# REDUCTION OF SCALING IN INDUSTRIAL WATER COOLING CIRCUITS BY MEANS OF MAGNETIC AND ELECTROSTATIC TREATMENT

WRC Report

submitted to the Water Research Commission

by

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AR | analar |
| B | Magnetic inductance |
| COC | Cycles of concentration |
| DC | Direct current |
| EDTA | Ethylenediaminetetraacetic acid |
| F | Force |
| H-bonds | Hydrogen bonds |
| HF | High frequency |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| M | Molar concentration |
| NMR | Nuclear Magnetic Resonance |
| PVC | Polyvinyl chloride |
| PWT | Physical Water Treatment |
| q | electric charge |
| RF | Radiofrequency |
| SEM | Scanning electron microscopy |
| TDS | Total dissolved solids |
| v | velocity |
| XRD | X-ray diffraction |
| µ | micron or micro |
| Δt | Delay time |

# EXECUTIVE SUMMARY

The formation of scale in practically all systems where water is transported through conduits or treated in containers at temperatures even slightly above ambient, is a major problem around the world. The problems range from reduction in heat transfer efficiency, blocked systems to wastage of large volumes of make-up and blowdown water.
There are two methods of reducing the impact of these problems. The first option is *chemical treatment*, where the scale formation characteristics of water are inhibited by the addition of chemicals, for instance scale inhibitors like polyphosphates or polyacrylates. These chemicals are expensive, require sophisticated dosing and dosing control equipment with concomitant supervision, and also end up in the environment through the blowdown water. The second option is *physical water treatment (PWT)* which consists of a simple flow-through system in which the water is exposed to some form of electromagnetic field. It is then claimed that the properties of water are changed and/or dissolved or suspended solids present in the water undergo physical changes leading to a range of effects. An influence on scale and scale forming salts is only one, albeit predominant effect. This treatment, if successful, then circumvents the problem of chemicals, dosing control and environmental pollution. PWT is especially attractive at the thousands of small-scale heat exchange systems where the cooling water circuit is a small, minor component of the operation. It has also found application in large industrial installations like power stations and the paper mills.

Physical water treatment, however, despite its potential benefits, is currently met with scepticism by the broader technical community. The first reason is that there is no plausible, commonly accepted fundamental mechanism by which the results of physical treatment can be explained. In the absence of such a mechanism, manufacturers frequently revert to extraordinary claims and hypotheses which, without supporting scientific data, do more harm than good. The second reason is that the units do not always have the same degree of success in all installations, and in some cases do not succeed at all. These cases, often highly publicized, lead to even greater scepticism. Physical water treatment has been around since the last century, but there is continuing doubt as to whether the process works at all. The literature abounds with reports, both from full-scale practical installations as well as research laboratories, which are in direct conflict. Some report substantial effects, others no effects at all. Also from South Africa, local suppliers of PWT equipment offer a number of well documented case histories of successful industrial application.

The current constraints on the use of PWT are basically twofold: i) the unpredictable behaviour of PWT devices in the industrial environment i.e. reports vary from very successful to total failure (ii) the total lack of understanding as to how PWT works.

## Objectives

The important parameters for magnetic and electrostatic treatment fall into two general categories. The first category deals with the *physical* parameters of the treatment device, which would include factors such a field strength, flow velocity, exposure time to the field, orientation of the field to the flow direction, and others. The second category deals with the *chemical* composition of the water to be treated, such as degree of supersaturation, temperature, nature and concentration of suspended solids, presence of precipitation nuclei, presence of trace elements of iron, zinc and vanadium, and others. It is fairly evident from the literature that the latter group plays the major role towards the success of the process. Our approach was, therefore, to concentrate our efforts on the role of chemical parameters.

The objectives of the project were:

- To determine the efficiency of electrostatic water treatment in a number of simulated industrial applications
- To verify and test the efficiency of magnetic and electrostatic treatment devices under rigorously controlled laboratory conditions
- To compile guidelines for the industrial application of magnetic and electrostatic treatment devices

## Summary of the work done

To achieve these objectives we used a two- pronged approach, namely (i) simulated full-scale investigations and (ii) laboratory investigations where the problem was studied at the molecular level

(i) *The main thrust of the laboratory investigations can be summarised as follows:*

- The development of laboratory test methods to verify the effects of physical water treatment in as short as possible experimental run times. The batch method based on measuring the rate of $CaCO_3$ precipitation ( pH vs time), was developed for this purpose. Tests were run on 5 commercially available PWT devices, 3 magnetic, 1 electric and 1 catalytic converter, and a 2 tesla variable laboratory electromagnet, using the above methods..
- The experimental verification under controlled conditions of the occurrence of some effects listed in the literature. The effect of PWT on the rate of crystallisation (by implication scale formation), crystal morphology (by implication adhesion properties of scale), and the effect of impurities released by the devices were studied in detail.
- The evaluation of the two main mechanistic models, namely the water structure model and the nucleation model.

