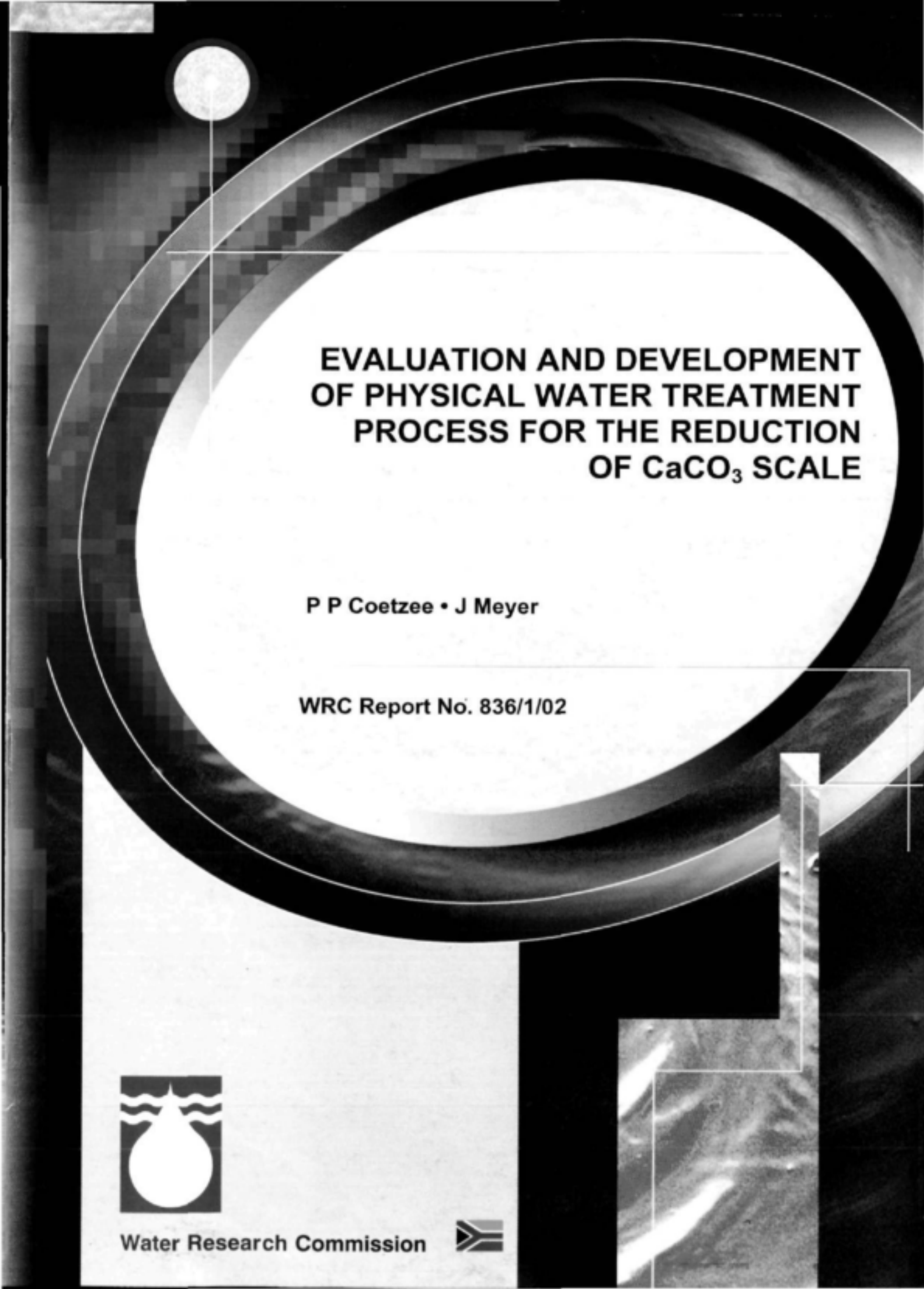

EVALUATION AND DEVELOPMENT OF PHYSICAL WATER TREATMENT PROCESS FOR THE REDUCTION OF $CaCO_3$ SCALE

P P Coetzee • J Meyer

WRC Report No. 836/1/02

Water Research Commission

EVALUATION AND DEVELOPMENT OF PHYSICAL WATER TREATMENT PROCESSES FOR THE REDUCTION OF $CaCO_3$ SCALE

by

PP COETZEE* and J MEYER[+]

Department of Chemistry and Biochemistry * and Department of Mechanical Engineering[+]
Rand Afrikaans University
Auckland Park, Johannesburg, 2006

Report to the Water Research Commission on the Project
"Evaluation and development of physical water treatment processes for the reduction of $caco_3$ scale in domestic and industrial heating and cooling circuits"

Head of Department:	**Professor PP Coetzee**
Project leader:	**Professor PP Coetzee**

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1. BACKGROUND AND MOTIVATION

Physical water treatment (PWT) for the reduction of scale has been actively promoted as alternative for chemical treatment of water since the first PWT patent was registered in 1945. This patent was for magnetic water treatment (Vermeiren, 1958). Other techniques that gained in popularity, in particular during the last decade, include non-intrusive devices based on varying frequency electric fields induced through wrap-around coils and intrusive "catalytic conversion" devices where water is treated electrochemically by exposure to a metal alloy surface. The potential reward to industry and the environment should physical water treatment prove to produce consistent scale reduction effects, is enormous. This is the reason why, despite the fact that more than 50 years of intensive research into the effects of electromagnetic fields on scaling processes did not produce a generally accepted theory to explain the mechanisms involved, research and technical development continues unabated. Although PWT technology has changed substantially in some respects since 1945, the basic claims and effects (Baker and Judd, 1996) remained essentially the same. These include: the formation of a soft scale with weak adhesion properties, reduced kinetics of crystallisation, a memory effect of up to 3 days, changes to crystal morphology, reduced or increased particle sizes, descaling and dissolution of existing scale, and decreased zeta potential and surface tension.

The current status is, however, that these claims and effects cannot always be demonstrated experimentally under controlled laboratory conditions in a reproducible way. The reasons why PWT technology sometimes produces excellent results and then seem to stop working altogether, are therefore not clear and will not become clear until the mechanisms involved in these processes are fully understood. In this project the approach was to develop laboratory methods in conjunction with an industrial size testing facility to provide the means for the acquisition of reliable data that could be used to substantiate mechanistic models.

The project follows up on the recommendations for further research expressed in a previous WRC sponsored project (Coetzee and Haarhoff, 1997) on the reduction of scaling by magnetic water treatment. The main finding of this report was the discovery that small amounts of free metal ions, in particular Zn^{2+}, released from magnet surfaces during water treatment, play a major role in the scale reduction properties of PWT devices in cases where the water is in physical contact with the device surface during treatment. This finding, including its potential use in scale reduction processes, was patented by the WRC in 1996 (Coetzee, 1996). The report, did not find conclusive evidence of scale reduction effects that could be attributed to electromagnetic fields. It was, however, recommended that the search for evidence of electromagnetically induced effects on scaling processes be continued using new state-of-the-art analytical technology such as atomic force microscopy.

2. OBJECTIVES

The main objectives of the project were addressed in three parts. The objectives for each of the parts are summarized below.

- **Fundamental research**:
    - To develop theoretical models to explain the mechanisms involved in physical water treatment.
    - To develop laboratory testing methods to demonstrate under rigorously-controlled experimental conditions the effect of electromagnetic fields on particle-producing chemical reactions such as scale forming processes.
- **New scale reduction technology**:
    - To develop a Zn-based electrochemical system for scale reduction and compile guidelines for its use.
- **Testing facilities for scale reduction technology**:
    - To develop a testing facility which can be used as an independent evaluation center for physical water treatment devices.

3. FUNDAMENTAL RESEARCH AND THE DEVELOPMENT OF LABORATORY TESTING METHODS

3.1. Hypotheses

The focus was on the fundamental chemistry and physics of the processes involved in physical water treatment, the development of experimental and analytical methods to study the effects of physical fields on systems where scaling can occur, and the formulation of theoretical models to explain the mechanisms involved.

The approach was to find a common denominator, which would link the claimed effects listed in the background section, and would make possible a plausible mechanistic explanation. It was assumed that scale formation proceeds through the processes of nucleation and crystal growth on exposed surfaces or in the bulk of the liquid phase followed by the attachment of crystalline particles to a surface, forming a layer prone to further growth. It was argued that if PWT was to affect scale formation at all, it should be measurable as an effect on the rates of nucleation and crystal growth processes and on the characteristics of the precipitate or scale, in particular its crystal morphology. The next step was to use existing theories of crystallisation to predict possible effects of electromagnetic fields on the processes involved and to design experiments to study these effects. These experimental techniques included the measurement of crystallisation kinetics, force-distance measurements using an atomic force microscope, and zeta potential studies.The methods were also used to test a number of commercial devices.

It was hypothesized, based on existing crystallization theories, that a possible distortion or polarization of the charge distribution in the solid-liquid interface during scaling by electromagnetic fields could increase the interfacial energy. If this happened the equations show that the nucleation rate will be decreased and the crystal growth rate increased.

3.2. The role of Zn in crystallisation processes

Experiments with several PWT devices, showed that nucleation rate was indeed decreased as can be measured from the time difference between the onset of precipitation of $CaCO_3$ in a control solution and test solution of calcium bicarbonate that was exposed to physical water treatment. Typical pH-vs-time curves given in Figure 1 clearly show that the induction time for the test sample is longer than for the control.

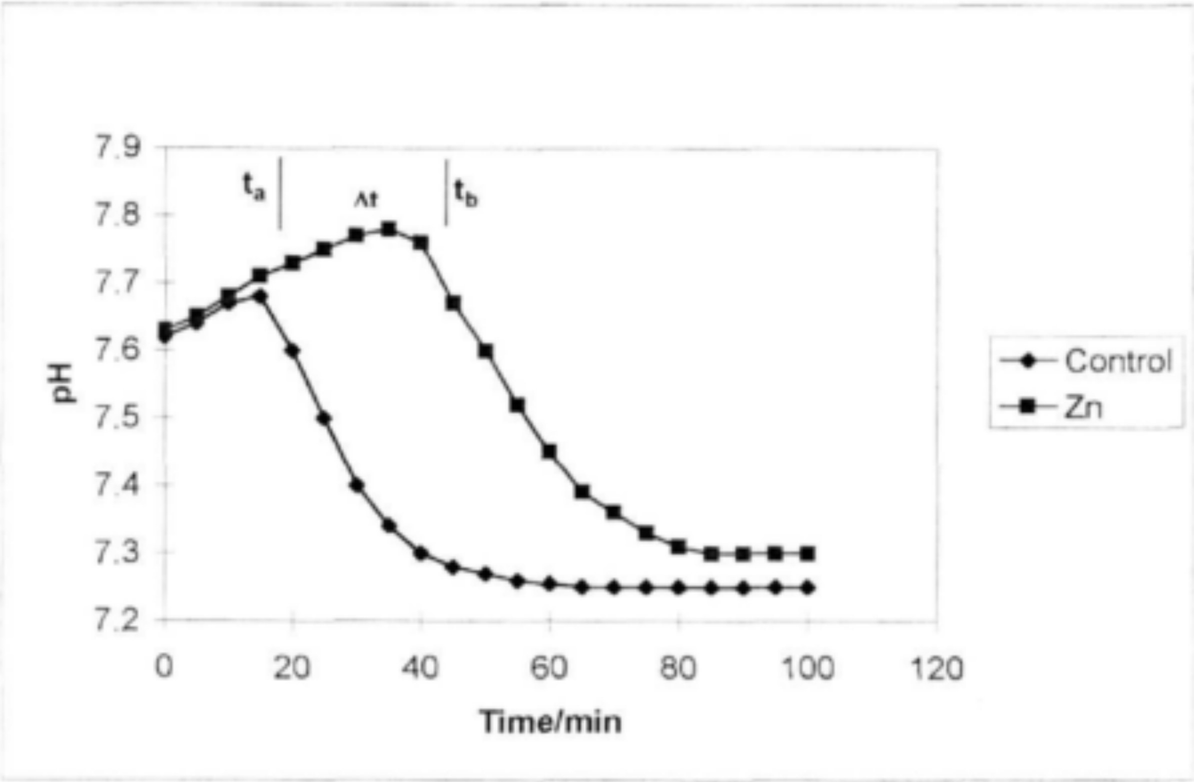

Figure 1.
pH vs time curves for the precipitation of $CaCO_3$ from a 150 mg.L^{-1} Ca control solution and a 150 mg.L^{-1} Ca + 50 μg Zn.L^{-1} test solution, respectively. Delay time ($\Delta t = t_b - t_a$) is the difference between induction times of the control and test solution.

The difference in induction times, t_a and t_b between the two curves, a test curve and a control, is denoted by the delay time, Δt. The precipitation curve for calcium carbonate precipitated from electromagnetically conditioned water (contact type device) and water spiked with trace amounts of zinc gave the predicted decrease in nucleation time.

The important role played by Zn^{2+} ions in increasing the delay time as the Zn/Ca concentration ratio becomes larger is illustrated in Figure 2.

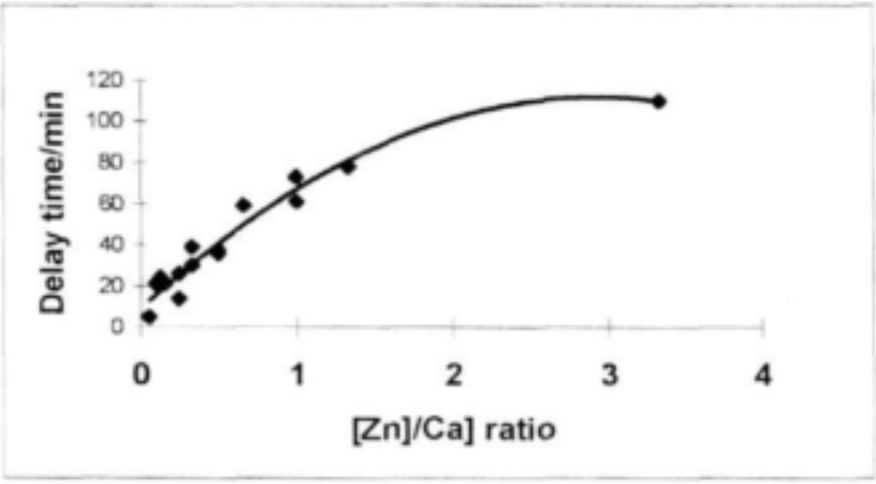

Figure 2.
Delay time as a function of [Zn] /[Ca] ratio

3.3. Atomic force microscopy experiments

Atomic Force Microscopy (AFM) was used to study electric double layer characteristics by acquiring force-distance data in different electrolyte media using modified AFM tips and an atomically flat substrate such as mica. It was proven that the double layer contraction as a function of increasing electrolyte concentration could experimentally be measured at the nanometer level in terms of repulsion forces in the order of pico newton. AFM results, shown in Figure 3, indicate that a decrease in surface charge (smaller repulsion force between cantilever tip and substrate) is triggered by exposure of electrolyte to electromagnetic fields. This is a far-reaching result which, if it can be confirmed by further experimental work, means that an electromagnetic field can affect the characteristics of the solid-liquid interface. This would broadly be in line with the hypothesis proposed in this project. It was not possible within the time constraints of this project to generate enough data to confirm these results.

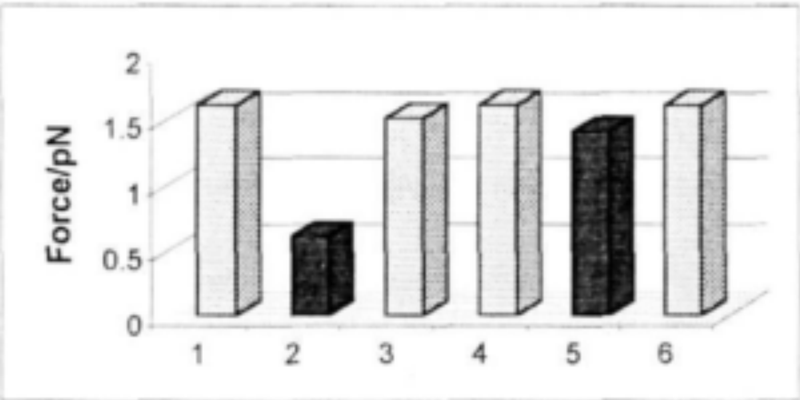

Figure 3.
Effect of a 0.45 T magnetic field on the apparent surface charge. Run 1, 3, 4, and 5 are controls. Run 3 is the repulsive force after 10 min exposure to the magnetic field and run 5 is the test sample after 5 min ultrasonic treatment.

3.4. Zeta potential measurements

The zeta potential of a colloid is an indication of the charge distribution around a colloidal particle in solution and is determined by measuring its electrophoretic mobility or its velocity when exposed to an electric field in a solution of known viscosity. The objective of the zeta potential experiments was to establish whether magnetic fields could have an effect on the surface charge distribution around colloidal particles or could cause a distortion in the electric double layer. Both these effects should under proper experimental conditions be reflected in zeta potential variations. The results summarized in Table 1 show a 10 % difference between control and magnetically treated samples. The decrease in zeta potential after exposure to the magnetic field is consistent with the AFM results.

Table 1 Zeta potentials (mV) for 220 nm poly styrene latex (PSL) particles in 0.001 M NaCl at pH 5.6 before and after a 10 min treatment in a 0.7 tesla magnetic field.

	Control	Field 0.7 T	Control	Field 0.7 T
Zeta ave	67.9	60.2	68.1	59.2
Std dev	1.1	1.4	1.0	1.9

3.5. Conclusions

The zeta potential studies seem to support the AFM results and points to a double layer distortion mechanism. The experimental evidence is, however, too inconsistent at this stage to form the basis for the formulation of a theoretical explanation of the effect of electromagnetic fields on chemical systems.

4. FREE METAL ION SCALE INHIBITOR BASED ON ZN

4.1. Introduction

The development of a **Zn-based free metal ion scale inhibitor** or sacrificial anode system followed the discovery of the effect of free metal ions, Zn^{2+} in particular, on nucleation and crystal growth processes in the calcium carbonate system in a previous WRC-sponsored project (Coetzee and Haarhoff, 1997) conducted by the Department of Chemistry and Biochemistry, RAU. The idea to use this effect as a means of scale inhibition was patented by the WRC in 1996 (Coetzee, 1996). In the current project a prototype Zn-based free metal ion scale inhibitor was developed, tested, and guidelines (from a chemical perspective) for its use compiled.

4.2 Principles and mechanisms of zinc-based scale reduction

It is important to note that the free Zn^{2+} ion is the active species in the scale inhibition process. In the scale inhibition process Zn^{2+} ions are introduced into scale forming solutions containing HCO_3^- ions at a concentration of up to 50 000 times more than the initial free $[Zn^{2+}]$. This means that the speciation of the solution will change over time resulting in a decrease in free $[Zn^{2+}]$. 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. The effectiveness of free Zn^{2+} species to produce delays in the precipitation of $CaCO_3$ is therefore dependent on the rate at which the deactivation of zinc occurs through complexation with ligands present in the system.

4.3 Design of a prototype free metal ion scale inhibitor

A diagram of the prototype Cu/Zn electrode system consisting of a hollow Zn rod inserted into a Cu pipe and provided with suitable electrical connections for connecting to an external DC power source, is shown in Figure 4. Controlled release of Zn was achieved by regulating the current through the cell.

The potential use of these phenomena in scale reduction applications was investigated in trial experiments by pumping ($14\ L.h^{-1}$) supersaturated $Ca(HCO_3)_2$ solutions 300 $mg.L^{-1}$ in Ca^{2+} and the zinc concentration controlled at 100 $\mu g.L^{-1}$ through glass coils (1m × 6 mm) immersed in a water bath at 70 °C. The amount of scale formed was determined by pumping 6 % nitric acetic acid through the coils to dissolve the scale and then determining the Ca concentration by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Scale reduction of 77±6 % was achieved.

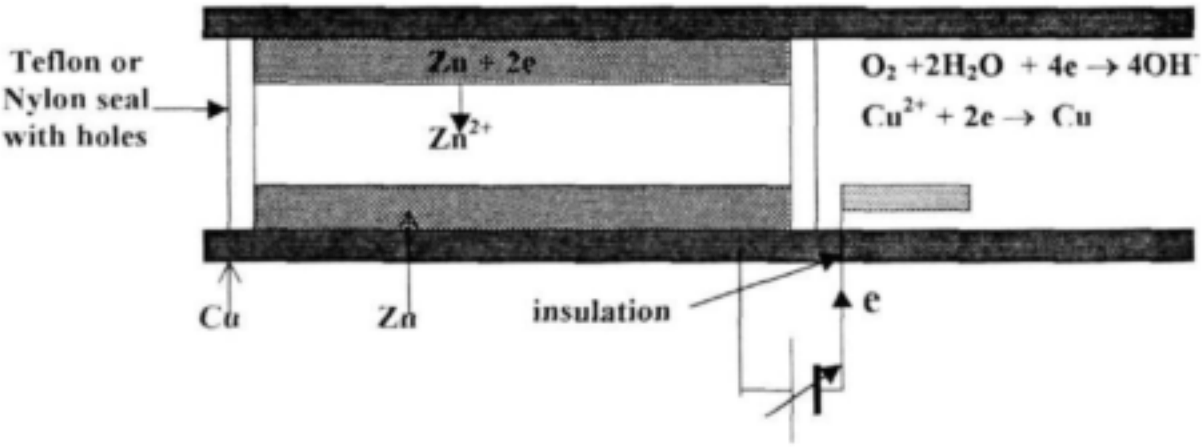

Figure 4.
Free Metal Ion Scale Inhibitor

4.4 Conclusion

Trace amounts of Zn can substantially inhibit the nucleation rate of $CaCO_3$ at Zn/Ca concentration ratios greater than 0.06×10^{-3}. The preferential formation of aragonite rather than calcite has been demonstrated to occur for Zn/Ca concentration ratios above the limiting value. The needle-like crystal morphology of aragonite crystals is believed to reduce the adhesion of scale onto surfaces. It was demonstrated that the presence of zinc as free metal ions reduced the formation of $CaCO_3$ scale in simple laboratory applications. Tests provided insight into possible limiting conditions. For instance, Zn^{2+} ions were deactivated by complexation with certain organic species such organic acid anions that could be present in water.

