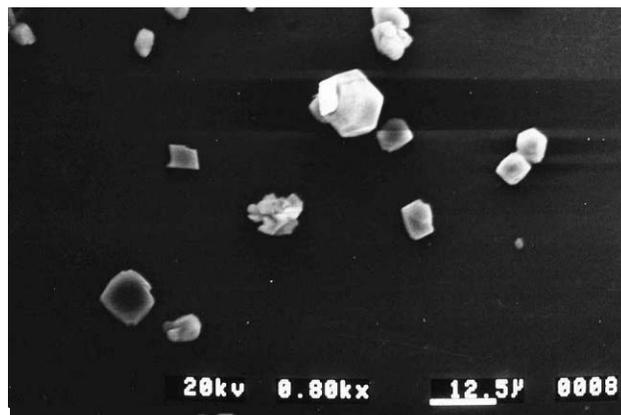
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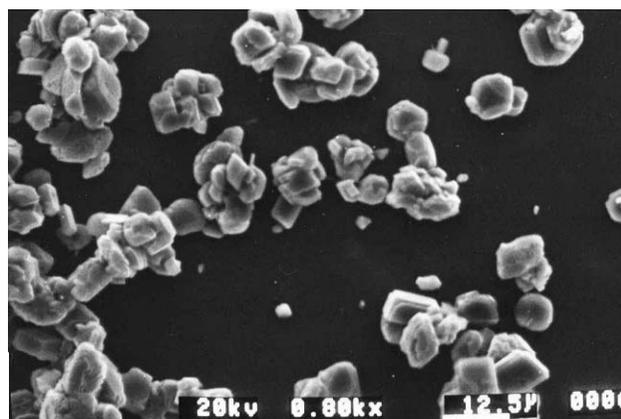
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Figure 8. Scanning electron microscope images of (A) untreated system scale and (B) magnetically treated system scale.

varied with the experimental conditions. Three basic forms were observed:

(1) Calcite—formed in sedimentary scale (magnetically-treated and blank). Calcite was found to be the main constituent of scale grown from deformation and was evident in magnetically-treated samples. This deformation took the form of reshaping of the crystal into more rounded shapes, due to non-uniform growth.

At temperatures below 60°C the scale grown on the heat exchanger surface was of a calcite form. Again deformations were observed in the magnetically-treated samples.

(2) Aragonite—formed on heat exchanger surfaces when the temperature was above 60°C. Although no irregular shapes were observed in magnetically-treated samples, the crystal sizes in these samples were significantly larger than those found in the blank solutions.

(3) Vaterite—observed only in the magnetically-treated reservoir.

CONCLUSIONS

The treatment of calcium carbonate solutions with orthogonal magnetic fields (7000 Gauss) can, depending on the solution chemistry, reduce precipitation of scale on heat exchanger surfaces by up to 80%. Results have shown

that colloidal stability is influenced by the application of a magnetic field; this will lead to accelerated coagulation confirmed by the increased agglomerates found in the scale. Nucleation and crystal growth rates are also reduced, leading to the formation of irregularly shaped crystal forms.

The evidence gathered from this study and from other credible experimental reports supports the theory that the magnetic effect is an interfacial effect. The reason for the drop in zeta potential is not clear but it does point indirectly to magnetic treatment increasing the coagulating tendency of the suspension by decreasing double-layer repulsion. Krylov et al[30] proposed, for a similar observation in a colloidal system, that when the $CaCO_3$ suspension is subjected to some degree of magnetic treatment, coagulation begins leading to a decrease in surface area. This in turn causes adsorbed ions to enter the liquid phase. This leads to a reduction in the thickness of the diffuse layer and hence a proportional decrease in the surface charge.

Gamayunov[31,32] proposed a theoretical model of the possible action of the magnetic effect on the electrical double layer present at any solid-liquid interface, where Lorentz forces are acting on a moving charged particle in a magnetic field, Lorentz forces causing isotropic distortion of the diffuse layer. The author proposed that the displacement of co- and counter-ions by Lorentz forces leads to a change in the charge distribution within the electrical double layer, resulting in a semi-permanent change in the charge and potential at the boundary of the Stern layer. This mechanism is particularly interesting as it could explain both coagulation and crystallization behaviour whilst offering a quantifiable performance parameter in the form of the zeta potential. What it does not explain is the effect magnetic treatment has on static systems.

Whether it is Lorentz forces that induce changes within the system, or another mechanism, is still unclear and further research is required to define fully when magnetic treatment will work and in particular the efficiency of different flow rates through the magnetic field.

SUMMARY

(1) Magnetic treatment can reduce calcium carbonate scale formation by up to 80%.
(2) The degree of the magnetically-induced change is dependent on solution chemistry.
(3) Magnetic amelioration of scaling is removed when the system's pH is controlled.
(4) Surface charge is reduced by an average 16% in the reported experiments.
(5) Nucleation and crystal growth rates are reduced, leading to the formation of irregularly shaped crystal forms.
(6) Magnetic treatment is an interfacial effect.

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