5. Testing facility

It was the objective to develop an experimental set-up where different types of physical water treatment devices could be tested and compared. Three testing facilities were designed, constructed and tested: a tube testing facility, a heat exchanger testing facility, and a domestic hot water storage testing facility.

The tube testing facility consisted of three parallel tubes each receiving the same water at the same temperature. Scale formation caused the flow resistance to increase with a concomitant decrease in the flow rate. In this facility it was possible to measure changes in flow rate very accurately. Experiments, with PWT device and without, were conducted over a period of two years using municipal water (Rand Water Board) spiked with calcium bicarbonate. The results were erratic and no conclusions could be made on the effectiveness of PWT devices.

The second testing facility consisted of two identical heat exchangers connected in parallel and receiving the same feed water (cold water and hot water at the same temperatures). Scaling was measured by determining the overall heat transfer coefficient as function of time. As scaling progressed the resistance for heat transfer decreased and the logarithmic mean temperatures changed, causing the overall heat transfer coefficient to decrease. To increase the rate of scale formation the concentration of calcium carbonate in one test line was increased to 1 200 $mg.L^{-1}$. Experiments were conducted over two periods of six months each over a time span of 18 months. Several experiments were conducted with and without PWT devices. The PWT devices were randomly commuted between the inlets of the two heat exchangers. No evidence was found that PWT devices reduced scale formation in heat exchangers.

Hot water storage tanks were used in the third testing facility. Initially two hot water storage tanks (geysers) were connected in parallel. The same volume (8 000 L) of water in each tank was heated to a predetermined temperature before being drained. The scale formed was then removed from the tanks and the mass determined. Ten experiments, in which a permanent magnet device was connected to the inlet of one of the tanks, were conducted. Scale formation was on average 36% less (minimum was 17% and maximum was 70%) than in the reference tank. These experiments were conducted over a period of 12 months during the period 1999/2000.

In subsequent experiments, running over 10 months, 6 hot water storage tanks were used in a testing facility where 5 devices could be tested simultaneously using the same input water. One tank was used as reference. Seven experiments were conducted where different PWT devices were compared. The results indicated that scale formation in all 5 circuits where PWT devices had been installed was reduced between 19% and 80%. In the last two experiments a permanent magnet device was installed onto the tank that was used as a reference for the first five experiments. The results, however, contradicted the scale reduction behaviour observed in the first five experiments, as the amount of scale in the tank with the permanent magnet was 52% to 70% more than in the tank without a PWT device. Drastic changes in the composition of Rand Water Board water occurred during this time as a result of the introduction of new treatment procedures using poly amines as coagulents. Incidentally, the zinc concentration during this period was also higher than during the first period. The exact reason for the change in the scaling behaviour during these tests is, however, not clear.

6. CONCLUSIONS

6.1 Summary of the work done

The work done to achieve the objectives of this project can be summarised as follows:

- the development of experimental procedures for the acquisition of reliable data on the effects of electromagnetic fields on scaling systems: These include crystallisation kinetic methods, zeta potential measurements, and AFM force-distance techniques.
- the formulation of theoretical models to explain possible mechanisms.
- the evaluation of commercial devices using crystallisation kinetic methods.
- the development and testing of a prototype free metal ion scale inhibitor based on a zinc/copper electrochemical cell.
- the development and construction of three different types of experimental testing facilities:

6.2 Synthesis of the main findings

6.2.1 Proposed mechanisms

The study showed that at least two completely different mechanisms could be involved in explaining the effect of physical water treatment on scale reduction. The first involves the effect of metal ions released by physical water treatment devices and the second has to do with the effect of electromagnetic fields produced by some PWT devices on the solid-liquid interface during the crystallisation process.

Metal ions, Zn^{2+} ions in particular, present in trace quantities reduce the rate of nucleation and crystal growth during $CaCO_3$ crystallisation. The crystal morphology of precipitated $CaCO_3$ is also predominantly aragonite in stead of calcite when Zn^{2+}

ions are present during the precipitation process. These effects may be explained in terms of the blocking of specific growth sites on the crystal surface by impurity ions of the right dimensions and chemical form.

It is proposed that the effect on electromagnetic fields on the crystallisation process may be interpreted in terms of a mechanism involving the polarisation or distortion of electric double layers around precipitating or scaling particles or ionic atmospheres around ions participating in the scaling process. Results obtained from atomic force microscopy measurements showing a reduction in double layer repulsion and a contraction of the double layer thickness and zeta potential measurements showing a reduction in zeta potentials on exposure to magnetic fields, support this hypothesis. Experimental evidence produced in this study was, however, not sufficiently reliable to confirm this hypothesis.

6.2.2 Free metal ion scale inhibitor

Results show that the performance of zinc as a scale reduction agent is predictable in clean systems using deionised water. Tests provided insight into possible limiting conditions that might occur in tap water or industrial water. Deactivation of Zn could for instance be caused by complexation reactions with organic and inorganic species in water. It was shown that electrochemically introduced zinc behaves in very much the same way as zinc introduced by chemical dosing. A prototype free metal ion scale inhibitor was designed, constructed and tested.

6.2.3 Testing facility

In experiments, running over 10 months, 6 hot water storage tanks were used in a testing facility where 5 devices could be tested simultaneously using the same input water. One tank was used as reference. Seven experiments were conducted where different PWT devices were compared. The results indicated that scale formation in all 5 circuits where PWT devices had been installed was reduced between 19% and 80%.

7. RECOMMENDATIONS

The nature of the processes involved in physical water treatment and the difficulty in monitoring these processes, make research into the fundamentals of electromagnetic effects on scale forming a challenging and very time-consuming effort. It is, nonetheless, recommended that further work be undertaken to address the following important aspects:

- Field tests and possible commercialization of the free metal ion scale inhibitor.
- Continuation of fundamental research, in particular using atomic force microscopy and zeta potential studies, with the aim of unravelling the mechanisms involved in the effect of electromagnetic fields on scaling reactions.
- Continuation of experimentation a longer period of time to verify the integrity of the testing facility.

- The effect of metal impurities on $CaSO_4$ scale formation.
- The effect of electromagnetic fields on $CaSO_4$ scale formation.
- A comprehensive survey of scaling problems in South Africa.
- The effectiveness of physical water treatment at high temperatures.

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- The Water Research Commission who provided the major part of the funding for this project.

- The steering committee responsible for this project consisted from time to time of the following persons:

Mr J N Bhagwan	Water Research Commission (Chairman)
Mr G Steenveld	Water Research Commission
Mr R van der Merwe	Water Research Commission (Committee Secretary)
Mrs C Smit	Water Research Commission (Committee Services)
Prof C A Buckley	University of Natal
Mr F J du Toit	Sastech)
Mr A J Vietti	De Beers Research Laboratory
Prof C F Schutte	University of Pretoria
Prof R Loewenthal	University of Cape Town

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- Rand Afrikaans University for providing laboratory facilities.

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ABBREVIATIONS AND DEFINITIONS

PWT	Physical Water Treatment
ICP-AES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
AFM	Atomic Force Microscopy
PSL	Polystyrene latex (particles)
PVC	Polyvinyl chloride
ISB	Ion Scale Buster
EDTA	Ethylenediaminetetraacetic acid
Δt	Delay time: The difference in induction times between control and test samples.

1. INTRODUCTION

1.1 BACKGROUND

Physical water treatment (PWT) for the reduction of scale has been actively promoted as alternative for chemical treatment of water since the first PWT patent was registered in 1945. This patent was for magnetic water treatment (Vermeiren, 1958). Other techniques that gained in popularity, in particular during the last decade, include non-intrusive devices based on varying frequency electric fields induced through wrap-around coils and intrusive "catalytic conversion" devices where water is treated electrochemically by exposure to a metal alloy surface. The potential reward to industry and the environment should physical water treatment prove to produce consistent scale reduction effects, is enormous. This is the reason why, despite the fact that more than 50 years of intensive research into the effects of electromagnetic fields on scaling processes did not produce a generally accepted theory to explain the mechanisms involved, research and technical development continues unabated. Although PWT technology has changed substantially in some respects since 1945, the basic claims and effects (Baker and Judd, 1996) remained essentially the same. These include: the formation of a soft scale with weak adhesion properties, reduced kinetics of crystallisation, a memory effect of up to 3 days, changes to crystal morphology, reduced or increased particle sizes, descaling and dissolution of existing scale, and decreased zeta potential and surface tension.

The current status is, however, that these claims and effects cannot always be demonstrated experimentally under controlled laboratory conditions in a reproducible way. The reasons why PWT technology sometimes produced excellent results and then seem to stop working altogether, are therefore not clear and will not become clear until the mechanisms involved in these processes are fully understood. In this project the approach was to develop laboratory methods in conjunction with a testing facility industrial size heating circuits to provide the means for the acquisition of reliable data that could be used to substantiate mechanistic models.

The project follows up on the recommendations for further research expressed in a previous WRC sponsored project (Coetzee and Haarhoff, 1997) on the reduction of scaling by magnetic water treatment. The main finding of this report was the discovery that small amounts of free metal ions, in particular Zn^{2+}, released from magnet surfaces during water treatment, play a major role in the scale reduction properties of PWT devices in cases where the water is in physical contact with the device surface during treatment. This finding, including its potential use in scale reduction processes, was patented by the WRC in 1996 (Coetzee, 1996). The report, did not find conclusive evidence of scale reduction effects that could be attributed to electromagnetic fields. It was, however, recommended that the search for evidence of electromagnetically induced effects on scaling processes be continued using new state-of-the-art analytical technology such as atomic force microscopy.

1.2 OBJECTIVES

The objectives of the project were:

- To develop laboratory testing methods to demonstrate under rigorously-controlled experimental conditions the effect of electromagnetic fields on particle-producing chemical reactions such as scale forming processes.
- To develop theoretical models to explain the mechanisms of such effects if any.
- To develop a Zn-based electrochemical system for scale reduction and compile guidelines for its use
- To develop a testing facility which can be used as an independent evaluation center for physical water treatment devices.

1.3 OUTLINE AND STRUCTURE OF THE REPORT

The report consists of three parts reflecting the three main objectives of the project: **Part A** Fundamental Research, **Part B** Free Metal Ion Scale Inhibitor based on zinc, and **Part C** Testing Facilities for PWT devices. The main findings for the project as a whole and recommendations for future work are presented in the chapters **Conclusions** and **Recommendations**, respectively. The **Appendix** lists the publications ensuing from this project and gives details on the archiving of data.

Part A: Fundamental Research

The focus in Part A is on the fundamental chemistry and physics of the processes involved, the development of experimental and analytical methods and the formulation of theoretical models

It was the objective to find a common denominator, which would link the claimed effects listed in the introduction and would make possible a plausible mechanistic explanation. The assumtion was made that scale formation proceeds through the processes of nucleation and crystal growth on exposed surfaces or in the bulk of the liquid phase followed by the attachment of crystalline particles to a surface, forming a layer prone to further growth. It was argued that if PWT was to affect scale formation at all, it should be measurable as an effect on reaction rate, that is, on nucleation and crystal growth processes and the characteristics of the precipitate or scale, in particular its crystal morphology. The next step was to use existing theories of crystallisation to predict possible effects of electromagnetic fields on the processes involved. Nucleation and crystal growth theories and experiments designed to verify the predictions are summarised in **Part A Chapter A1** and **A2**, respectively. The suitability of atomic force microscopy (AFM) and zeta potential measurements to study the effect of electromagnetic fields on the solid-solution interface (electric double layer) during scale formation is discussed in **Part A Chapter A3** and **Chapter A4.** Part A is concluded in **Chapter A5** with the laboratory evaluation of several types of commercial scale reduction devices.

Part B: Free Metal Ion Scale Inhibitor

Part B reports on the development of new scale reduction technology in the form of a free metal ion descaler based on the electrochemical generation of free Zn^{2+} ions according to a patented process (Coetzee, 1996).
The principles and the design and testing of a prototype Free Metal Ion Scale Inhibitor based on a Zn/Cu electrochemical cell system is discussed in **Part B Chapter B1** and **B2,** respectively.

Part C: Testing facility

Part C reports on the construction and use of different industrial size testing facilities for physical water treatment using commercial heating circuits and commercial PWT devices.

It was the objective to develop an experimental facility where different types of physical water treatment devices can be tested and compared.
Three different types of experimental testing facilities have been developed. They are:

- Tube testing facility.
- Heat exchanger testing facility.
- Domestic hot water storage systems with two or 6 six tanks.

PART A

FUNDAMENTAL RESEARCH AND THE DEVELOPMENT OF LABORATORY TESTING METHODS

In Part A relevant theories (Chapter A1), i.e. nucleation and crystal growth theory and the electric double layer theory, that may be used to explain some of the effects of electromagnetic fields on scaling processes or particle-producing reactions, are discussed. A short description of the experimental methods and instrumental techniques namely scale formation kinetics (Chapter A2), AFM measurements (Chapter A3), zeta potential measurements (Chapter A4), and the results of laboratory tests performed on different types of commercial PWT equipment (Chapter A5), is given. A more detailed reference to theoretical treatment of the subject and a detailed review of the literature may be found elsewhere (Coetzee and Haarhoff, 1997, Baker and Judd, 1996).

A1. CRYSTALLISATION THEORY

A1. 1 Nucleation and crystal growth theory

Crystallisation can be seen as consisting of two distinct processes:

- **nucleation** where a small number of ions constituting the precipitate, aggregate to form microscopic nuclei
- **crystal growth** where particles larger than a critical size will increase their size through a diffusion and adsorption-controlled growth process

The nucleation process is strongly dependent on the degree of supersaturation and also involves the formation of a solid-liquid interface when nuclei are formed. It can be shown (Beruto and Giordani, 1995) that the rate of nucleation, dN/dt, here given in a much simplified form, is directly proportional to the supersaturation, S, and is inversely proportional to interfacial energy, σ. Note that the relationship is exponential:

$$\frac{dN}{dt} \propto e^{-\sigma^3/(\ln S)^2} \qquad (1)$$

where

$$S = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{sp}} \qquad (2)$$

Crystal growth rate, dC/dt, here also given in simplified form, is directly proportional to interfacial energy and supersaturation. Note that this relationship is linear:

$$\frac{dC}{dt} \propto \sigma\left(\sqrt{S}-1\right)^2 \qquad (3)$$

Careful consideration of all the factors in the final equations led to the conclusion that the interfacial energy would be the most likely candidate to show any sensitivity for electromagnetic effects. It can therefore be argued that a possible distortion or polarisation of the charge distribution in the solid-liquid interface by electromagnetic fields would increase the interfacial energy, i.e. the energy of formation of the solid-liquid interface. It is clear from the equations above that the nucleation rate will be exponentially dependent on the supersaturation and interfacial energy whereas crystal growth rate will only show a linear dependency. This hypothesis then predicts that the effect of electromagnetic fields would be that of slowing down the rate of nucleation and enhancing the crystal growth rate. The end result would be fewer but larger crystals.

This hypothesis may also be used to make predictions with regard to the crystal morphology of precipitated particles. In the case of calcium carbonate two crystal forms occur. At 37 °C, calcite is the preferred crystal form (rhombohedral or "cubes") and above 60 °C the aragonite form (rhombic or "needles) predominates. However, should an electromagnetic field distort the solid-liquid interface or polarise the electric double layer, the hypothesis predicts that the crystal growth rate will increase. The formation of calcite, being the more stable crystallographic form should then be even more favoured. It should, however, be noted that many reports on magnetic water treatment claim that the formation of calcium carbonate in the aragonite form is favoured in treated systems.

A1.2 Electric double layer theory

A distortion of the solid-liquid interface should also affect the electric double layer around a colloidal micro crystal of the formed precipitate. The structure and properties of the electric double layer are adequately described by the electric double layer theory (Atkins, 1994) in terms of the electric potential across the solid-liquid interface.

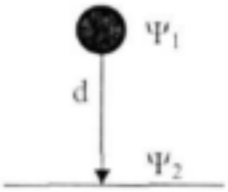
The potential energy arising from the repulsion of double layers on particles of radius, a, (first term) and the Van der Waals attraction (second term) at distance, d, has the form:

$$V = \frac{Aa^2\zeta^2}{R}e^{-d\kappa} - \frac{B}{d} \qquad (4)$$

where ζ is the zeta potential, A and B are constants, R is the separation of centers, d is the separation of surfaces or d = R-2a, and κ is the inverse double layer thickness given by:

$$\frac{1}{\kappa} \approx \sqrt{\frac{k}{I}} \qquad (5)$$

where I is the ionic strength of the solution and k is a constant. The double layer thickness therefore decreases with increasing electrolyte concentration. These equations were used to derive an expression for the repulsive force between a colloidal particle and a similarly charged flat surface with surface potential, ψ, here given in a simplified form:



$$F \approx \frac{\Psi_1 \Psi_2}{\kappa} e^{-\kappa d} \qquad (6)$$

A distortion of the double layer by an electromagnetic field or a change in the ionic strength would therefore be reflected as a change in the force-distance relationship. The invention of the atomic force microscope allowed molecular forces to be measured on the molecular scale for the first time. In particular, force-distance measurements by AFM (see Chapter A3) provide a means of directly studying the electric double layer and associated surface charges.

A2. EFFECT OF ELECTROMAGNETIC FIELDS ON CRYSTALLISATION KINETICS

A2.1 Experimental procedures

To test the predictions of the hypothesis that interfacial energy during nucleation and crystal growth may be affected by elctromagnetic fields (see Section A1.1), experiments were designed to study the possible consequences with regard to crystallisation kinetics of precipitation reactions and crystal morphology of the resulting precipitates as a function of exposure to electromagnetic fields. Crystallisation kinetics can conveniently be studied by following the pH, metal ion concentration of the precipitating salt, or other parameters of the precipitating solution, over time. Data can then be presented as precipitation curves, i.e. curves of a measured parameter vs time, for example, pH vs time curves. Other parameters that were monitored include, conductivity, turbidity, particle size, zeta potentials and crystal morphology.

Two types of precipitation reaction were studied:

- the precipitation of calcium carbonate
- the precipitation of barium oxalate

Typically, supersaturated calcium carbonate solutions were prepared by mixing calcium nitrate and sodium bicarbonate solutions. The calcium concentration (50 to 300 mg.L^{-1}) was chosen in such a way that the solution was metastable with regard to precipitation. This means that precipitation could take place thermodynamically but kinetically nucleation was slow. Precipitation thus only started after prolonged heating at 37 °C allowing enough time for a proper measurement of the precipitation curve. The precipitation reaction was then monitored by measuring different parameters for electromagnetically conditioned solutions and the results compared with that obtained from identical but unconditioned solutions. Reaction conditions such as temperature at 37 °C, stirring and mixing rates, initial pH and level of supersaturation were kept constant during experiments. Extreme care was taken to ensure that all experimental conditions were exactly the same for test and control. Electromagnetic fields used in the experiments were generated by commercial physical water treatment devices, laboratory electromagnets or specially constructed Helmholtz coils. Intrusive and non-intrusive types were used. Magnetic fields varied between 0.1 mT to 1.5 T. No extraeneous electromagnetic fields apart from the earth's magnetic field were measureable.
Details of test loops, instrumentation, experimental conditions and methods are described elsewhere (Coetzee et al., 1996; Coetzee, 1998; Howell, 1996).

The precipitation of barium oxalate was monitored by measuring with ICP-AES, the residual Ba concentration, that is the Ba remaining in solution as a function of time after mixing barium chloride and sodium oxalate solutions. Test solutions were exposed to 1200 Hz electromagnetic fields generated by Helmholtz coils wrapped around the reaction vessel.

A2.2 Effects on the precipitation of calcium carbonate

Data, graphically presented as precipitation curves, can be used to calculate induction times, i.e. the time from mixing of reagents to the start of precipitation. Induction time is then taken as a measure of nucleation rate, being inversely proportional. The curves, as shown in Figure

A2.1, are characterised by a gradual rise in pH caused by an initial slow release of CO_2 from the solution as the temperature is increased from ambient to 37 °C (optimum temperature for the formation of calcite). The sharp downward adjustment in the pH marks the onset of precipitation of solid calcium carbonate according to the reaction given below, and the beginning of the crystal growth phase.

$$Ca^{2+} + 2HCO_3^{-1} \rightarrow CaCO_3 + CO_2 + H_2O$$

Details of the chemistry of $CaCO_3$ scale formation and crystallisation characteristics may be found elsewhere (Coetzee and Haarhoff, 1997; Howell, 1996; Mubenga, 1998)
The difference in induction times, t_a and t_b between the two curves, a test curve and a control, is denoted by the delay time, Δt. The precipitation curve for calcium carbonate precipitated from electromagnetically conditioned water (contact type device) and water spiked with trace amounts of zinc gave the predicted decrease in nucleation time. In Figure A2.1 a delay time of 20 min is indicated for water containing 50 µg $Zn.L^{-1}$ and 150 mg $Ca.L^{-1}$. No difference in slope is, however, measureable in the crystal growth phase of the curve.

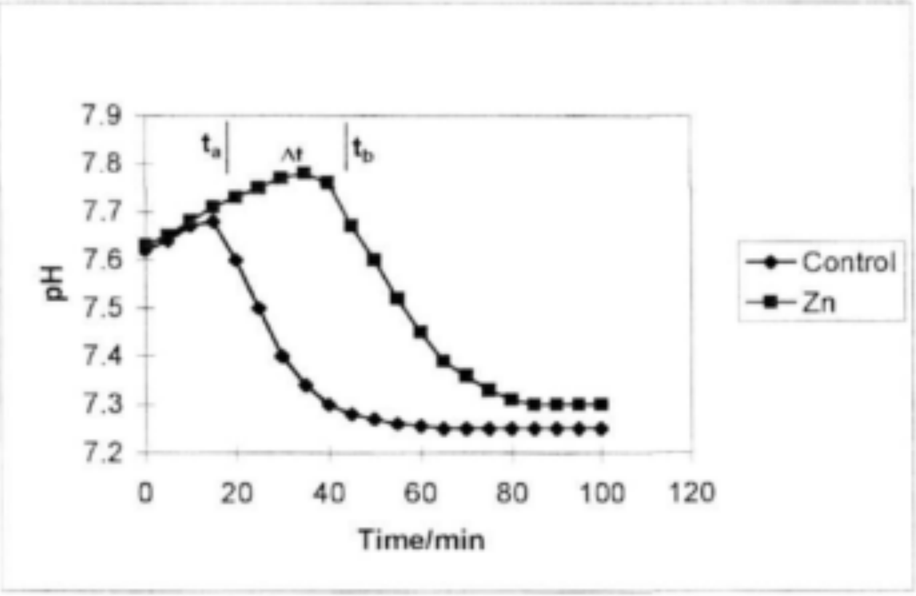


Figure A2.1.
pH vs time curves for the precipitation of $CaCO_3$ from a 150 $mg.L^{-1}$ Ca control solution and a 150 $mg.L^{-1}$ Ca + 50 µg $Zn.L^{-1}$ test solution, respectively. Delay time ($\Delta t = t_b - t_a$) is the difference between induction times of the control and test solution.

Investigation of the crystal morphology of the precipitates by scanning electron microscopy indicated the formation of aragonite in preference to calcite for conditioned solutions in all cases where intrusive devices were used. These included, magnetic, electric, and catalytic conversion types. The results did, therefore, not completely support the hypothesis.

The fact that aragonite was formed and it is well known that trace ionic impurities can influence crystal morphology and cause a decrease in crystal growth rate (Meyer 1984), indicated that metal impurities released from surfaces in contact with the conditioned water might be the cause of this anomaly. In subsequent experiments all internal surfaces that came into contact with the test solution were coated with a silicone-based polymer and the experiments repeated. Results showed that by eliminating direct contact with internal surfaces the delay times were reduced to zero and the crystal form reverted to calcite. ICP-MS analysis of deionised water pumped through the uncoated devices revealed minute amounts of metal ions, such as Cu, Zn, Fe, Co, Ni and Mg released into solution (Coetzee et al, 1996). Extensive tests on different metals showed that ultratrace amounts of Zn ions have a pronounced effect on the nucleation rate of calcium carbonate. In fact, the addition of trace amounts (μg.L^{-1}) of Zn ions to the test solution, equivalent to the concentration released by the device, produced identical results as before.

The effect of Zn on crystallisation of calcium carbonate was studied comprehensively. The results are published elsewhere (Coetzee et al, 1998). Results shown in Figure A2.2 reveal that initially the delay time increases almost linearly with zinc concentration, but eventually levels off when the [Zn]/[Ca] ratio becomes larger than 0.002 μgZn/μgCa. Mass ratios as low as 10 parts Zn per million parts Ca can still result in measurable delay times which means that about 1 μg.L^{-1}of Zn would be enough to produce effects on the crystallisation of calcium carbonate in scale forming water containing 100 mg.L^{-1} Ca. Tests to evaluate the potential of Zn to reduce scale showed that a 80% reduction in the amount of scale formed was achieved when solutions containing 300 mg.L^{-1} Ca and 200 μg.L^{-1} Zn were pumped through glass coils at 70 °C.

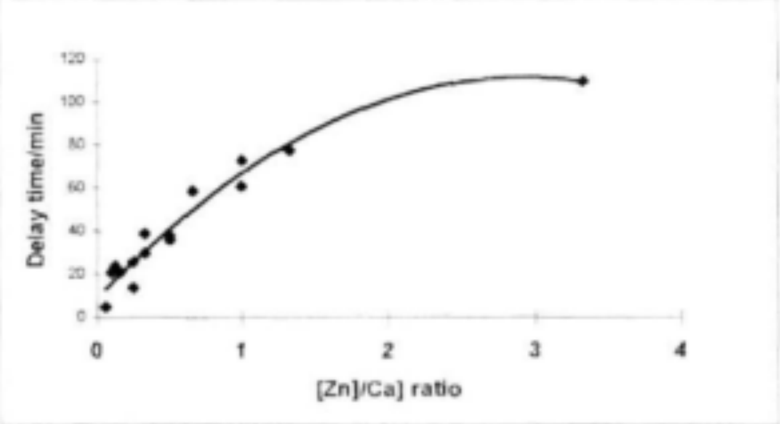


Figure A2.2.
Delay time as a function of [Zn] /[Ca] ratio

A 2.3 Effect on barium oxalate precipitation

A useful method (Coetzee et al, 1998, Berton et al, 1993) for studying precipitation reactions, measures a suitable property of the precipitating solution, in this case metal ion concentration remaining in solution, as a function of time. This method was applied to study the effect of low frequency electric fields, such as those generated by commercial wrap-around coil devices, on the precipitation of barium salts. Devices based on this principle and included in this study were: Scale Watcher (The Netherlands) and Scale Ban (UK). Barium salts were chosen because the barium precipitation reaction is independent of CO_2 and therefore much easier to control than the calcium carbonate precipitation reaction. Barium salts can also cause scale.

The rate of precipitation of barium oxalate was monitored by measuring (ICP-AES) the barium concentration remaining in solution as a function of time after mixing barium chloride and sodium oxalate solutions. Test solutions were exposed to 1200 Hz electromagnetic fields generated by specially constructed Helmholtz coils wrapped around the reaction vessel. The associated magnetic field was very low, about 3 mT. Results previously published (Berton et al., 1993) and obtained using a similar system, seem to indicate a decreased rate of nucleation as predicted by the hypothesis. The results from this study compared in Figure A2.3, however, show identical behaviour of control and test sample and therefore do not support the hypothesis.

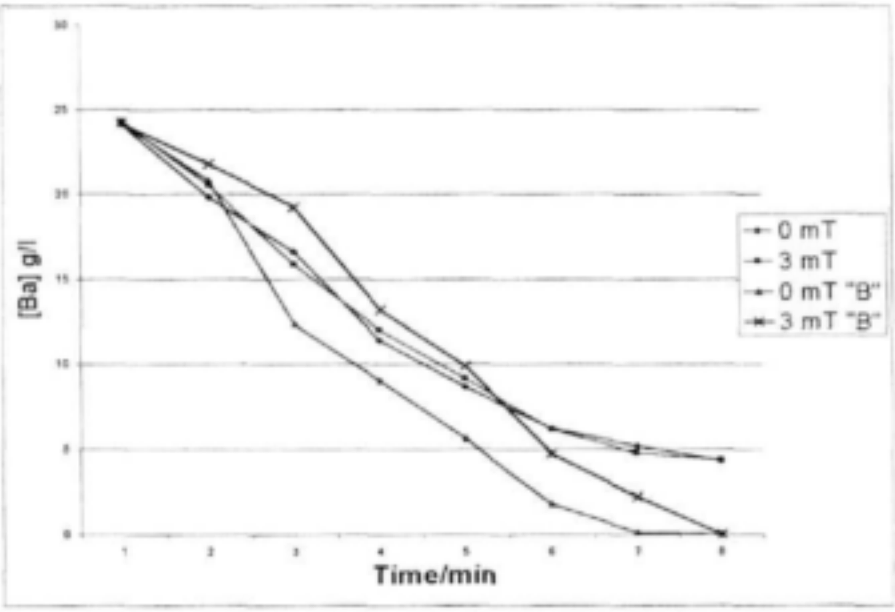


Figure A2.3:
Ba cocentration remaining in solution as a function of time for the precipitation of barium oxalate exposed to a 1200 Hz magnetic field. "B" indicates results by Berton (Berton et al., 1993).

A2.4 Conclusions

- Free metal ions, in particular Zn^{2+} released by PWT devices or pipes as a result of electrochemical reactions induced by the field, can cause a reduction in nucleation rate and changes in crystal morphology which could lead to a reduction in scale formation.
- Experimental results obtained from barium oxalate precipitation curves were not sufficiently reproducible to confirm the hypothesis based on the modification of the surface energy by electromagnetic fields.

A3. ATOMIC FORCE MICROSCOPY EXPERIMENTS

A3.1 Introduction

The objective of these experiments was to investigate the suitability of AFM to study the possible effect of electromagnetic fields on surface charge and the electric double layer around colloidal particles. If this effect could be demonstrated experimentally it would give an important indication of the mechanisms involved in magnetically modified scale formation. AFM is an extremely powerful modern surface analysis technique whereby the forces across the electric double layer can be measured using the force-distance acquisition mode. In this mode the probe, cantilever and tip, with a known force constant, is brought into contact with a surface and the forces of attraction or repulsion between the tip and surface determined by measuring the shift in the reflected laser beam. The bending of the cantilever is proportional to the force experienced by the cantilever. When this experiment is performed in liquids, the characteristics of the electric double layer can be obtained

In the experiments, modified AFM cantilevers were used to acquire force-distance data across the particle - solution interface, or the double layer. The modified probe was made by gluing a 9µ poly styrene latex (PSL) particle to the tip of the AFM cantilever. This is a highly specialised procedure which was performed with the aid of micro manipulators under a microscope. Force-distance data were then compared to predictions for double layer characteristics based on double layer theory. The first objective was to demonstrate that small changes in electric double layer characteristics as a function of electrolyte concentration, could indeed be measured by AFM using a colloid probe. Once this was proven the technique could be adapted to study the effects of electromagnetic fields on the surface-solution interface. AFM measurements were performed at the Department of Biophysics at Nottingham University, UK and since January 1999 with identical AFM equipment (Topomerix Explorer) at RAU.

Figure A3.1 gives a diagram of the experimental setup to perform force-distance measurements using a Topometrix Explorer Atomic Force Microscope. A modified tip was used as a probe to measure the force between particle and substrate (a piece of atomically flat mica or oxidised electronic grade silicon) in different electrolytes by using the z-scanner (2µ Topometrix liquid scanner.) to move the tip into the substrate over a distance of 200 nm.

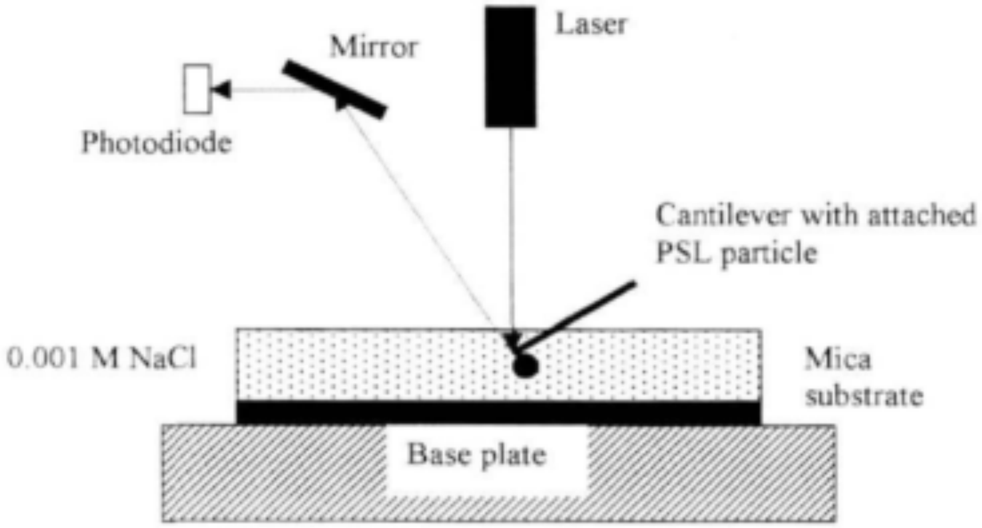


Figure A3.1
Experimental setup for AFM force-distance measurements showing a PSL particle glued to the cantilever tip.

A3.2 Effects of electromagnetic fields on the electric double layer

Table A3.1 summarises the effect of electrolyte concentration and pH on the apparent surface charge, indicated by the repulsive force (F in pN) between probe and an atomically flat mica substrate, and double layer thickness (S in nm).

Table A3.1 Effect on repulsive force (F) and double layer thickness (S) of different electrolytes

[NaCl] at pH 8	Force pN	Distance (S) nm
1E-5	1.2	65
1E-4	1.1	39
1E-3	0.9	25
1E-2	0.7	10

Repulsive forces and double layer thickness increased with decreasing concentration as expected according double layer theory. These results are highly significant because for the first time analytical technology allows the direct measurement of electric double layer characteristics at the molecular level and provides an excellent tool to study the small effects caused by electromagnetic fields in aqueous media. Figures A3.2 and A3.3 give a graphical representation of the observed effects.

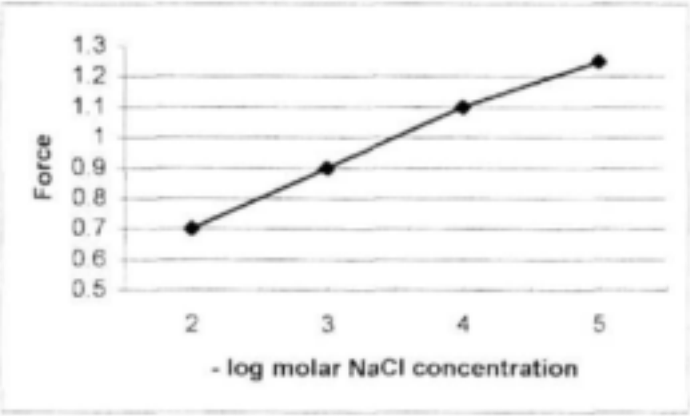


Figure A3.2

The effect of electrolyte concentration on apparent surface charge.

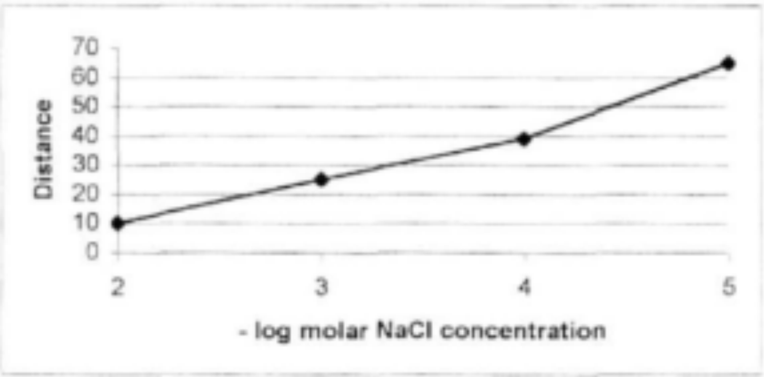


Figure A3.3

The effect of electrolyte concentration on double layer thickness.

The increase in double layer thickness as concentration of the electrolyte decreases can clearly be seen in Figure A3.3. This is in agreement with the predictions according to equation 6 (Section A1.2). These results prove that changes in very small repulsion forces in the order of pico newton over very small distances (0 to 50 nm) can be measured reliably by modern AFM equipment.

Exposing the electrolyte, eg 0.001 M NaCl, to a magnetic field of 0.45 T under static conditions for 10 min and then performing the force-distance measurements produced a 60 % reduction in the repulsive force between tip and substrate and an increase in double layer thickness. A reduction in repulsive force was also observed when a fresh sample of the 0.001 M NaCl electrolyte was circulated through the magnetic field for 10 min. The same NaCl solution used for the static experiment was subsequently subjected to sonic treatment for 5 min in an ultrasonic bath after the cantilever and tip were plasma cleaned.

Typical results are shown in Table A3.2 and Figure A3.4.

Table A3.2 Effect of a magnetic field of 0.45T on electric double layer characteristics

Experimental details	Static		Recirculate		Ultrasonic	
	Force pN	Distance(S) nm	Force pN	Distance(S) nm	Force pN	Distance(S) nm
Control	1.6	54	3.2	61	4.1	73
Treated	0.6	43	2.1	43	3.5	76
Control	1.5	71	3.1	72	4.2	68

The larger values of the repulsive force observed for the recirculation and ultrasonic treatment experiments could in part be ascribed to the effect of using a plasma-cleaned tip which enhanced sensitivity. The fact that the two ultrasonically treated controls and the static control gave the same values for the repulsive force, F and double layer thickness, S in a highly reproducible manner indicates that the high values reflect a change in the condition of the tip. It could be argued that exposing the tip to an ultrasonically treated solution somehow affected the tip because the static control sample which measured 1.5 pN in the first experiment also gave a value of 4.1 using this tip. The absolute values of the three experiments are therefore not directly comparable.

It is very interesting to note that the statically treated sample, even after ultrasonic treatment, still give a repulsive force slightly less than the controls. This could indicate that the effect caused by the magnetic field is indeed very robust - a difficult scenario to explain from a theoretical point of view. Similar observations were also published by Higashitani (Higashitani et al,1997).

		Force pN	σ n=30
1	CONTROL	1.6	0.1
2	MAGNETISED*	0.6	0.1
3	CONTROL	1.5	0.2
4	CONTROL US**	1.6	0.1
5	MAGNETISED US	1.4	0.1
6	CONTROL US	1.6	0.2

* 0.45 tesla field
** 5 min ultrasonic treatment

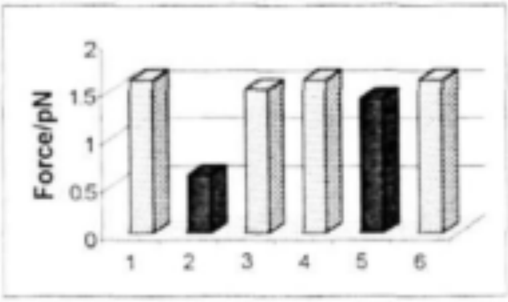


Figure A3.4
Effect of a 0.45 T magnetic field on the apparent surface charge. Ultrasonic values are normalised to the static control.

If this result could be confirmed and reproduced in other laboratories it would be the first directly measurable effect of electromagnetic fields on the solid-solution interface on the near molecular level. However, possible artefacts, largely unknown at this stage, but inherent in force-distance measurements with AFM, which could produce the observed results, must in follow-up work first be excluded before these results could be accepted with certainty.

A3.3 Conclusions

AFM force-distance measurements indicate, but not as yet confirm, a contraction of the electric double layer and a redistribution of surface charge on precipitating particles or a distortion of the hydration sphere around ions caused by the electromagnetic field.

A4. ZETA POTENTIAL MEASUREMENTS

A4.1 Introduction

The zeta potential of a colloid is an indication of the charge distribution around a colloidal particle in solution and is determined by measuring its electrophoretic mobility or its velocity when exposed to an electric field in a solution of known viscosity. The ionic strength and pH of the solution are important determinants of zeta potential and must be controlled. Changes in the surface charge of a particle or charactistics of the electric double layer will be reflected in the zeta potential.

The objective of the zeta potential experiments was to establish whether magnetic fields could have any effect on the surface charge distribution around colloidal particles or could cause a distortion in the electric double layer. Both these effects should under proper experimental conditions be reflected in zeta potential variations.
The fundamental assumption was that a distortion of the double layer or polarisation of the surface charge would lead to an apparent reduction in electric mobility and a shrinkage of the double layer. If this hypothesis was correct a lowering of zeta potentials after exposing colloids to magnetic fields was to be expected.

A4.2 Experimental procedures

Zeta potential measurements were performed using state of the art equipment at Malvern Laboratories, England and with an identical system (Malvern Zetamaster) at RAU. An aliquot of a 220 nm PSL particle size standard from Duke Scientific was suspended in a 0.001 M NaCl solution which was then exposed to magnetic fields of either 0.7 tesla or 0.1 tesla for 10 min.

A4.3 Effect of electromagnetic fields on zeta potentials

The results of zeta potential measurements are summarised in Table A4.1.

Table A4.1 Zeta potentials (mV) for 220 nm poly styrene latex particles in 0.001 M NaCl at pH 5.6 before and after 10 minutes treatment in a 0.7T magnetic field.

	Control	Field 0.7 T	Control	Field 0.7 T	Sonic 5 min	Sonic 0.7 T
Zeta ave	67.9	60.2	68.1	59.2	61.3	31.4
Std dev	1.1	1.4	1.0	1.9	1.4	1.1

A 10 % difference between control and treated samples was observed. These results obtained at Malvern Laboratories, caused great excitement among the researchers working on this project, in particular the apparently synergistic effect of ultrasonic treatment combined with magnetic treatment. The experiments were subsequently repeated at RAU with identical equipment. Great care was taken to control all experimental conditions. The results obtained at Malvern Laboratories (UK) could, however, not be confirmed. A probable cause of this

discrepancy could be the presence of colloids in the test solutions. It is known that silicates leached from glass can affect zeta potential measurements.
In subsequent experiments colloidal silica suspensions with a narrow particle size distribution (average particle size 300 nm) were exposed to magnetic fields of 0.22 tesla in a circulating system and the zeta potentials measured over time. Results show a decrease in zeta potential over time compared to an identical control colloid which was not exposed to the magnetic field. The remarkable observation was that the differences only became evident 24 hours after exposure to the field. The same result was obtained in 5 consecutive experiments.

A4.4 Conclusions

The zeta potential studies seem to support the AFM results and points to a double layer distortion mechanism. The experimental evidence is, however, too inconsistent at this stage to form the basis for the formulation of a theoretical explanation of the effect of electromagnetic fields on chemical systems.

A5. EVALUATION OF COMMERCIAL DEVICES

A5.1 Introduction

Different types of antiscaling devices were evaluated using rapid laboratory screening tests. These tests were designed to give a preliminary indication whether antiscaling or scale reduction effects could be expected for a particular device. Two tests were performed:

(i) trace metal ion releases after test water was passed through the device.

(ii) precipitation curve measurements.

Identification of trace quantities of certain metal ions, eg Zn, Fe and Cu, and increases in nucleation time as determined in precipitation curve experiments, could indicate possible scale reduction effects.

A5.2 Permatrade

Description of device

The Permatrade device (manufactured in Germany) is based on a permanent magnet system where the magnets are arranged in a NN-SS array. The treated water follows a corkscrew motion through the device passing through several magnetic field gradients.

Experimental

The experimental test loop consisted of a 25 L polyethylene reservoir, 20 mm PVC pipes, a peristaltic pump, and the Permatrade device. In the identical control loop a glass tube replaced the magnetic unit.

A set of runs was carried out to investigate the possible release of trace metals from the device. Deionised water was circulated through the system for 3 h and samples taken after every hour. ICP-AES was used to determine the following metals: copper, aluminium, barium, iron, magnesium, cobalt, nickel, chromium, and zinc.

Results and discussion

Metals released

Only Zn was found in the test solutions and the concentration of zinc increased with circulation time. One possibility was that it could be released from the device. Another option was that this zinc might be released from the new PVC pipes. A set of tests involving the circulation of deionised water through the system was carried out to determine the source of zinc. The results showed that the concentration of the zinc decreased with each test run. Deionised water was alternately circulated through the test loop and the control loop with the objective of checking if zinc concentration was still decreasing. This trend in the decrease of zinc was confirmed. It was clear that the observed zinc was released from the new PVC pipes. Water was circulated through the system for 24 h to leach the remaining zinc from the pipes.

Precipitation curves

A solution of calcium nitrate (Ca^{2+} concentration = 100 mg.L^{-1}) and sodium bicarbonate was circulated through the test loop for 10 min. Samples were then heated in a water bath at 37 °C and the precipitation of calcium carbonate followed by taking pH measurements over time. Precipitation curves were constructed and delay time calculated in the same way as was illustrated in Figure A2.1. The delay times are given in Table A5.1.

Table A5.1: Delay times in the precipitation of calcium carbonate for the Permatrade device.

RUN	DELAY TIME (min)
CONTROL	93
TEST	93
CONTROL	90
TEST	90

No difference in delay times were found between control and test. These results indicate that the Permatrade device had no effect on the precipitation kinetics of calcium carbonate.

A5.3 Ion Scale Buster

Description of the device

The Ion Scale Buster (ISB) device (made in the UK) consists of a Zn tube joined to an outer Cu pipe. The device was to be earthed when installed.

Experimental

The test solution consisted of a $Ca(NO_3)_2$ solution mixed with a solution of $NaHCO_3$ with a final Ca^{2+} concentration of 100 mg.L^{-1}. The pH of the $NaHCO_3$ solution was adjusted to approximately 7.5 before mixing. One liter of the test solution was circulated through the system consisting of a 2 L glass reservoir and a treatment loop that permits a continuous re-circulation of the solution through the ISB device. A second loop similar to the test loop but without the unit was used as a control loop.

One set of the experiments was carried out with the ISB device earthed and the other set with the ISB device not earthed. The glassware used for the precipitation experiments was cleaned with 10 % nitric acid solution, rinsed in de-ionised water, steam cleaned for 10 min, and finally rinsed with de-ionised water.

The solutions were circulated for 10 min and then left to stand for 15 min before heating in a water bath set at 37 °C prior to recording the precipitation curves. Graphs of pH versus time were plotted and the delay times of the test and control solutions were calculated.

Results and discussion

The summary of the metal ions released from the device over time is shown in Table A5.2.

Table A5.2 Concentrations in mg.L^{-1} of metal ions released from the ISB device and the corresponding delay times.

Run	Zn		Cu		Δt
	Test	Control	Test	Control	min
Earthed					
1	1.45	0.03	0.12	0.27	54
2	0.87	0.002	0.03	0.03	90
3	0.59	0	0.015	0.017	104
4	0.39	0.008	0.022	0.045	174
5	0.19	0.001	0.017	0	117
Not earthed					
6	0.13	0	0	0	58
7	0.11	0	0.006	0.014	72
8	0.22	0	0.023	0.017	57
9	0.07	0	0.013	0.01	24
10	0.12	0	0.063	0.053	36
11	0.12	0	0.051	0.05	36
12	0.08	0	0.030	0.031	18
13	0.10				
14	0.12				
15	0.09				
16	0.05				
17	0.04				

The results are characterised by a steady decrease in the concentration of zinc released over time or number of times the test calcium bicarbonate solution was circulated through the device. This is graphically illustrated in Figure A5.1.

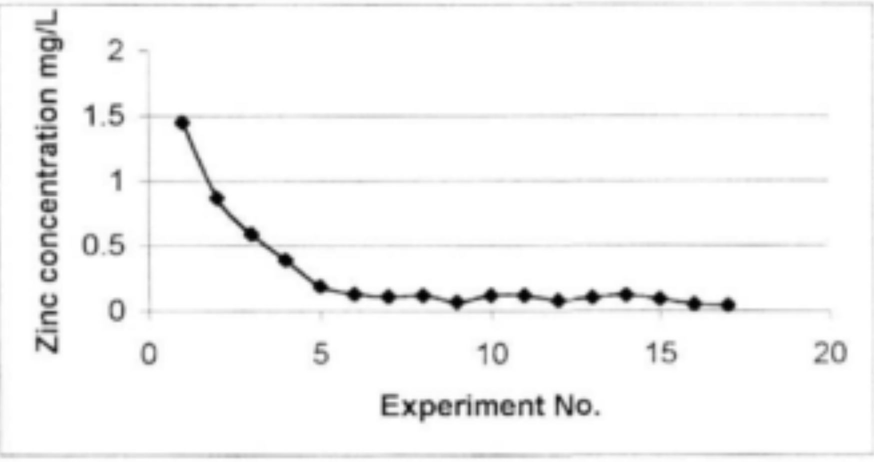


Figure A5.1
Decrease in zinc released by the ISB device over time or number of experiments.

Before the start of experiment 1 the system, including the device, was cleaned by pumping 0.1 M acetic acid through the loop followed by rinsing with deionised water. The increasing delay times measured for runs 1 through 5 while the zinc concentrations were steadily diminishing, could be due to residual acid in the system being removed. The general trend is, however, a gradual decrease in the release of zinc due to the scaling of the active surface of the device and a commensurate decrease in delay time or the precipitation of calcium carbonate. The system, including the device was again cleaned with 0.1 M acetic acid solution and the metal ion concentrations determined after repeated runs with deionised water and tap water. Table A5.3 summarises the results.

Table A5.3 The concentrations of Zn, Cu and Fe in mg.L^{-1} released from the ISB device after c leaning with 0.1 M acetic acid and circulating deionised water and tap water.

Run	Zn		Cu		Fe	
	Test	Control	Test	Control	Test	Control
Deionised water						
1	0.84	0.04	0.43	0.88	0	0
2	0.16	0	0.02	0.06	0	0
3	0.08	0	0.02	0.04	0	0
4	0.08	0	0.02	0.03	0	0
Tap water						
5	0.75	0.04	0.10	0.14	0.04	0.04
6	0.36	0.04	0.05	0.05	0.04	0.04
7	0.33	0.08	0.05	0.04	0.04	0.05
8	0.33	0.11	0.06	0.04	0.05	0.05

Again an initial decrease in Cu and Zn was noticed. The release then quickly stabilised. The release of Zn into deionised water is very low compared to the concentrations released into tap water. This is an important indication that electrochemical reactions are required in this device for its successful operation. Without ionic conductance and the presence of small amounts of copper ions in solution this device will not work properly.

Conclusion

The ISB device would under certain conditions release enough zinc to slow down the nucleation process for calcium carbonate and also change its crystal morphology. This could lead to decreased scale formation.

A5.4 Superior

Description of device

The Superior C-100 device (made in the UK) consists of a magnet of unknown configuration which is in contact with the water passing through the device.

Experimental

The same experimental test loop and experiments were used as before.

Results and discussion

Zn was released by the Superior in significant amounts. The release of zinc did not tend to decrease with time as was the case with the ISB device which had no magnet as part of its design. The concentration of Zn released into the test solution circulating for 10 min and containing 2 L calcium bicarbonate (100 mg.L^{-1}) remained constant at 0.3 mg.L^{-1} over time.

The average delay time for the precipitation of a 100 mg.L^{-1} calcium carbonate solution treated with the Superior C-100 for 10 min was 170 min. Typical precipitation curves are given in Figure A5.2. The Zn concentration released into the solution was much higher than in the case of the ISB and the delay times also significantly longer.

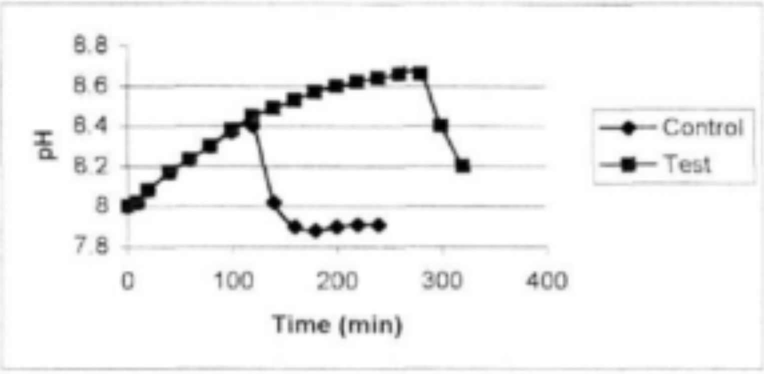


Figure A5.2

Precipitation curves for a 100 mgCa.L^{-1} calcium carbonate solution treated with the Superior C-100 device. Δt = 171 min

Impurities

A set of experiments was conducted to study the effect of an inorganic ligand, such as chloride, on the delay time when the Superior C-100 device was used. For this purpose NaCl solutions with different concentrations, 100, 500, and 1000 mg.L^{-1} were circulated through the system and the delay times determined. The results are shown in the Table 2.7. The results indicate that chloride ions have an increasingly detrimental effect on the delay times as the [Cl$^-$] increases. This confirms previous work (Coetzee, 1998) with regard to the importance of free zinc ions being present in the treated solutions to facilitate scale reduction effects. In high chloride concentrations zinc will be complexed as the $ZnCl_3^-$ species rendering it ineffectual in decreasing the nucleation rate of calcium carbonate.

Table A5.4: Effect of Chloride ions on the delay time

Exper. No	$[Cl^-]$ mg.L^{-1}	$[Zn^{2+}]$ µg.L^{-1}	Delay min
1	100	1014	110
2	500	3630	63
3	1000	3545	18
4	1000	3630	16

Conclusion

Our results indicate that the Superior C-100 has a significant effect on slowing down the nucleation rate of calcium carbonate. One would expect this device to have scale reduction properties provided the treated water is free from inorganic and organic ligands that could form coordination complexes with zinc.

A.5.5 Scale Watcher

Description of device

The Scale Watcher (made in the Netherlands) is a variable frequency wrap-around coil device.

Descaling eperiments

The aim was to determine the descaling effects on calcium carbonate deposits, if any, of a radio frequency (RF) field produced by the Scalewatcher coil wrapped around a scaled-up pipe.

Preparation of the scaled-up coils:

The four glass coils (1 m x 6 mm i.d.) were washed in a 10 % nitric acid solution to ensure that the inside of the coils were clean and free of foreign matter. The coils were then thoroughly rinsed with de-ionised water. De-ionised water was also flushed through each of the coils to remove any traces of the nitric acid. After flushing, the coils were dried by using compressed air.
The scale growth loop was prepared in such a way as to build equal amounts of scale in each set of two coils under identical conditions. A 500 mg.L^{-1} calcium carbonate solution was circulated through the coils placed in a water bath maintained at 78°C throughout the duration of the scaling process. The aim was to achieve an equal velocity of calcium carbonate solution through both sets of coils.

Preparation of the test and control loops for descaling:

The control and test loops were both constructed identically i.e. from the same length of tubing and the same size of tubing. The loops (coils excluded) were flushed with 1% nitric acid solution for 20 min. The loops were then flushed with de-ionised water until free of acid. After rinsing, the loops were disassembled into component form and the connectors rinsed in de-ionised water, dried with compressed air and reassembled. Once fully assembled (excluding coils) the loop was again flushed out with compressed air to make sure all water was expelled from the system.

Experimental procedure for descaling:

Two coils each were installed in the test loop (including the Scale Watcher device) and in the control loop (without device). De-ionised water was circulated simultaneously through the loops at the manufacturers recommended flow rate of 410 mL/min. Samples were taken from each system every 15 min. The Scale Watcher device in the test loop was not turned on at this stage. The aim was to allow the calcium concentration to stabilise before the unit was switched on. Thus if a substantial increase in calcium concentration was to be observed it could only be attributed to the effects of the Scalewatcher itself. The calcium concentration was found to stabilise in both systems after sample 5 was taken, i.e. 90 min after circulation was started. The Scalewatcher was switched on immediately after sample no 5 had been taken. Further samples were taken with increasing time intervals until an interval of 2 h was reached. The experiment was terminated after 53 h. Analysis of the samples in question was conducted by means of ICP-AES.

Results and Discussion

As is evident from the data, graphically presented in Figure A5.3, there is no conclusive evidence of a descaling effect. The increase in Ca concentration in the test and control loops appears to be at the same rate although the concentrations measured in the test loop were consistently higher than in the control loop.

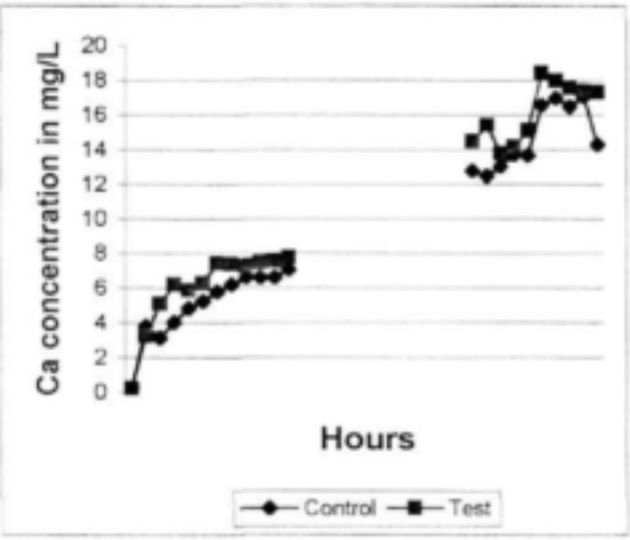


Figure A5.3

The release of calcium from scaled-up coils over a period of 53 hours. Top curve with Scale Watcher on, bottom curve is the control.

Conclusion

A descaling effect due to the presence of the Scale Watcher device was not observed under the experimental conditions described above.

PART B

FREE METAL ION SCALE INHIBITOR BASED ON Zn

Part B covers two aspects related to the development of zinc technology for the reduction of scale. In Chapter B1 the fundamental chemistry of zinc in relation to its effect on the kinetics of the $CaCO_3$ precipitation reaction and $CaCO_3$ crystal morphology is discussed. In Chapter B2 the design and testing of a prototype Zn electrode to demonstrate in principle that dosage control can be achieved electrochemically is described.

B1. Principles and mechanisms of Zn-induced scale reduction

B1.1 Introduction

The principles and mechanisms of the scale inhibition effect of Zn^{2+} ions and to a lesser extent other metal ions, in water containing Ca^{2+} and HCO_3^- ions have been studied in detail during this project. The most important aspects are briefly discussed in this section. More information may be found in the relevant published work (Coetzee et al, 1996, Coetzee et al 1998, Coetzee PP 1996).

B1.2 Effect on nucleation rate and crystal growth rate

The discovery that Zn^{2+} ions decreased the rate of nucleation during $CaCO_3$ crystallisation and promoted the formation of $CaCO_3$ in the aragonite in stead of the more stable calcite form, are key aspects in understanding the scale inhibition effect of zinc. Although it is known (Meyer 1984) that Zn^{2+} and other metal ions can inhibit crystal growth processes the effect of Zn on nucleation rate was not reported before. Another important finding is that non-stoichiometric amounts of Zn at extremely low concentrations, as low as 1 μg.L^{-1}, can produce measureable effects on the nucleation rate. In this report the effect on nucleation rate is expressed in terms of the delay time, Δt (see Part A Section 1.4).

B1.3 The importance of free Zn^{2+} ions

It is important to note that the free Zn^{2+} ion is the active species in the scale inhibition process. In the practical application of Zn scale inhibition, Zn^{2+} ions are introduced into scale forming solutions containing HCO_3^- ions at a concentration of up to 50 000 times more than the initial free $[Zn^{2+}]$. This means that the speciation of the solution will change over time resulting in a decrease in free $[Zn^{2+}]$. 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. The effectiveness of free Zn^{2+} species to produce delays in the precipitation of Ca CO_3 is therefore dependent on the rate at which the deactivation of zinc occurs through complexation with ligands present in the system. To study this equimolar solutions of $NaHCO_3$ containing 50 μg.L^{-1} of Zn^{2+} and 150 mg.L^{-1} 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 Figure B1.1. It is evident that about 40 % of the Zn^{2+} ions is 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 municipal water supplies.

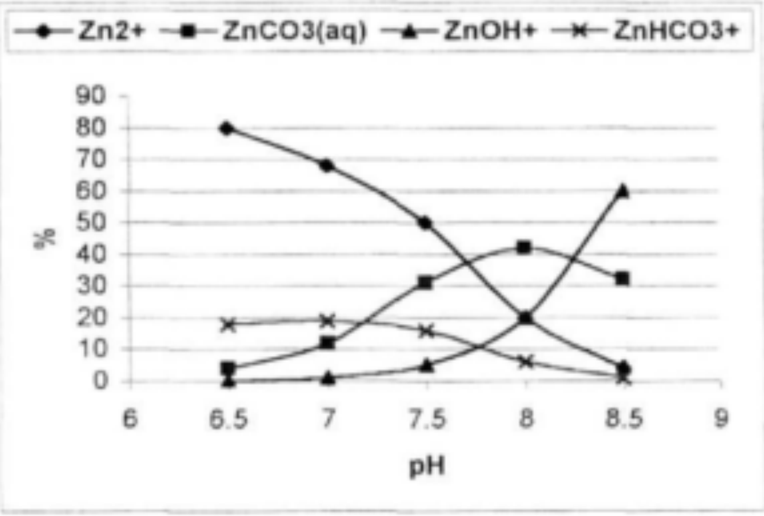


Figure B1.1
Distribution diagram for Zn species in a 150 mg.L^{-1} $Ca(HCO_3)_2$ solution containing 100 µg.L^{-1} Zn.

B1.4 Effect on crystal morphology

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. At Zn/Ca mass ratios larger than 0.5×10^{-3}, 100 % aragonite was produced with no traces of calcite. For smaller ratios down to 0.06×10^{-3}, increasing amounts of calcite were found precipitating with the aragonite. Below 0.06×10^{-3}, calcite was formed predominantly.

B1.5 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.L^{-1} Ca and 100 µg.L^{-1} Zn it was found that up to 400 mg.L^{-1} Cl^- could be tolerated before a decrease in Δt became noticeable. At 1 600 mg.L^{-1} Cl^-, Δt was decreased by 40 %. At a concentration of 1 mg.L^{-1}, organic acid anions such as acetate caused a 70 % reduction in Δt 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.

B1.6 Effect of other metal and anionic species.

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, affect the nucleation rate of $CaCO_3$ to varying degrees ranging from large increases in induction times induced by certain phosphates, to almost no effect at all by metals such as Ni and negative effects by chelating agents such as EDTA. Cu^{2+} gave rise to Δt values about half of that for Zn^{2+} while Mg^{2+} was much less effective, requiring concentrations 1 000 times more than that for Zn to produce comparable effects. Effects on crystal morphology also seemed 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.

The effect of Fe, both dissolved Fe and colloidal iron oxides, was studied in detail because of the 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 $\mu g.L^{-1}$ Fe, it was decided to test a $Ca(HCO_3)_2$ solution with 50, 100 and 1000 $\mu g.L^{-1}$ 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 $Ca(HCO_3)_2$ solution. The effects on nucleation rate and crystal morphology were minimal.

Tests done on the haematite sol produced results which indicated reduced induction times, i.e. increased nucleation rates. Increased nucleation rates make sense because the haematite colloids could act as seed crystals which would then enhance heterogeneous nucleation.

B1.7 Proposed mechanism

The question as to why Zn^{2+} seems to be more efficient than other metal ions to induce decreased nucleation rates and to promote the formation of aragonite rather than calcite is beyond the scope of this report 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^{2+} in carbonate media shown in Figure B1.2 is compared to the distribution for Zn^{2+} shown in Figure B1.1, 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. The results obtained in this study therefore indicate the involvement of Zn^{2+} ions during nucleation whereas results reported by Meyer applied to the crystal growth phase of the crystallisation process.

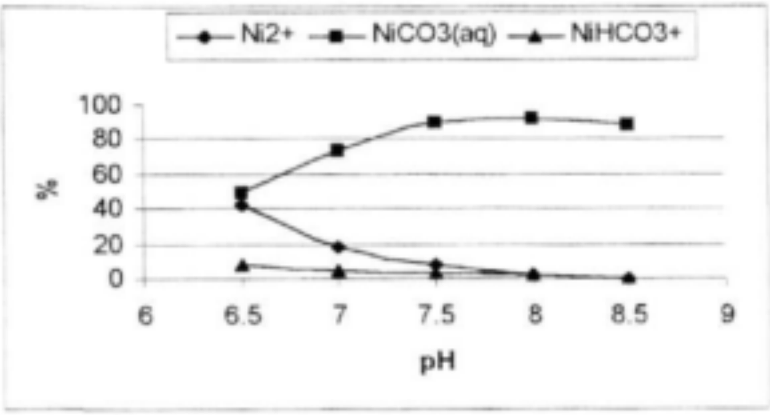


Figure B1.2

Distribution diagram for Ni species in a 150 mg.L^{-1} Ca(HCO$_3$)$_2$ solution containing 100 µg.L^{-1} Ni.

B2. Design and testing of a prototype free metal ion scale inhibitor

B2.1 Design of the Free Metal Ion Scale Inhibitor.

A Cu-Zn electrode system, consisting of a Zn rod (6x100 mm) as anode and Cu as cathode, was used in preliminary experiments to test the feasibility of electrochemical Zn dosing. The current, I that must be supplied to the electrode to electrolytically release Zn at the required rate can readily be calculated from Faraday's law:

$$I = \frac{nFm}{t}$$

A current of ca. 3 A is for example required to maintain a dosage of 1mgZn/s. The duration of the current can be electronically adjusted depending on flow rates.

A diagram of the prototype Cu/Zn electrode system consisting of a hollow Zn rod inserted into a Cu pipe and provided with suitable electrical connections for connecting to an external DC power source, is shown in Figure B2.1.

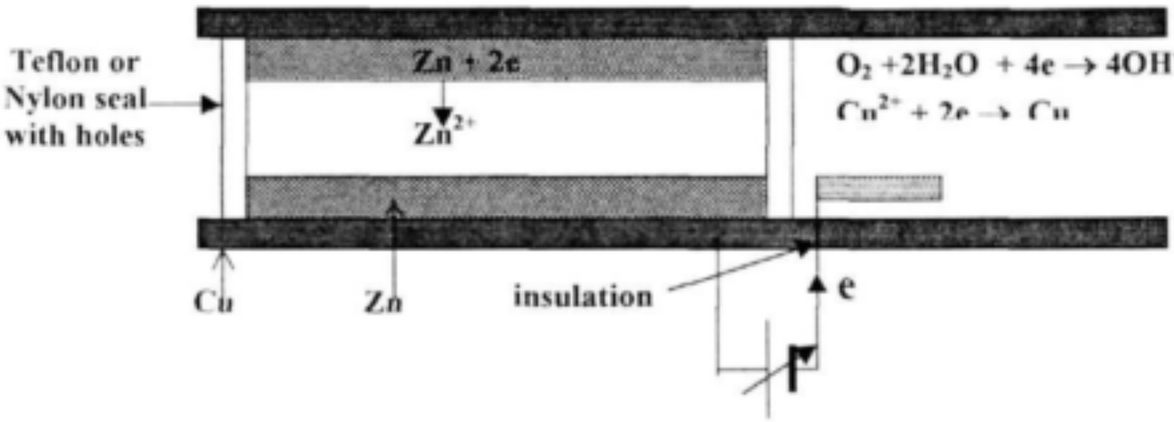


Figure B2.1.
Free Metal Ion Scale Inhibitor

B2.2 Testing of the Zn/Cu electrode system

The performance of the electrode system was evaluated by running the following tests. The aim was to characterise the system and to ascertain its potential usefulness as a scale inhibition system. The most important aspect tested was the factors controlling the amount of zinc released into the system.

The electrode system consisted of Cu and Zn metal in contact. Hence, the electrochemical cell created when conducting water was passed through it caused the spontaneous release of Zn at a low level ($\mu.L^{-1}$) without having to switch on the power. The rate at which Zn is released could of course not be controlled in this mode of operation.

Test solutions were circulated through the test loop for 60 min. Samples were taken every 10 min and analysed for zinc by ICP-AES. The release of Zn is expected to depend on the composition of the water passing through the cell, in particular the presence of Cu^{2+} and

$Ca(HCO_3)_2$. This was investigated by using test solutions consisting of 0.0005 M Cu^{2+} in 0.001 M NaCl and 0.005 M $Ca(HCO_3)_2$ in 0.001 M NaCl.

The results, shown in Figure B2.2, indicate that the presence of Cu^{2+} in the solution caused a significant increase in the rate at which Zn was released. This is explained in terms of the oxidation-reduction reactions given below which clearly show that the overall reaction leading to the dissolution of Zn^{2+} will thermodynamically be more favourable at increased Cu^{2+} concentrations in the water.

$$\begin{array}{lr} Cu^{2+} + 2e = Cu & E^\circ = 0.337\ V \\ \underline{Zn = Zn^{2+}} & \underline{E^\circ = -0.763\ V} \\ Cu^{2+} + Zn = Cu + Zn^{2+} & \end{array}$$

The addition of $Ca(HCO_3)_2$ caused a reduction in the release of zinc. This was due to the formation of a layer $CaCO_3$ on the zinc electrode surface.

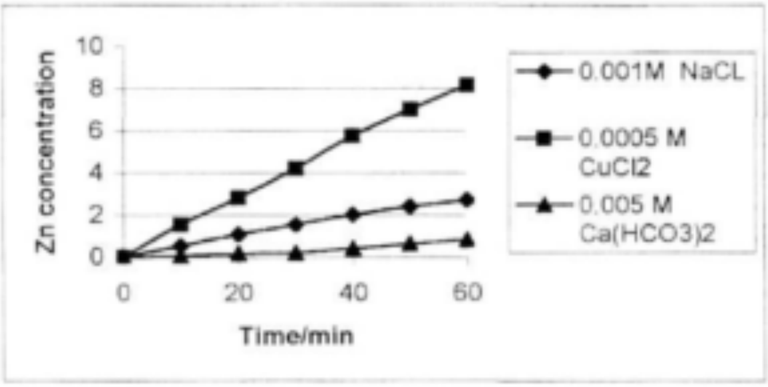


Figure B2.2
The release of Zn in μg.L^{-1} over time in a Cu/Zn electrode system for different test solutions.

Controlled release of Zn was achieved by regulating the current through the cell. The release of Zn as a function of current through the Free Metal Ion Scale Inhibitor is shown in Figure B2.3.

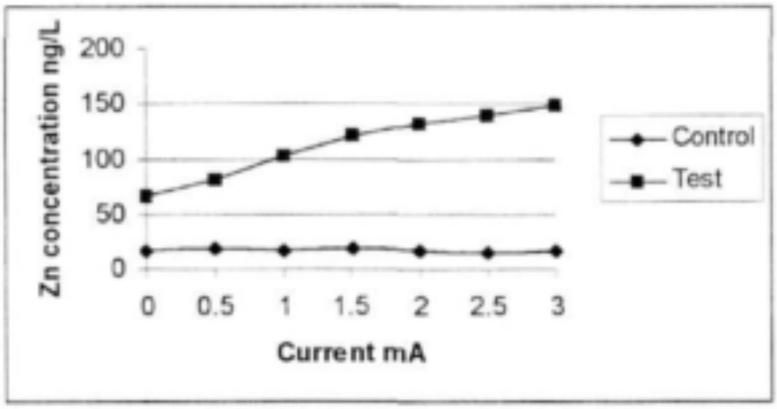


Figure B2.3
The release of Zn in μg.L^{-1} over time in the Free Metal Ion Scale Inhibitor as a function of cell current in 0.001 M NaCl solution.

B2.3 Possible application: Reduction in scale formation

The potential use of these phenomena in scale reduction applications was investigated in trial experiments by pumping (14 $L.h^{-1}$) supersaturated $Ca(HCO_3)_2$ solutions at 300 $mgCa.L^{-1}$ and the zinc concentration controlled at 100 $\mu g.L^{-1}$ through glass coils (1m × 6 mm) immersed in a water bath at 70 °C. The amount of scale formed was determined by pumping 6 % nitric acetic acid through the coils to dissolve the scale and then determining the Ca concentration by ICP-AES. Scale reduction of 77±6 % was achieved.

B2.4 Conclusion

Trace amounts of Zn can substantially inhibit the nucleation rate of $CaCO_3$ at Zn/Ca concentration ratios greater than 0.06×10^{-3}. The preferential formation of aragonite rather than calcite has been demonstrated to occur for Zn/Ca concentration ratios above the limiting value. The needle-like crystal morphology of aragonite crystals is believed to reduce the adhesion of scale onto surfaces. It was demonstrated that the presence of zinc as free metal ions reduced the formation of $CaCO_3$ scale in simple laboratory applications. It was shown that zinc can be deactivated by complexation with certain inorganic and organic species such as Cl^- ions and organic acid anions that could be present in water.

PART C

TESTING FACILITY FOR PHYSICAL WATER TREATMENT DEVICES

In Part C three testing facilities are presented which were constructed and tested. The testing facilities consisted of: a tube testing facility (Chapter C1), a heat exchanger testing facility (Chapter C2), and a domestic hot-water storage testing facility (Chapter C3).

C1. TUBE TESTING FACILITY

C1.1 Introduction

Pipes and tubes are very important components in industry as they are used as carriers of water from one component to another or from one system to another. For this reason a testing facility was developed that would be able to measure the possible influences of physical water treatment devices on scale formation.

C1.2 Free flow tube system

The experimental set-up was designed to measure change in flow rate through three tubes when scale formation occurs. The experimental set-up is shown schematically in Figure C1.1.

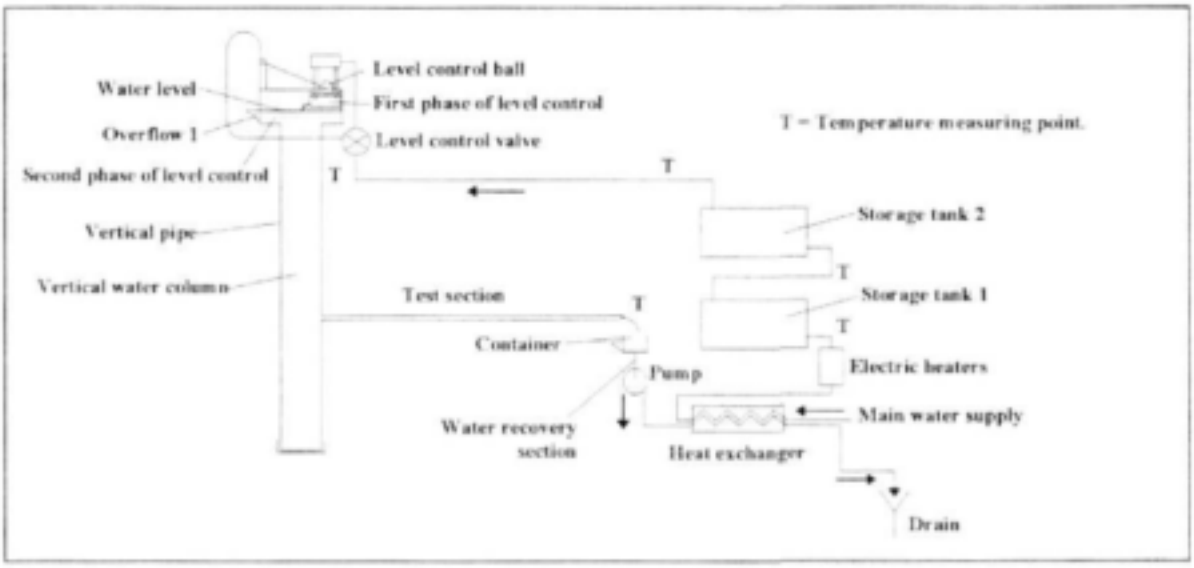


Figure C1.1
Schematic representation of experimental set-up.

To indicate the test section more clearly a top view of the part just before the fouling tubes is shown in Figure C1.2.

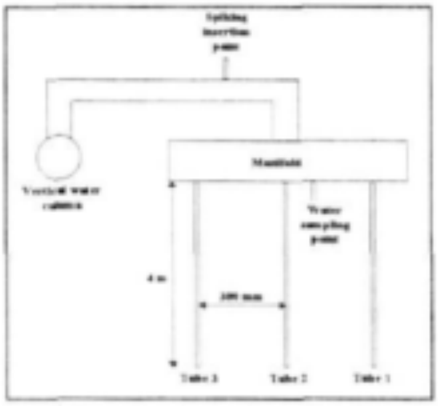


Figure C1.2
Top view of test section.

The experimental set-up in Figure C1.1 receives water from the main water supply (Rand Water) with temperatures of between 16°C (winter) and 20°C (summer). It is first heated to approximately 38°C with a 21 kW counterflow tube-in-tube heat exchanger made from copper tube. The water used for the heating is hot water, which has passed through the system and would have been drained directly. The system is therefore a once through system and the water is not recirculated. This heat exchanger gives an energy saving of 54%. After the heat exchanger the water is further heated with five 4 kW electric heaters. These electric heaters have no temperature controllers connected onto them and the heaters stay on permanently.

The water is then finally heated in two 200 *l* storage tanks (geysers) connected in series, each having its own 4 kW element and temperature controller. The purpose of the first geyser is to increase the temperature of the water close to the desired value of 53.5°C. This temperature is chosen as scale forms better at higher temperatures and the temperature cannot be increased above 60°C. The PVC used for the vertical pipe and manifold cannot withstand such high temperatures. The second geyser is used to do only a small amount of heating and can thus control the water temperature more accurately. With this set-up it is possible to control the water temperature variation to within ± 0.5°C. The first storage tank is equipped with a normal on/off type controller with a J-type thermocouple. The second storage tank is equipped with a digital temperature PID controller. The probe used to determine the water temperature is a PT 100 class A probe. Testing was done to determine the best location for this probe to obtain the best possible temperature control. It was found that the best temperature control was obtained when the probe was placed in the water close to the electrical heating element.

After the storage tanks the water passes through a level control section which consists of a level control valve, level control indicator and level control ball. The ball is used to indicate if water must be added to the set-up or if the flow must be stopped to keep the water level constant. The level control indicator and ball are connected to the level control valve by means of a tube. The ball is situated in the first phase level control container. The first and second phase level control is used to control the height of the water to a constant value. Although the height of the water in the first phase container may vary by up to 60 mm it was found that the height of the water in the second phase stays constant to within ± 1 mm.

The first phase container has three holes which are used to supply water to the second phase container. These holes are large enough to support the flow in the fouling tubes when no fouling has occurred. The second phase container has an overflow through which the excess water flows. A sampling point is inserted at the overflow which is used to get water samples of the water entering the vertical water column. The water flow rate increases through the overflow, when fouling takes place in the fouling tubes. This method of level control was selected after different methods were evaluated to keep the water level constant.

The water is added to the first phase container from the top and the device which is used to add the water is not fixed to the set-up. This is done because water hammer is caused by the level control valve which opens and closes. If the water supply device was fixed to the set-up this vibration would be transferred to the set-up and the fouling tubes which might influence the experimental results.

The vertical water column is used to ensure a constant pressure head. The height of the water in the vertical column to the centre line of the fouling tubes is 4.16 m. This height ensures a velocity of approximately 2 m/s in the tubes of the test section.

The manifold is used to divide the flow into three. This water flows through the three fouling tubes used as test sections. A spiking insertion point is added to the set-up as indicated in Figure C1.2. This is done so that chemicals can be added to the water if necessary. The second sampling point is inserted just before the fouling tubes. The fouling tubes used in the set-up are soft drawn copper tubes having an inside diameter of 6.52 mm at 20°C and a length of 4 m. This length tube is used because the Physical Water Treatment devices should be placed on a tube to allow approximately 3.048 m of straight tube after the Physical Water Treatment device installation for optimum performance. The tubes are placed inside steel pipes for support.

When the water has passed through the test section the water is gathered in an energy recovery section where its energy is transferred to the incoming water supply by pumping it through a tube-in-tube heat exchanger. After the heat exchanger the water is directed to a drain. The flow rate of the water in each of the fouling tubes is also measured after the test section.

The flow rate through the test section or fouling tubes is determined by measuring the time it takes to fill a known volume. More details in this regard are given in the next section. The container which is bveing filled, is designed in such a way that the time necessary to fill the container can be measured accurately. This method was used after different concepts were considered and evaluated. The container which was used is made from PVC, has a volume of ± 215 *l*, is 1.82 m high and is shown in Figure C1.3.

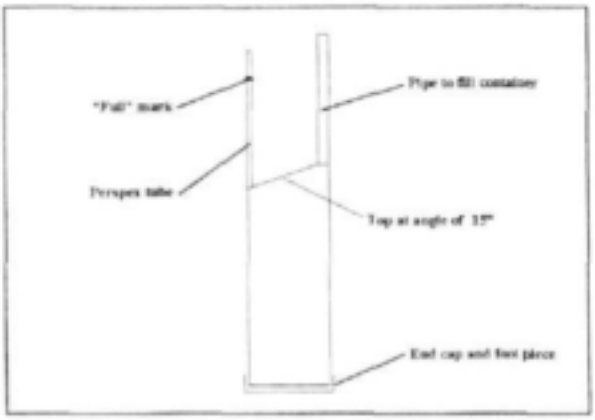


Figure C1.3.
Schematic representation of container used to determine flow rate.

While the container is being filled the water level in the bottom part of the container increases very slowly. When the water reaches the perspex tube the water level increases rapidly so that it is easy to see when the water level passes the "full" mark. The top of the container is placed at an angle so as to prevent any air being trapped in the container while the container is being filled, and in this way change the volume of the container. The volume is also kept constant by following a specific experimental procedure by which it is not necessary to completely dry the inside of the container before each experiment. For the analyses done it is important to know the volume of the container at different temperatures and for this reason, calibration of the container was done. The method relies on the fact that the amount of water remaining inside the container is the same for each experiment if the time taken to empty the container is kept constant.

If the volume of the container stays constant it is only necessary to compare the time necessary to fill the container for the different experiments to be able to say if the flow rate is changing. The container is made with a drain plug at the bottom which is used to drain the water after the experiment has been done. The container is placed on a metal foot piece with which it is possible to make adjustments so that the container stands vertically for every experiment.

A parameter which is very important and must be controlled is the temperature of the water in the fouling tubes (within ± 0.5°C) and for this reason the whole set-up is covered with insulation. The insulation is between 100 and 130 mm thick which ensures that the water temperature stays constant to within ± 0.09°C if the difference in temperature between the surroundings and the water is 15°C. Temperatures are also measured at various points with K type thermocouples to monitor the temperature changes throughout the set-up. These thermocouples were calibrated to ensure accurate temperature measurements. The points where the temperature is measured are indicated in Figure C1.1.

C1.3 Design of the experimental set-up

The primary aim with the experimental set-up was to detect any volumetric flow variations. A decrease in the volumetric flow would indicate that scale was forming. The diameter of the tube in which fouling is going to occur will decrease and this change will increase the flow resistance and thus the flow rate through the tube, which can be measured accurately. This change in velocity will then in turn influence the Reynolds number.

The design of the experimental set-up was done to ensure that changes in flow rate of less than 1% could be measured. The height of the water in the vertical pipe was taken into consideration as well as temperature changes and changes in friction. Detailed sensitivity studies were done to ensure that changes in flow rate of 1% could be measured. The design and sensitivity study is reported elsewhere (Da Veiga, 1999). The result was that a 1% change represents a 22 m*l*/min change in flow rate so that the set-up is sensitive enough to pick up such small volumetric flow rate variations.

C1.4 Experimental procedure

The experimental set-up described in the previous chapter was used in different phases so that the effectiveness of the permanent magnetic (Eneflow Fluid Dynamic Power Cells) PWT devices could be determined by monitoring the volumetric flow rate through the tubes. In each of these phases a specific experimental measuring procedure (Da Veiga, 1999) was used to determine the volumetric flow rate in the fouling tubes. To determine if the volumetric flow rate was changing, it was only necessary to compare the time necessary to fill the flow rate measurement container, because the volume of the container was kept constant for all the tubes. A change in the time necessary to fill the container indicated that the amount of scale formed was changing. The amount of scale formed could also be influenced by the chemical composition of the water and therefore the water was analysed. It was also possible that the magnetic field of the magnetic PWT device on the one tube could influence the scale formation in the other tube. Therefore magnetic field strength experiments were also done.

The experiments were done over a period of two years (721 days). The experimental results were divided into sixteen phases and are summarised in Table C1.1. In each phase the time necessary to fill the container for each of the three tubes were measured.

As explained, the time necessary to fill the container was used as an indication of the scale formed. In all the graphs/results the time necessary to fill the container is indicated on the y-axis and is shown as the minutes above 47 minutes (47:38.4 is indicated as 38.4 s) and the day number on the x-axis.

Table C1.1 Description of different phases of experimental period.

Phase	Period [days]	Description
1	72	Calibration and cleaning
2	6	Spiking with calcium solution
3	65	No PWT device
4	70	PWT device attached onto tube 3
5	222	No PWT device
6	14	PWT device attached onto tube 3
7	22	No PWT device
8	6	Spiking with calcium solution
9	58	No PWT device
10	6	Spiking with calcium solution and PWT device attached onto tube 3
11	29	PWT device attached onto tube 3
12	51	No PWT device
13	6	Spiking with calcium solution
14	76	No PWT device
15	6	Spiking with calcium solution
16	12	No PWT device

C1.5 Results

For each phase given in Table C1.1, detailed graphs, corresponding chemical analysis of the water, and analyses of results were generated. As these results (Da Veiga, 1999 and Da Veiga, 2002) are so elaborate, just the summarised results are given here.

The experimental results for all the phases combined are indicated in Figure C1.4. To indicate the results for the last stages more clearly, the results for phases 7 to 16 are indicated in Figure C1.5.

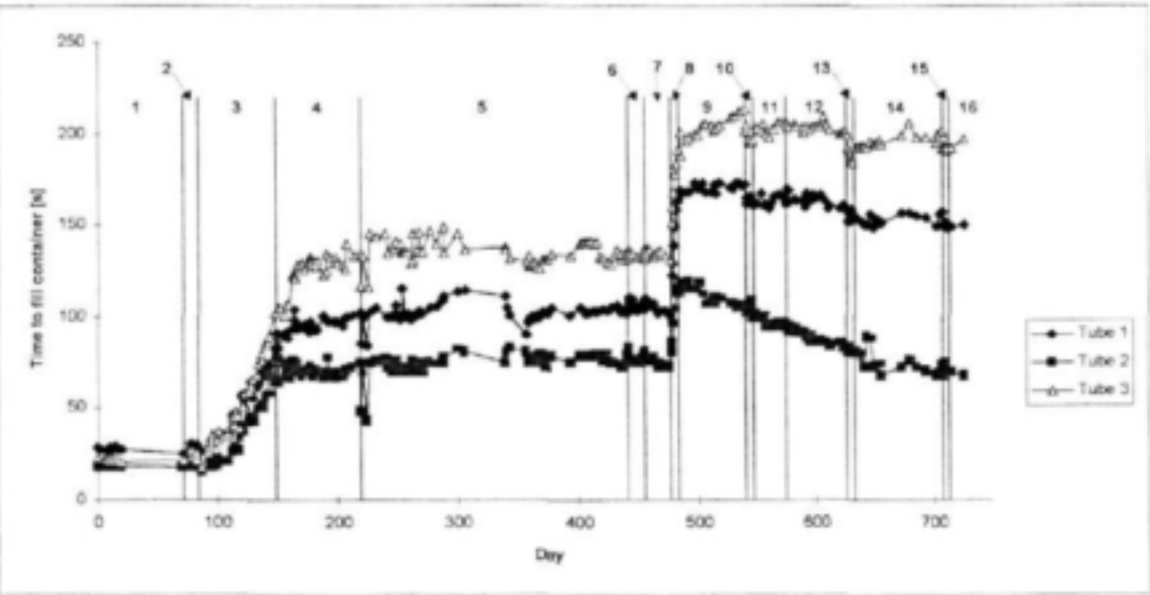


Figure C1.4.
Combined experimental results for the different phases.

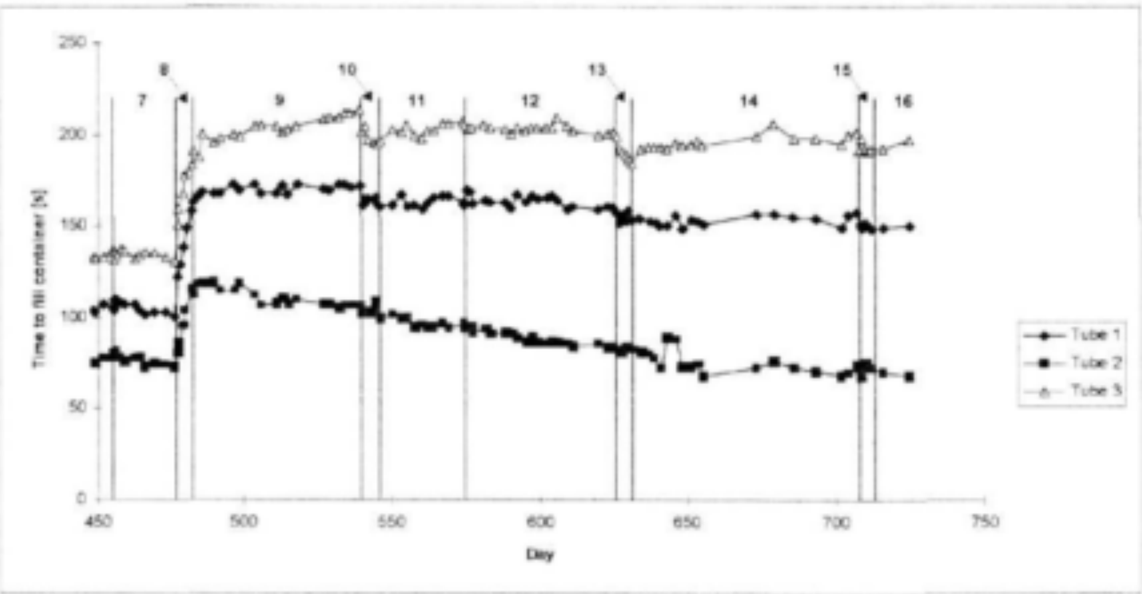


Figure C1.5.
Combined experimental results for phases 7 to 16.

As the experimental results obtained could be influenced by the chemical composition of the water, graphs for the variation of the chemical composition in the different phases was also generated. The average of each of the chemical properties for each phase in these graphs was used. The graph for the average calcium concentration is given in Figure C1.6, while graphs for magnesium, sodium, potassium, conductivity, pH, hardness, turbidity, silica, zinc, and iron are given in Da Veiga (2002).

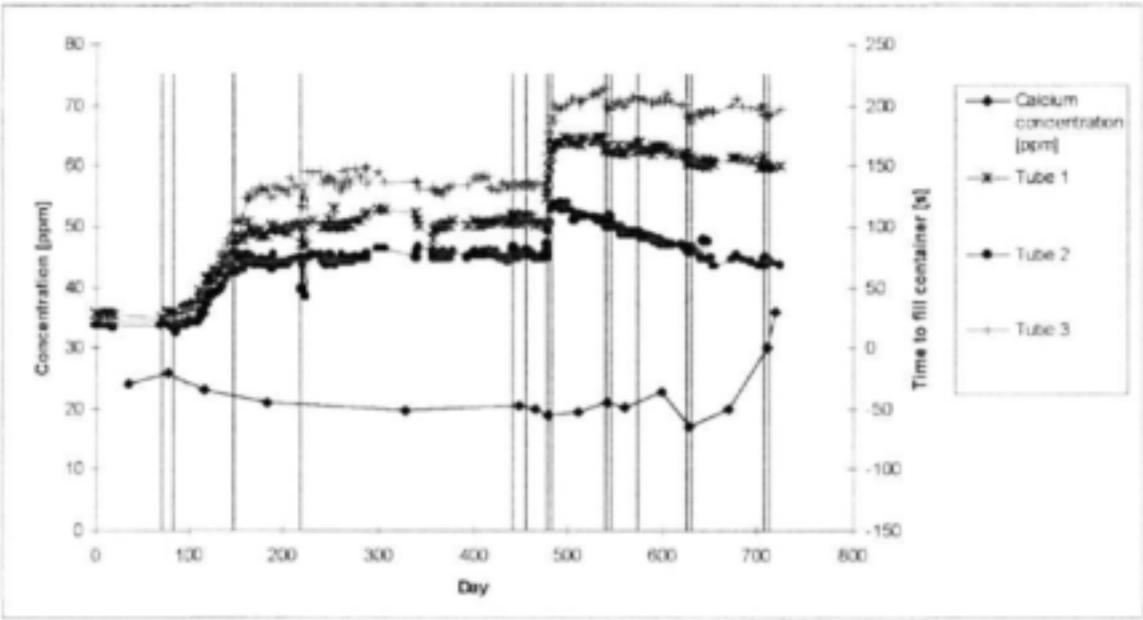


Figure C1.6.
Variation of the average calcium concentration during the experiments.

C1.6 Discussion of results

It follows from Figures C1.4 and C1.5 that there was no scale formation for phases 1 and 2 and that in phase 3 the scale formation increased. Almost the same amount of scale formed in phases 4 and 5. There was thus a decrease in scale formation from phase 3 to 4 when the PWT device was attached onto tube 3, but the reduction was not only in tube 3 but in all the tubes. The increase in scale formation which was hoped for to indicate that the magnets had the effect of reducing the scale formation in all three tubes was not present from phase 4 to 5. There was, however, a sudden decrease in time necessary to fill the container in all three tubes when the magnets were removed from tube 3 in phase 5. This sudden decrease in time necessary to fill the container was, however, not present in phase 7.

There was no change in scale formation rate between phases 5 and 6 when the magnets were attached onto tube 3 which indicated that the PWT device had no influence on the scale formation rate. It could be argued that the magnets would only have an influence on the scale formation rate when scale was forming and for this reason the solution was spiked in phase 8 to increase the scale formation rate. A contradiction exists between the results in phase 2, where spiking did not cause scale formation to increase, and phase 8 where spiking definitely caused an increase in scale formation. After the spiking in phase 8 the scale formation rate decreased in phase 9 in all three tubes which differed from the results in phase 3 where the scale formation rate increased after the spiking in phase 2. At this point it would thus be possible to test the effectiveness of the PWT device by spiking the solution, which should cause the scale formation rate to increase, and adding the magnets simultaneously. This was done in phase 10. The effect was that there was a decrease in scale formation rate in all three tubes compared to phase 8. This once again indicated that the PWT device had an influence on the scale formation rate and the influence was not only on the tube on which it was attached but on all three tubes. This result could not be verified since the results in phases 13 and 15 gave similar scale formation rates as in phase 10 but the magnets were not attached onto tube 3.

The results obtained in the three tubes could be influenced by the magnetic field caused by the magnets attached onto tube 3. Therefore the vertical and horizontal magnetic fields in and around the magnets were measured (Da Veiga, 1999) and monitored. According to the results obtained the field strength around the magnets and the changes which took place in the field strength over time were very small in comparison to the field strength between the magnets. This emphasises the observation that the results obtained in this phase were not caused by the magnets.

The other possibility is that the chemical composition of the water changed in such a way as to cause the results obtained. According to the values for the average calcium concentration the following were concluded: there is not a definite decrease or increase in calcium concentration from the start of the experiments to the end. The average calcium concentration decreased from phase 3 to 4 and that is the reason for the decrease in scale formation rate between phase 3 and 4. This is, however, contradicted by the fact that the scale formation rate did not increase from phase 15 to 16 where the average calcium concentration increased. If the average concentration for the incoming water for phase 2 and phase 8 is compared, it can be concluded that with a higher concentration spiking does not cause an increase in scale formation. This is, however, contradicted by the results in phases 8 and 13 where the concentration is lower in phase 13 than in phase 8. From these explanations it can thus be concluded that the calcium concentration did not influence the experimental results.

The variation in average pH as well as potassium concentration between the phases is very small so that it could also not affect the results. There is no correlation between the changes in average sodium concentration, zinc concentration, total silica concentration, conductivity, hardness, turbidity and the results obtained. Therefore these variations did not influence the experimental results.

There is, however, a correlation between the magnesium concentration and the tendency for scale formation when spiking is done as it was found that when the magnesium concentration is high enough (phase 8), spiking causes scale formation and when the concentration is low (phases 2, 10, 13 and 15), spiking does not cause scale formation. This contradicts the findings of Meyer (1984) in which it was found that adding magnesium causes a reduction in calcite scale.

It was also found that there is a correlation between the amount of iron and an increase in scale formation when spiking is done. From the results it follows that when the iron concentration is high, spiking does not cause scale formation (phases 2, 10, 13 and 15) and when the iron concentration is low, spiking causes scale formation (phase 8). This corresponds with the findings of Herzog *et al.* (1989) in which it is stated that iron inhibits the formation of $CaCO_3$.

C1.7 Summary

From the results and explanations given it follows that in certain phases it seemed as if the magnets had an effect, in other phases it seemed that the magnets had no effect and there were phases which contradicted one another. These different phases can be grouped as follows:

Phases in which it seemed as if the magnets had an effect :

a. As soon as the magnets were attached onto tube 3 in phase 4, the scale formation decreased in all three tubes.
b. As soon as the magnets were removed from tube 3 in phase 5 there was a sudden decrease in scale formation in all three tubes.
c. When the solution was spiked and the magnets were attached onto tube 3 in phase 10, there was a decrease in scale formation compared to phase 8.

Phases in which it seemed as if the magnets had no effect :

a. The sudden decrease in scale formation in phase 5 could not be reproduced in phase 7.
b. The scale formation rate did not return to the formation rate as in phase 3 after the magnets were removed in phase 5.
c. The results obtained in phase 10 with the magnets were similar to the results in phases 13 and 15 with no magnets which indicated that the magnets had no effect.

Phases which contradicted one another

a. Spiking in phases 2, 10, 13 and 15 did not cause the scale formation rate to increase, while the spiking in phase 8 caused an increase in scale formation rate.
b. After the spiking in phase 2 the scale formation rate increased in phase 3. This increase was not present in phases 9, 11, 14 and 16.

From the above explanation it follows that many contradictions exist in the experiments which were done. From the analyses done it follows that the chemical composition of the water could cause these contradictions. Magnesium and iron were identified as the only two substances which could explain the results obtained. There could, however, be other chemicals or properties which could cause these variations. It is not possible to know which chemicals or properties could cause this, because the variations of these chemicals or properties were not monitored. It is thus not possible to determine the efficiency of PWT devices on this tube testing facility due to the many contradictions and uncertainties.

C1.8 Conclusion

An experimental set-up (tube testing facility) was designed and built with which very small amounts of scale could be measured by monitoring the time necessary to fill a container.

Many contradictions exist in the results obtained in the different phases. The chemical analyses of the water showed that the results obtained in the different phases could be caused by the chemical composition of the water. Magnesium and iron concentrations were the only two properties which could explain the experimental results. Other properties could also influence the results but were not monitored. Due to these contradictions it is not possible to determine the efficiency of the magnets as PWT devices. The duration of the experiments (720 days) could have caused the contradictions, because many variables changed during the experimental period. The duration makes it difficult to repeat the experiments to get reproducible results.

It can thus be concluded that the flow rate measuring technique used gives very accurate results. However, it was found that the testing facility is not a practical solution as a testing facility for the following reasons: it takes very long before usable results are generated and it has high running costs.

C2. HEAT EXCHANGER TESTING FACILITY

In this chapter the second testing facility, which was designed, constructed and tested is discussed.

C2.1 Introduction

Heat exchangers are very important components in industry as they are the active components where heat is transferred and where most scaling occurs. For this reason a heat exchanger testing facility was developed.

C2.2 Experimental set-up

The heat exchanger testing facility developed is shown schematically in Figure C2.1. It consists mainly of two closed loop systems, a cold-water system and a hot-water system.

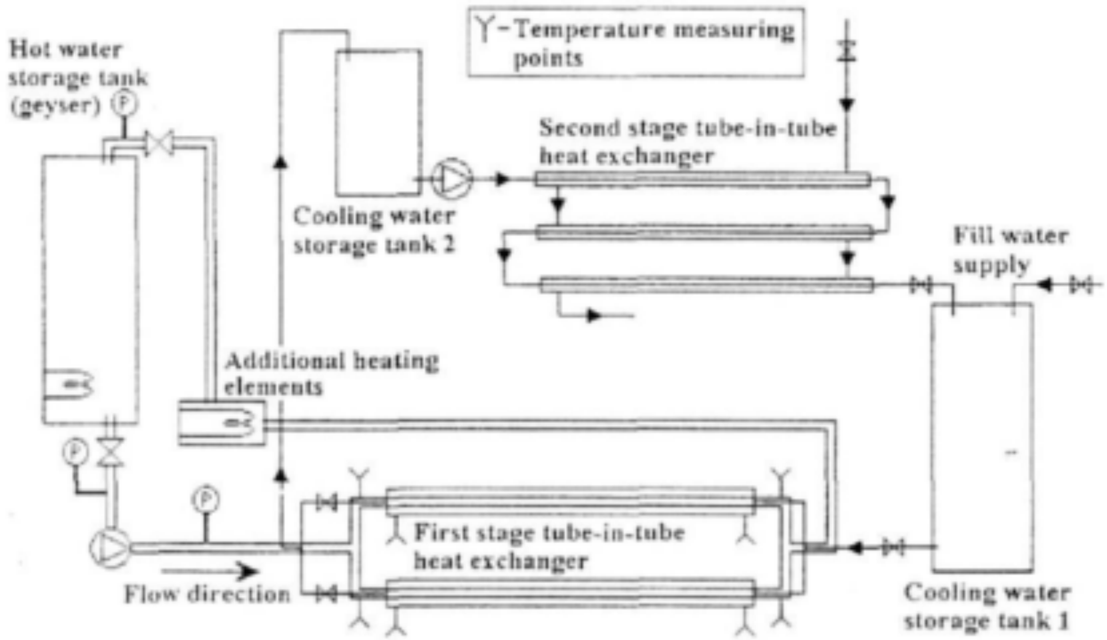


Figure C2.1
Schematic representation of experimental set-up

The hot-water system consists of a storage tank (geyser), a pump, a heat exchanger and three additional heating elements. The make-up water is provided by the municipal supply (Rand Water) at about 18°C, and is then heated in the storage tank (geyser) to approximately 62°C to 64°C. The storage tank uses a 4 kW heating element. It is then pumped through the annulus of a counter flow tube-in-tube heat exchanger, made out of copper tubing, where the temperature drops to approximately 57°C to 60°C. Thereafter it passes through three 4 kW heating elements after which it enters the storage tank again.

The cold-water loop consists mainly of a storage tank, a solenoid valve, primary and secondary heat exchangers and a supply pump. After the test solution has been mixed and prepared, it is pumped into the storage tank (±285 *l*). The solution then flows freely through the primary counter-flow tube-in-tube heat exchanger to storage tank 2. The solution enters the heat exchanger at about 22°C to 24°C and leaves the heat exchanger at about 34°C to 37°C. The solution is then pumped through a secondary counter flow tube-in-tube heat exchanger to reduce the temperature further to the inlet temperature of the primary heat exchanger. The cold water system is a free flow system that makes up only of gravity and head height of the solution in the storage tank.

The heat exchangers used in this set-up are two identical counter flow tube-in-tube heat exchangers with the hot water flowing through the annulus. The one heat exchanger is used to attach the PWT device to while the other heat exchanger serves as a reference. Eight temperature measurements were made on an hourly basis. The points of measurement are shown in Figure C2.2.

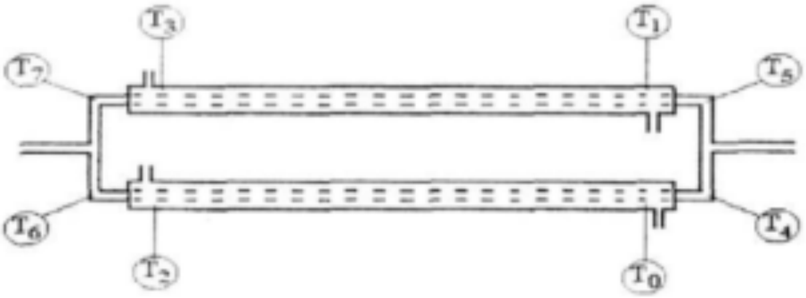


Figure C2.2
Schematic representation of the counter flow tube-in-tube heat exchanger with temperature (T) measuring points.

The inner tube of the two heat exchangers in Figure C2.2 are made of copper tubing with an inside diameter of 14 mm and outside diameter of 15.5 mm, while the outer tube is made of see-through PVC piping, to be able to view the scale as it forms. The inner diameter of the outer tube is 22 mm.

The PWT device used in the experiments was an *Eneflow Fluid Dynamic Power Cell*, manufactured and distributed by *Enecon Corporation*.

As the lengths and diameters of the two heat exchangers were exactly the same the water flow rates were the same and the heat exchangers would also receive the same quality of water.

C2.3 Experimental procedure

The heat exchangers were made operational and after they had stabilised, the temperatures as indicated in Figure C2.2 were measured as function of time (usually hourly). From the water flow rate and temperature differences the heat transfer (Q) in each heat exchanger was calculated. From the temperature measurements the logarithmic mean temperature differences (ΔT_{LMTD}) were calculated for each heat exchanger. As the heat transfer areas (A) are known the overall heat transfer coefficients (U) were calculated as $U = Q/(A.\Delta T_{LMTD})$. As scaling occurs the resistance for heat transfer increases from scale deposits and the overall heat transfer coefficient decreases.

The overall heat transfer coefficient (U) is therefore an indication of scale formation and the lower this value the more scale has formed.

To accelerate scale formation the test solution was spiked with equimolar solutions of calcium nitrate and sodium carbonate mixed with tap water such that the hardness of the test solution was equivalent to 1 200 ppm calcium carbonate.

Experiments were run for at least 16 hours, after which the system was cleaned before the next experiment was started. The system was cleaned by draining the test solution and then filling the storage tank with tap water. Nitric acid, with a concentration of 55%, was then added to the water and circulated through the system until it was properly cleaned.

Experiments were conducted over a period of six months from January to June 2000 and for another six months period from February to July 2001.

C2.4 Results

In Figure C2.3 typical results of the overall heat transfer coefficient are given during scale formation in the two heat exchangers, which are operated parallel to each other. It shows that the overall heat transfer coefficient decreases as function of time as scale formation occurs. Except for the fact that the initial heat transfer coefficients differ with approximately 9% the tendencies of the scale formation are approximately the same.

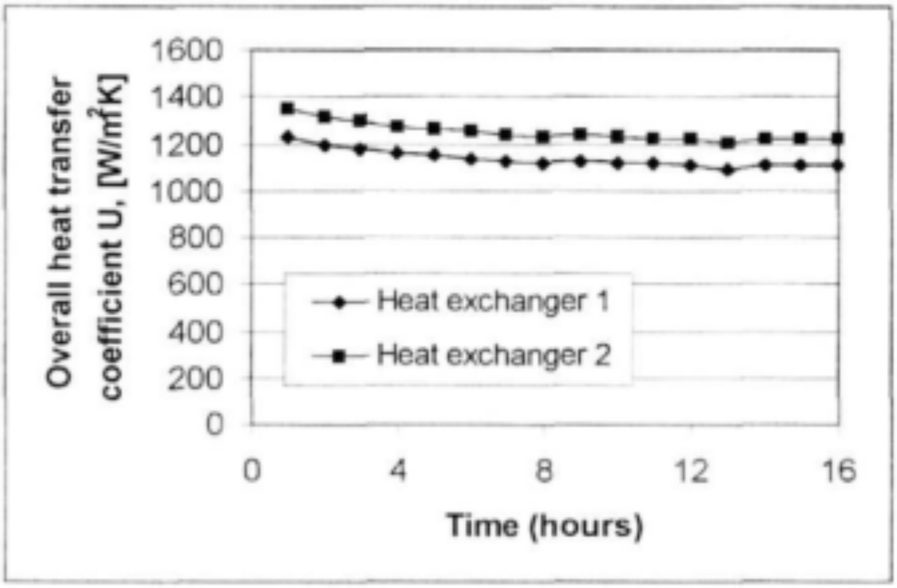


Figure C2.3
Overall heat transfer coefficient as function of time without any PWT devices.

Several experiments were conducted at random stages without any PWT devices to determine the repeatability of the experimental set-up. Although strange results were sometimes found the behaviour of the scale formation in the two heat exchangers were very similar. In Figure C2.4 an example of such an unexplained behaviour is shown, where scale formation was accelerated for an unknown reason after eight and nine hours of testing.

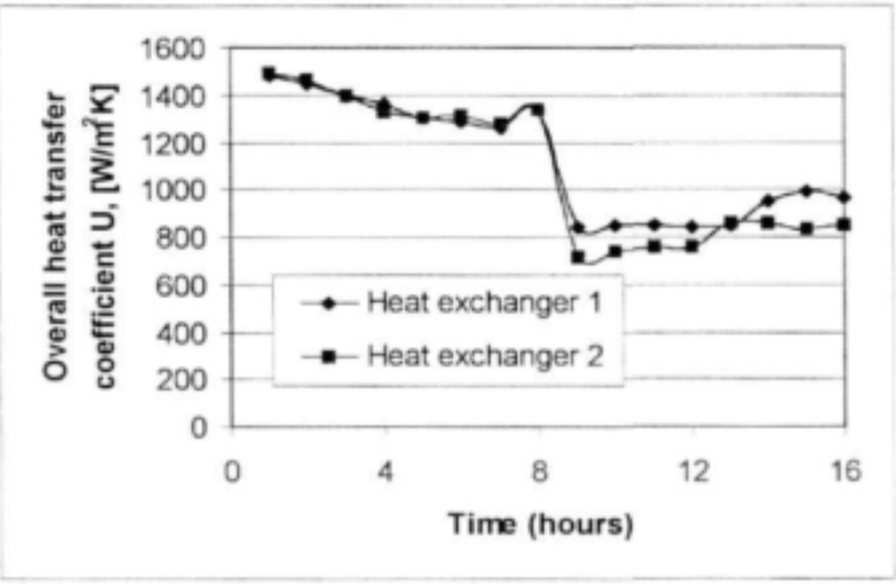


Figure C2.4
Overall heat transfer coefficient as function of time without any PWT devices with a sudden build-up of scale between eight and nine hours of testing.

In Figure C2.5 the overall heat transfer coefficient is given with a PWT device on heat exchanger 1. Many such results were generated (and over much longer periods of time than 16 hours) by Basson (2000) showing no effects on the overall heat transfer coefficients. During these experiments the PWT was randomly rotated between the two heat exchangers and in approximately 30% of the experiments it was not used at all.

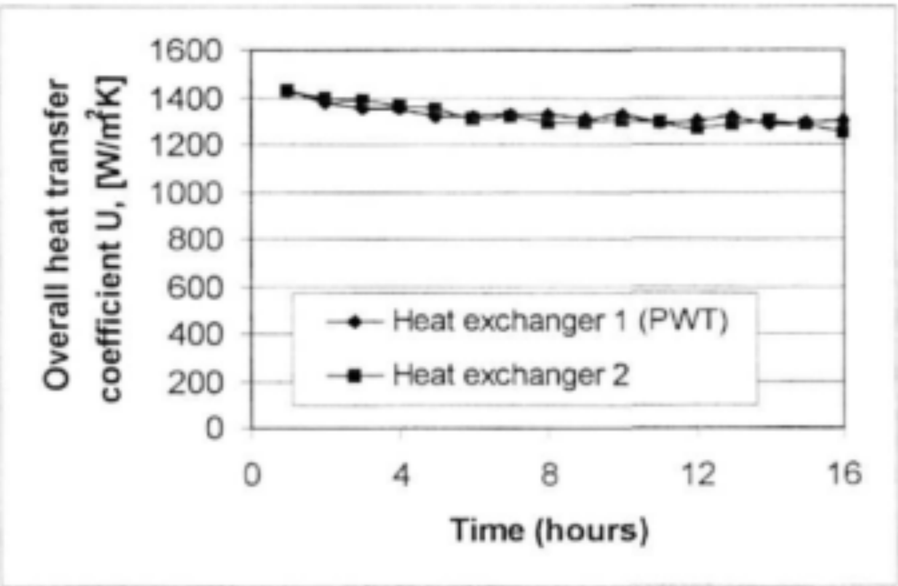


Figure C2.5
The overall heat transfer coefficients of the two heat exchangers with a PWT device connected to the first heat exchanger

In about 25% of the experiments, however, experimental results were generated showing that the heat exchanger with the PWT device had a slower build-up of scale as is shown in Figure C2.6. After 16 hours heat exchanger 2 had approximately 13% less scale than the other heat exchanger.

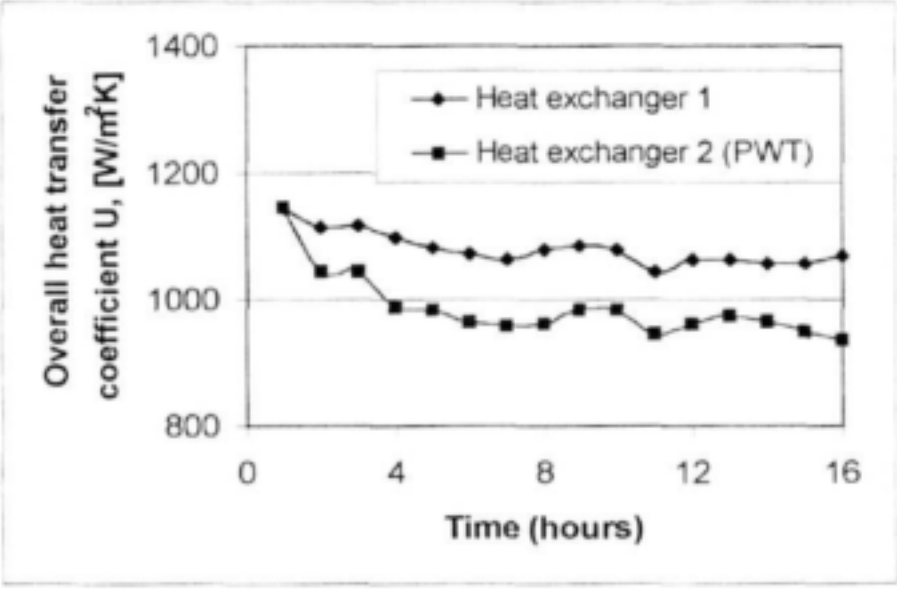


Figure C2.6
The overall heat transfer coefficients of the two heat exchangers with a PWT device connected to heat exchanger 2

C2.5 PWT devices

Four different types of PWT devices were also tested and no definite conclusions could be made that PWT devices reduce scale formation.

C2.6 Conclusion

Although a large number of experiments had been done over a period of two years in a heat exchanger testing facility, no repeatable evidence was found that PWT devices reduce scale formation.

C3. HOT-WATER STORAGE TANK TESTING FACILITY

In this chapter the third testing facility, which was designed, constructed and evaluated is discussed.

C3.1 Introduction

Domestic hot-water storage tanks, reservoirs and boilers are used daily in industry and it is well known that scale formation occurs in them. For this reason a hot-water storage tank (geyser) testing facility was developed and evaluated.

C3.2 Experimental set-up

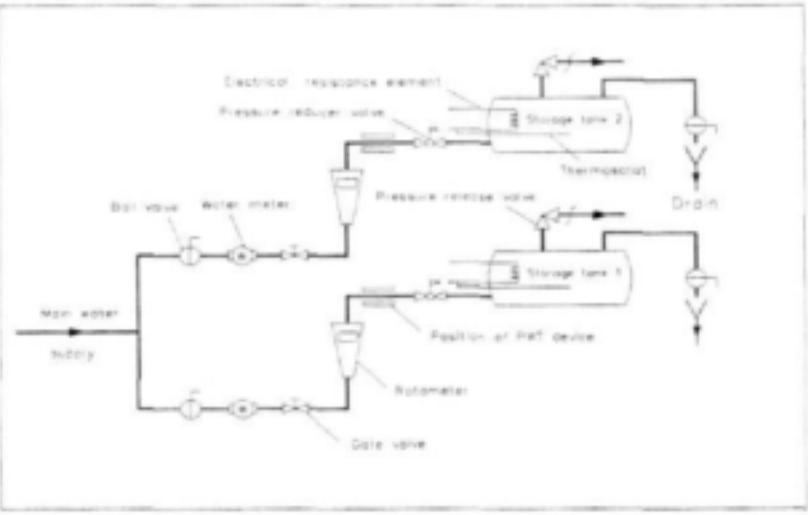


Figure C3.1
Schematic representation of the experimental set-up.

The experimental set-up is shown schematically in Figure C3.1. It consisted of two domestic, electrically heated, horizontal hot-water storage tanks, connected in parallel. Their measured capacities were 197 litres and 191 litres respectively for storage tanks one and two. The inside of the storage tanks was manufactured from mild steel coated with glass enamel. The tanks were insulated with 50 mm polyurethane and their standing losses were 2.6 kWh per day. The thermostat setting on both tanks that controlled the electrical current to the resistance elements was adjusted and calibrated to keep the water temperature constant at 75°C with an average error of ± 2°C. They were each fitted with electrical resistance elements with measured heating capacities of 2960 W and 2850 W each. The resistance elements were manufactured from copper plated with nickel. The average surface temperatures on the electrical resistance elements varied between 92°C and 97°C.

Both tanks received water from the same feed-water line connected to the municipal main water supply (Rand Water) of Johannesburg. Upstream of each tank a water meter and a flowmeter were installed. The water meter was of the positive displacement type that could measure the volume of water used with an error of ±2%. The flowmeter was a rotameter that could measure the flow rate with an error of ±4% at full scale. When the water was drained, the water temperature was measured in the water stream with a K-type thermocouple. The thermocouple was calibrated to an accuracy of ±0.1°C. All the tubes to and from the storage tanks were 22 mm (ID) copper tubes, which were soft soldered in position. The wall thickness of the tubes was 0.5 mm.

Upstream of each storage tank the distance to the position (when installed with cable ties) of the physical water treatment device (Figure C3.2) was 2 m. When installed, the length, width and height of the device when clamped into position were 128 mm, 66 mm, and 32 mm respectively.

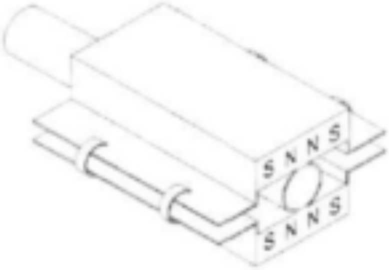


Figure C3.2
Schematic representation of the experimental set-up.

The maximum measured field strength of the physical water treatment device was 129 mT. Measurements were made with a digital teslameter with an inaccuracy of ±2% in a constant magnetic field between 10^{-5} and 1 T. The field strength distribution was measured on the centre line while the two halves of the magnet were clamped 23 mm from each other onto a similar copper tube used for the feed-water line. The measured field strength distributions are given in Figures C3.3 and C3.4. In Figure C3.3 the field strength distribution is as expected from the North (N) and South (S) orientation of the magnet, shown schematically in Figure C3.2. For this configuration the measurements along the magnet's length (Figure C3.4) on the centre line on the levels DD, EE and FF, should be zero because the magnetic field changes direction as the polarity changes. This is not the case, which indicates that the tube was not exactly in the centre of the magnet. It is, however, evident from these measurements that the magnetic field changes direction through its length which indicates that the power cell is a multi-axial unit.

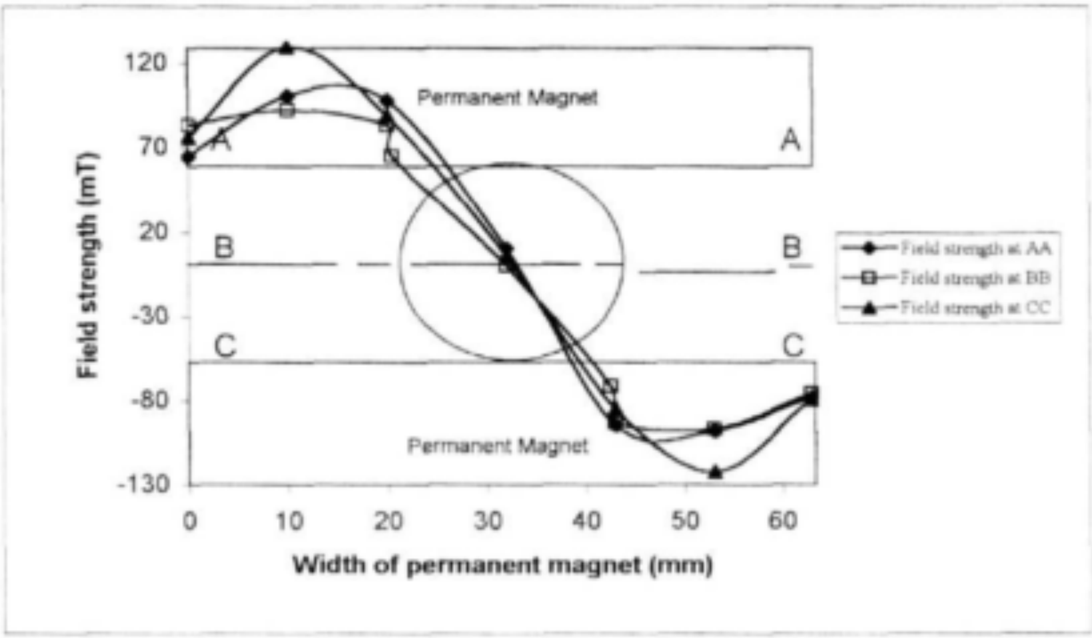


Figure C3.3
Measured field strength across and outside the tube over three sections. The orientation of the magnet relative to the tube is also shown.

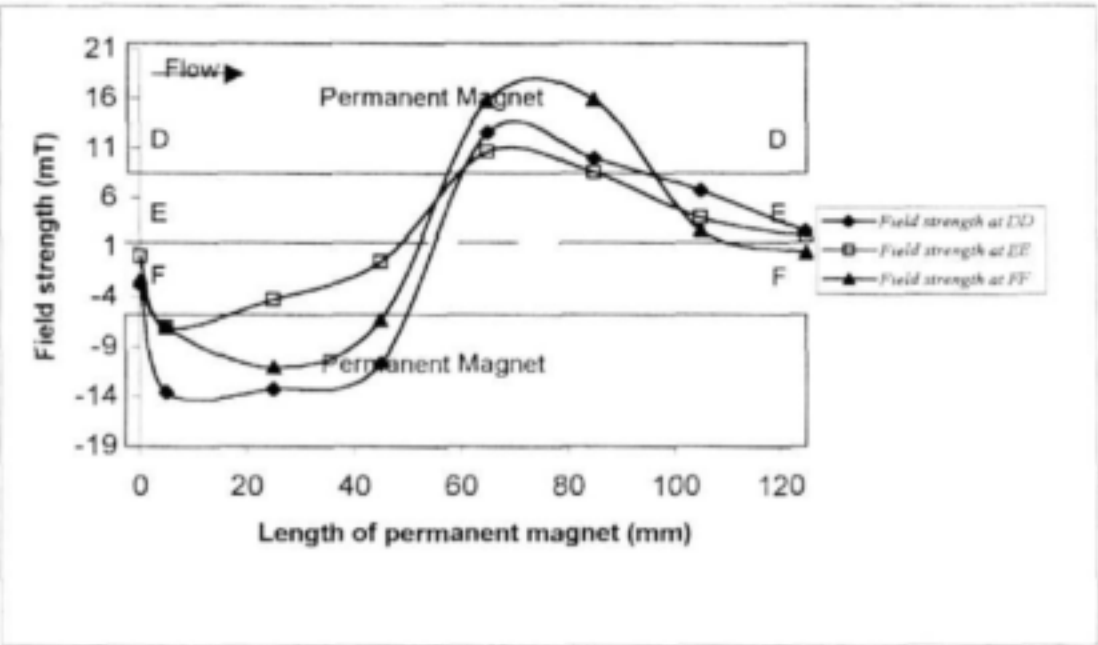


Figure C3.4
Measured field strength in the flow direction on three sections including the tube centre line. The orientation of the magnet relative to the tube is also shown.

The manufacturers of the physical water treatment device made four recommendations on the installation of the device, which were followed carefully. The device should be clamped onto the feed-water line as indicated in Figure C3.2. The flow direction through the tube should be in the same direction as indicated with an arrow on the device. The power cells should be installed in pairs where the number of pairs is determined by the size of the pipe diameter. Lastly, the device should be installed 2 m to 3 m upstream of the storage tank.

C3.3 Test procedure

Before any experiments were conducted, the tanks were cleaned with a 10% acetic acid solution and rinsed well with water. The hot-water storage tanks were simultaneously filled with water from the feed-water line at a flow rate that ensured an average velocity of 1.75 m/s in the tubes. Water samples were taken from the feed-water line for the monitoring of the average water quality. The measuring instrumentation used for measuring the average water quality for each experiment is summarised in Table. C3.1. After every 12 hours, 200 litres of water was drained from each tank, again at a flow rate ensuring an average of 1.75 m/s flow velocity through the tubes. This was repeated for a period of 28 days (672 hours), heating a total of 8 000 litres of water in each storage tank. The experiments were conducted from January 2000 to February 2001. The scale on the electrical elements and on the inside wall of the storage tanks was stripped with a fresh 10% acetic acid solution. Samples were taken every half an hour whereafter the maximum concentration of calcium content was measured.

Parameter	***Instrument***	***Precision***
Ca	*Absorption spectrometer*	*97%*
Fe and Zn	*Induction coupled plasma spectrometer*	*97%*
pH	*Portable pH meter*	*±0.01 pH*
Conductivity	*Conductivity meter*	*±99%*
Turbidity	*Nephelometric turbidity meter*	*±98%*

Table C3.1
Instrumentation used for measuring water quality.

Ten experiments were conducted. During experiments 1 to 3 the physical water treatment device was not used on any of the storage tanks. The purpose of these experiments was to determine the reproducibility of the mass of scale formed in the two tanks. In the next three experiments (experiments 4 to 6) the physical water treatment device was commuted between the two tanks. The device was therefore installed upstream of one of the storage tanks while the other storage tank had no device and was used for comparison purposes. In experiment 7 the experiment was again conducted without any device on either of the two tanks to verify reproducibility. In experiments 8-10 the physical water treatment device was again commuted between the two storage tanks.

C3.4 Results

The average water quality during each experiment represented by calcium concentration, alkalinity, conductivity, pH, pH$_s$ (saturation pH), zinc, iron and turbidity, is given in Smith (2000) as well as the Langelier Saturation Index and Ryznar Stability Index.

The total mass of calcium precipitated on the inside wall of each hot-water storage tank together with the mass of calcium precipitated on its heating element for each experiment is shown in Figure C3.5. The positions of the physical water treatment device for each experiment are also shown. The mass of calcium that precipitated during the first three experiments corresponds well. The differences were 1.3% (experiment 1), 5.2% (experiment 2) and 0.42% (experiment 3) from the average between the two tanks. The average difference is thus 2.3%. The largest difference between the two tanks is 5.2% for experiment 2. No physical water treatment device was used during these experiments, as the objective of the first three experiments was to compare the reproducibility between the two storage tanks. It was concluded that the reproducibility of these experiments was acceptable.

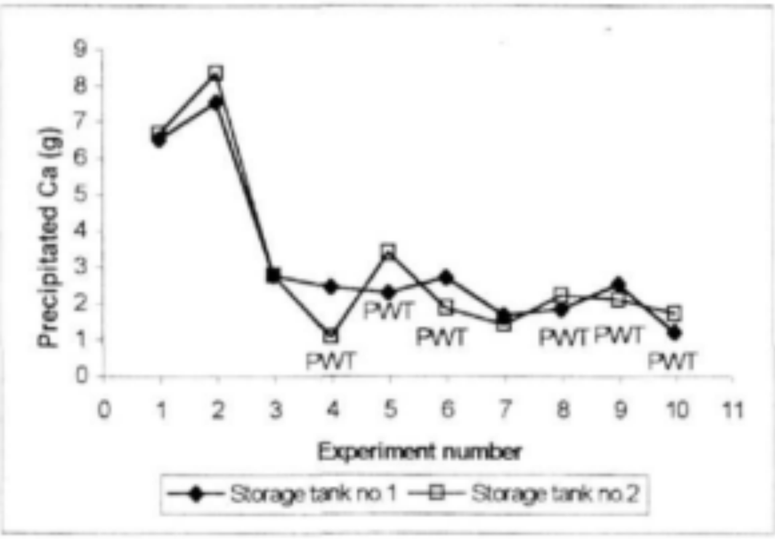


Figure C3.5

Mass of precipitated calcium in the storage tanks and the position of the physical water treatment (PWT) device when in use.

In experiment 4 the physical water treatment device was installed for the first time (onto the feed-water line of storage tank 2). The mass of calcium that precipitated into this tank was measured as 70% less than the tank without the physical water treatment device. In experiments 5 and 6 the device was commuted between the two tanks and every time the tank connected with the device it had less calcium (33% and 31% respectively for experiments 5 and 6).

In experiment 7 no device was used on either one of the tanks. The mass of calcium that precipitated in the two tanks differs by only 8%. This is higher than the average of the first three experiments of 2.3%. However, the mass of calcium measured in each tank was low, which could be contributed to the larger measuring error.

In experiment 8 the device was again installed onto storage tank 1 and commuted between the two tanks. With every experiment where the physical water treatment device was used, less calcium precipitated in the storage tank than in the storage tank without any device (i.e. 17%, 17% and 32% less calcium respectively for experiments 8, 9 and 10).

On average for the five times that the device was used, 36% less calcium precipitated than in the other tank which was run without any device. It can therefore be deducted that the physical water treatment device tested reduced calcium precipitation over the period that the experiments were conducted.

It was also observed visually after experiment 4, as shown in Figures C3.6 and C3.7, that the electrical resistance element of the storage tank where the physical water treatment device was used, was shinier/cleaner from deposits than the electrical resistance element operated without any device. Precipitates from each electrical element were studied with scanning electron microscopy. No morphological changes in the crystals could be observed. It was also found that the visual observation was more difficult and not that clearly defined for experiments 5 and 6 where the differences in calcium that precipitated between the two tanks were also smaller. Investigating morphological changes was difficult as only very small pieces of deposits could be removed from the electrical heating elements without influencing the experimental results of this study. It is recommended that similar experiments be conducted where the morphological changes are the subject of the investigation.

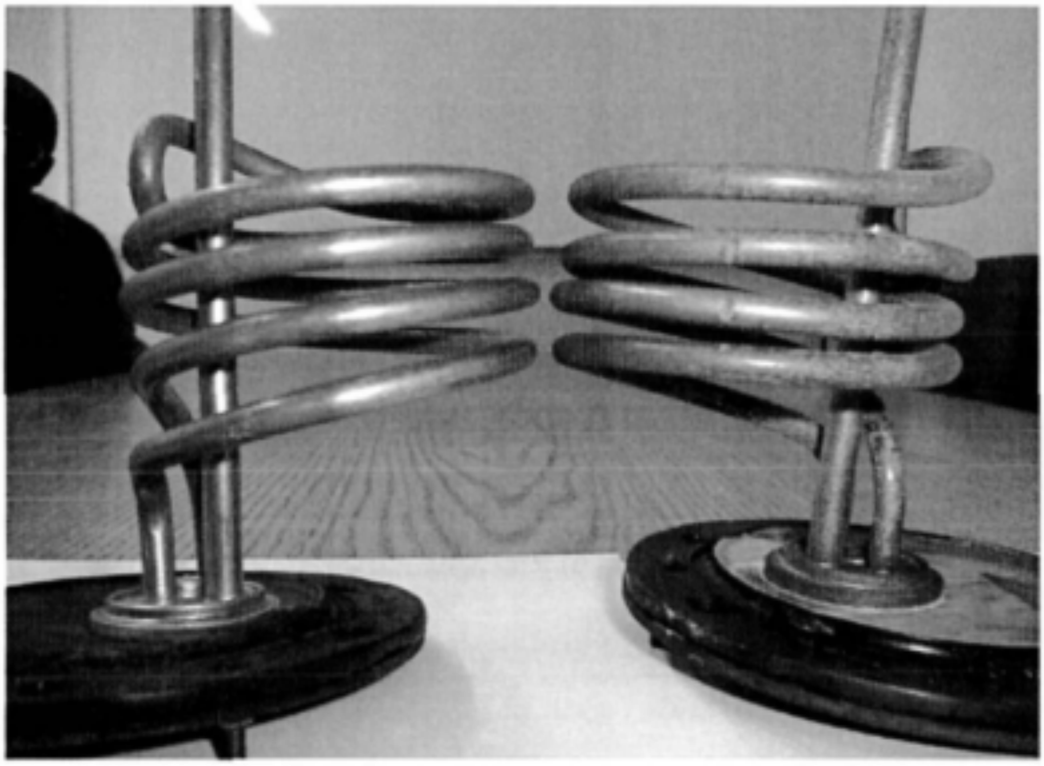


Figure C3.6

Precipitation on the electrical resistance elements of the two storage tanks. The physical water treatment device was on the system to the left in the photograph.

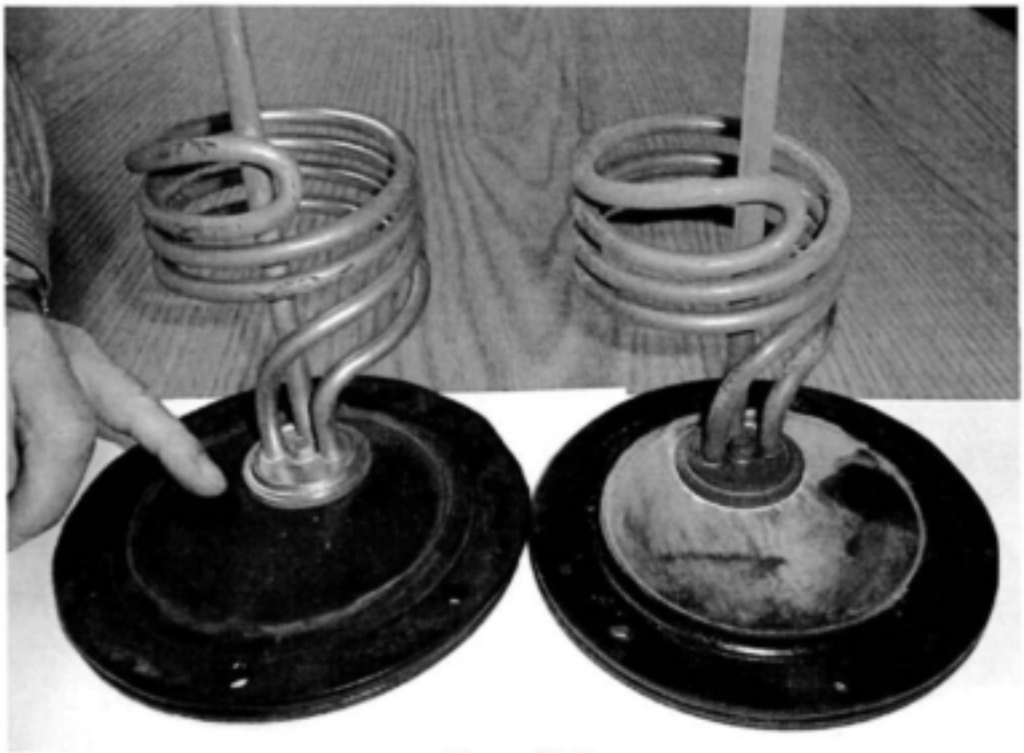


Figure C3.7

Precipitation on the base of the electrical resistance elements. The physical water treatment device was installed on the system to the left in the photograph.

C3.5 Summary of results

During this study an experimental set-up was built and experiments were done following a very simple experimental procedure. The results showed that the experiments with and without the permanent magnet were highly reproducible. Experiments without the permanent magnet showed a maximum of 5.2% deviance from the average amount of calcium precipitation in the storage tanks while the use of the permanent magnet successfully reduced the formation of scale in the hot-water storage tanks with an average of 34%. The maximum reduction in scale formation was 70% and the minimum 17%.

C3.6 Different PWT devices

Although good results were found with the storage tank facility the production of experimental data/results are very slow. The results in Figure C3.5 took 12 months to produce. Another four storage tanks were therefore installed parallel to the two in Figure C3.1. Six storage tanks are therefore available and more physical water treatment devices could therefore be tested at the same time, with the same source of water.

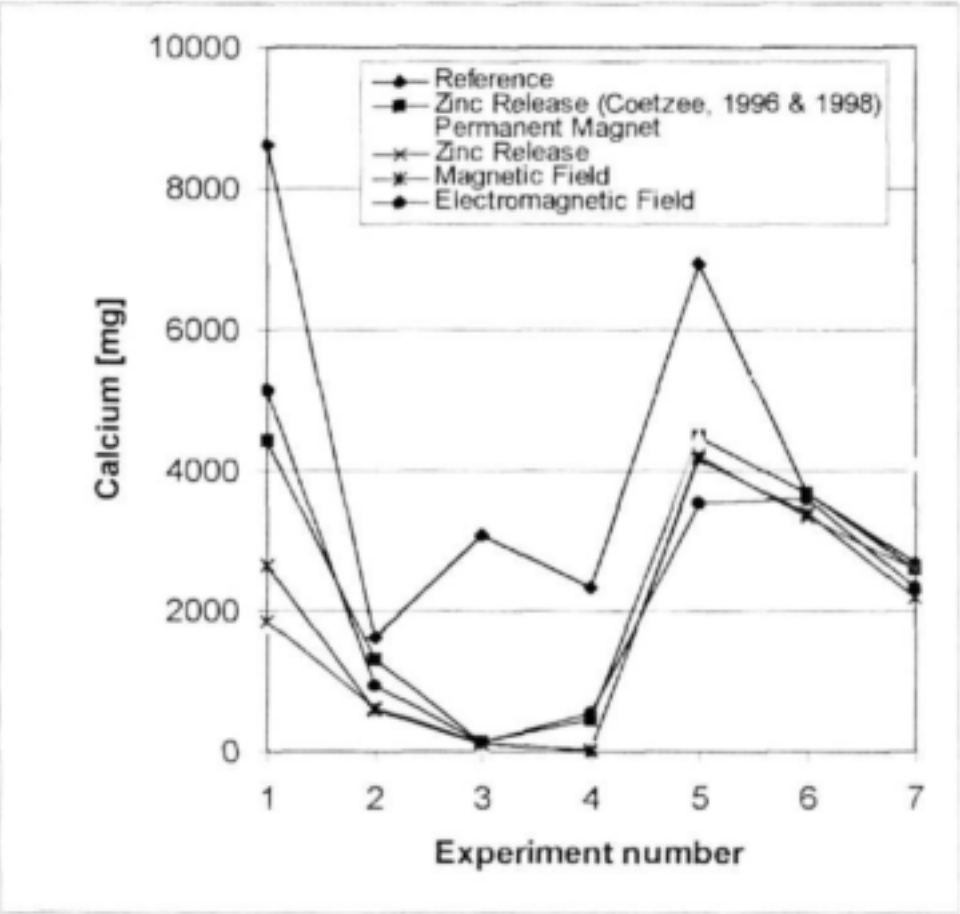


Figure C3.8
Mass of scale precipitated for five different types of PWT devices in hot water storage tanks fed with the same feed water.

Four commercially[1] available PWT devices were tested (Williamson, 2001) at the same time plus the recently patented PWT device of Coetzee (1996 & 1998). During the first five experiments the PWT devices were not commuted between the different tanks, as special care had to be taken to ensure that each was installed according to the instructions of the manufacturers. One tank was used as a reference. For the last two experiments the permanent magnet, which can be moved more easily, was installed onto the tank that was used as a reference for the first five experiments.

C3.7 Results

During the first five experiments it was found that tanks using PWT devices had less scale precipitation than the tank without any PWT device. The differences were substantial (between 19% and 80%). In the last two experiments a permanent magnet device was installed onto the tank that was used as a reference for the first five experiments. The results contradict the scale reduction behaviour observed in the first five experiments, as the amount of scale in the tank with the permanent magnet was 52% to 70% more than in the tank without a PWT device. Drastic changes in the composition of Rand Water Board water occurred during this time as a result of the introduction of new treatment procedures using polyamines as coagulant. Incidentally, the zinc concentrations during this period were also higher than during the first test period. The reason for the change in scaling behaviour during these tests is, however, not clear.

C3.8 Conclusions

It seems as if storage tanks as testing facilities do have potential but evaluations of PWT devices cannot be done without taking the quality of the feed water into consideration. Changes in the quality of the water can, however, be eliminated to an extent if experiments are conducted over a long period of time.

Many more tests need to be done to evaluate the effectiveness of PWT devices at different conditions (such as storage temperatures). The fundamental understanding of the possible working mechanisms of PWT devices are also essential to understand why in certain operating conditions such as in tubes and heat exchangers no positive effects of PWT devices are observed while in storage tanks positive effects are observed, but not always.

[1] The selection of the PNT devices was arbitrary and does not mean that the products are endorsed.

2. CONCLUSIONS

2.1 SUMMARY OF THE WORK DONE

This chapter presents a synthesis of the findings of the three parts of the project. The objectives of the three parts follow a logical sequence from **fundamental research** on the mechanisms of electromagnetic effects on crystallisation and scale formation and the formulation of theoretical models through a practical part focussing on the development of **new scale reduction technology** based on the scale inhibition effects of the Zn^{2+} ion to the construction and use of **testing facilities** for physical water treatment devices.

The work done to achieve these aims can be categorised as follows:

- the development of experimental procedures for the acquisition of reliable data on the effects of electromagnetic fields on scaling systems: These include crystallisation kinetic methods, zeta potential measurements, and AFM force-distance techniques.
- the formulation of theoretical models to explain possible mechanisms.
- the evaluation of commercial devices using crystallisation kinetic methods.
- the development and testing of a prototype free metal ion scale inhibitor based on a zinc/copper electrochemical cell.
- the development and construction of three different types of experimental testing facilities:

2.2 Synthesis of the main findings

2.2.1 Fundamental research

2.2.1.1 Theoretical models and mechanisms

The study showed that at least two completely different mechanisms are involved in explaining the effect of physical water treatment on scale reduction. The first involves the effect of metal ions released by physical water treatment devices and the second has to do with the effect of electromagnetic fields produced by some PWT devices on the solid-liquid interface during the crystallisation process.

Metal ions, Zn^{2+} ions in particular, present in trace quantities reduce the rate of nucleation and crystal growth during $CaCO_3$ crystallisation. The crystal morphology of precipitated $CaCO_3$ is also predominantly aragonite in stead of calcite when Zn^{2+} ions are present during the precipitation process. These effects may be explained in terms of the blocking of specific growth sites on the crystal surface by impurity ions of the right dimensions and chemical form.

It is proposed that the effect on electromagnetic fields on crystallisation process may be interpreted in terms of a mechanism involving the polarisation or distortion of electric double layers around precipitating or scaling particles or ionic atmospheres around ions participating in the scaling process. Results obtained from atomic force microscopy (AFM) measurements showing a reduction in double layer repulsion and zeta potential measurements showing a reduction in zeta potentials on exposure to magnetic fields, support this hypothesis. Experimental evidence produced in this study was, however, not sufficiently reliable to confirm this hypothesis.

2.2.1.2 Atomic force microscopy measurements

An important conclusion reached in this study was that AFM can be used to study electric double layer characteristics by acquiring force-distance data in different electrolyte media using modified AFM tips. It was proven that the double layer contraction as a function of increasing electrolyte concentration could experimentally be measured at the nanometer level. AFM results obtained during preliminary experiments at Nottingham University and RAU indicated that double layer contraction was triggered by exposure of electrolyte to electromagnetic fields. This is a far-reaching result which would enable the study of electromagnetic fields on solutions and colloids at the molecular level.

2.2.1.3 Zeta potential results

Results indicated a lowering of zeta potentials in magnetically treated colloidal suspensions. The zeta potential studies seem to support the AFM results and point to a double layer distortion mechanism. The experimental evidence is, however, too inconsistent at this stage to form the basis for the formulation of a theoretical explanation of the effect of electromagnetic fields on chemical systems.

2.2.2 Free metal ion scale inhibitor

Results show that the performance of zinc as a scale reduction agent is predictable in clean systems using deionised water. Tests provided insight into possible limiting conditions that might occur in tap water or industrial water. Deactivation of Zn could for instance be caused by complexation reactions with certain organic and inorganic species present in water. It was shown that electrochemically introduced zinc behaves in very much the same way as zinc introduced by chemical dosing. A prototype free metal ion scale inhibitor was designed, constructed and tested and guidelines for its use compiled.

2.2.3 Testing facility

Three testing facilities were designed, constructed and tested: a tube testing facility, a heat exchanger testing facility, and a domestic hot water storage testing facility.

It was found that the first two testing facilities were not suitable because the time required before measureable results were obtained was too long and the running costs too high for the tube facilty and in the case of the heat exchanger facility no effects could be observed when PWT devices were used.

Hot water storage tanks were used in the third testing facility. Ten experiments were conducted during which time a permanent magnet was connected to the inlet of one of the storage tanks. It was found that scale formation precipitation was on average 36% less (minimum was 17% and maximum was 70%) in the test circuit where the device had been installed compared with the control circuit.

In subsequent experiments, running over 10 months, 6 hot water storage tanks were used in a testing facility where 5 devices could be tested simultaneously using the same input water. One tank was used as reference. Seven experiments were conducted in which different PWT devices were compared. The results indicated that scale formation in all 5 circuits where PWT devices had been installed was reduced between 19% and 80%. In the last two experiments a permanent magnet device was installed onto the tank that was used as a reference for the first five experiments. The results, however, contradicted the scale reduction behaviour observed in the first five experiments, as the amount of scale in the tank with the permanent magnet was 52% to 70% more than in the tank without a PWT device. Drastic changes in the composition of Rand Water Board water occurred during this time as a result of the introduction of new treatment procedures using polyamines as coagulant. Incidentally, the zinc concentrations during this period were also higher than during the first test period. The reason for the change in scaling behaviour during these test is, however, not clear.

3. RECOMMENDATIONS

The nature of the processes involved in physical water treatment and the difficulty in monitoring these processes, make research into the fundamentals of electromagnetic effects on scale forming a challenging and very time-consuming effort. It is, nonetheless, recommended that further work be undertaken to address the following important aspects:

- Field tests and the possible commercialisation of the free metal ion scale inhibitor.

- Continuation of fundamental research, in particular using atomic force microscopy and zeta potential studies, with the aim of unravelling the mechanisms involved in the effect of electromagnetic fields on scaling reactions.

- Continuation of experimentation over a longer period of time to verify the integrity of the testing facility.

- The effect of metal impurities on $CaSO_4$ scale formation.

- The effect of electromagnetic fields on $CaSO_4$ scale formation.

- A comprehensive survey of scaling problems in South Africa.

- The effectiveness of physical water treatment at high temperatures.

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APPENDIX

Dissertations, research papers, conference contributions, and research visits

1. Simon Mubenga, The role of Zn in physical water treatment for the prevention of scale, *MSc thesis* (RAU) 1998

2. S Udol, Mitigation of calcium carbonate scaling by alternative methods *MSc thesis* (Univ of Cranfield, UK), 1997

3. PP Coetzee, M Yacoby, S Howell and S Mubenga, Scale reduction and scale modification effects induced by Zn and other metal species in physical water treatment, *Water SA 24*, 1998, 77

4. R Barrett, S Parsons and PP Coetzee, The effect of magnetic fields on the precipitation of calcium carbonate, *WISA Conference*, Cape Town, May 1998

5. PP Coetzee, The role of Zn in physical water conditioning, *Conference Proceedings: MAG 3 International Conference on Antiscale Magnetic Treatment*, Cranfield University, UK, April 1999

6. R Barrett, Magnetic treatment in static and flowing systems, *MAG3 International Conference on Antiscale Magnetic Water Treatment*, Cranfield University, UK, April 1999

7. Christo Smith, An evaluation of a magnetic physical water treatment device for the prevention of scale fouling in hot-water storage tanks, *M. Eng Thesis* (RAU) 2000

8. Reynaldo da Veiga, Evaluation of physical water treatment devices to decrease scale formation in tubes, *D.Eng. thesis*, RAU, 2002, (to be submitted)

9. Reynaldo da Veiga, Evaluation of a permanent magnet to decrease scale formation in a tube, *M.Eng Thesis* (RAU), 1999.

10. Smith, C., Coetzee, P.P. and Meyer, J.P., Treatment devices for preventing scale fouling in hot water storage tanks, *Proceedings of the International Conference on Applied Mechanics, SACAM 2000*, Edited by: Adali, S, Morozov, E.V. and Verijenko, V.E., pp. 635 – 640, 11-13 January 2000.

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12. Da Veiga, R, Coetzee P.P, and Meyer, J.P., The effect of a permanent magnet on scale formation in a tube, *Proceedings of the ASME-ZSITS International Thermal Science Seminar*, Bled, Slovemia, pp. 301 – 307, 11 – 14 June 2000.

13. Smith, C, Coetzee, P.P. and Meyer, J.P. ,The effectiveness of a magnetic physical water treatment device on scaling in domestic hot-water storage tanks, *Water Research*, (submitted for publication)

14. Veronique Williamson (2001), The influence of physical water treatment devices on the scaling of water at high temperatures in hot water storage tanks, *B.Ing. final year project*, RAU.

15. Ivan Basson, (2000), Scale prevention in tube-and-tube heat exchangers, using a magnetic physical water treatment device, *B.Ing. final year project*, RAU

Research visits

- Prof PP Coetzee, Visiting professor at the School of Water Sciences, Cranfield University, UK, April – October 1997, ESPRC Grant.
- R Barrett, Visiting researcher at Department of Chemistry and Biochemistry from Cranfield University, March – August 1998, WRC grant.

Archived data

All RAU dissertations are available in the RAU Main Library.

Other related WRC reports available

Research on the corrosion performance of various non-metallic piping materials and coatings in potable water

JS Ramatlhola, Dr C Ringa, R Cromarty

The objectives of this study were to critically evaluate the effect of mineralisation on the service performance of various non-metallic pipe materials and linings in the PWV/Klerksdorp areas, to determine which water parameters are important when selecting coatings and non-metallic piping materials for conveying potable water, and recommend candidate coatings and non-metallic piping materials such that internal corrosion of pipes can be reduced. Since there are many types of coatings available for use as linings on carbon steel piping, it was necessary to evaluate the performance of generic coating systems in a systematic, scientific manner. These results will allow local authorities to decide on what type of coating systems to use in their piping systems in a cost-effective manner so that costly failures are avoided. Non-metallic coatings, metallic coatings, non-metallic piping materials, cement mortar-lined and carbon steel pipe samples were exposed to potable water in a flow loop system. These samples were examined and evaluated every year for their corrosion performance and rated accordingly. The quality of the water was also monitored with a data acquisition system and was related to the corrosion rates of carbon steel pipe samples.

Report Number: 381/1/99 **ISBN 1 86845 532 7**

Exposure of generic coating systems in raw South African dam waters

JS Ramotlhola, R Cromarty, Dr C Ringas

An exposure program was undertaken over a period of three years to evaluate the performance of various metals, alloys and coatings in South African dam waters. A total of 2 250 coupons were exposed in three dams, namely the Vaal and Roodeplaat Dams in Gauteng and the Kleinplaas Dam in the Western Cape. The purpose of the exposure program was to evaluate the suitability of various generic coating systems for immersed applications in raw South African dam waters and the results will therefore not refer to specific coating brands. Strict control was exercised over the preparation of the panels in order to avoid any dispute at the end over the application of the coatings and the coatings were applied by the manufacturers themselves. Specimens were exposed at three levels in each dam, namely splash zone, totally immersed and in the mud/silt zone.

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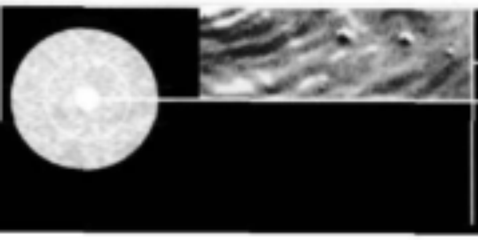

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