(ii) *The focus of the simulated full-scale investigations can be summarized as follows:*

- to design, construct and optimize a full-scale testing system to measure scale formation in heat exchanger pipes rapidly and quantitatively.

- to evaluate selected PWT devices for industrial applications.

## Summary of results

- Verification of effects. We have shown that the emission of metal ions, in particular zinc ions from three different types of PWT device can affect the rate of crystallisation of $CaCO_3$ and can cause changes to the crystal morphology of precipitates. Nucleation rates are decreased and the morphology of the scale changes from calcite rhombohedrons to aragonite needles. Presumably the adhesion properties differ between these two crystallographic forms of $CaCO_3$. Scale inhibition effects shown by these devices could therefore be attributed to these phenomena. Where devices released no measurable amounts of impurities, no effects were observed.

- Proposed mechanistic model. Results from experiments designed to test the water structure model, proved negative. The devices had no measurable effect on surface tension, infrared spectra or NMR spectra of water which would have indicated structural changes to water . The fact that after coating the inner surfaces of the devices with an impenetrable thin layer of polymer, the effects on nucleation rate and crystal morphology disappeared, indicated that the release of impurities from inner surfaces were responsible for the observed effects. In view of these results, a mechanistic model based on the substoichiometric blocking of crystal surface growth sites, is proposed. This means that metal ions, in particular free metal ions with the right stereochemistry are preferentially adsorbed at "kinks" and "steps" in the growing crystal. This blocks the preferred growth pattern of calcite, converting to an aragonite growth pattern which takes place at a slower rate.

- Full-scale investigations.
  A quick, reliable method was developed to determine the rate of scale formation in afull-scale test rig. The method comprised of stripping the scale from straight pipes with 10 % acetic acid and determining the Ca content after acid stripping. The reproducibility amongst different pipes, and amongst different experiments, were not as good as expected. Further work should be conducted to improve the reproducibility of the test rig before meaningful verification of PWT could be done on this rig.

## Research products

- *Free metal ion scale inhibitor.*

  In view of the results obtained, a scale inhibition procedure , was proposed based on the controlled addition of metal ions, such as zinc, to scale forming water. Broad operating guidelines were established. In experiments done with tap water and deionised water both spiked with $CaCO_3$ at concentrations up to 500 µg/l, scale reduction of between 50 and 80% was achieved. Strong ligands for Ca complexation like EDTA, when present in mg/l quantities, will destroy the beneficial effect of µg/l levels of active zinc. High concentrations of inorganic ions like chloride and sulphate may, however, be tolerated.

The addition of free metal ions to feed water may be achieved by controlled electrolysis via a pulsed DC power supply. This has the advantage of controlling the concentration of free $Zn^{2+}$ ions and preventing the zinc anode of becoming deactivated by formation of a protective ZnO coating or deposition of scale.

- *Dissertations*

1. M. Yacoby M.Sc.(Chemistry)(RAU)1996, with distinction:
   *The effect of magnetic and constant electric field antiscaling devices on the mechanism of $CaCO_3$ scale formation.*
2. S.S. Howell M.Sc.(Chemistry)(RAU) 1996, with distinction:
   *A critical evaluation of physical water treatment for the prevention of scale*
3. S.M. Canbulat M.Eng.(Civil Engineering) 1997
   *Measurement of scale formation in an experimental heat exchanger circuit.*

- *Research papers*

1. PP COETZEE, M YACOBY and SS HOWELL (1996) The role of zinc in magnetic and other physical water treatment methods for scale prevention. *Water SA* 22(4) 319-326

2. V KOCHMARSKY (1996) Magnetic treatment of water: Mechanisms and conditions for applications. *Magnetic and Electrical Separation* 7(2) 77-107

- *Patent*

*Process for treatment of water: Prevention of scale deposits* SA Patent No. 95/6807

- *Conference contributions*

1. PP COETZEE, *The role of metal surfaces in antiscale physical water treatment.* Plenary lecture at the International symposium: Antiscale Magnetic Treatment: How does it work? Cranfield University, Bedford, UK, 14 March 1996.

2. PP COETZEE, M YACOBY, SS HOWELL, *Magnetic water treatment for prevention of scale. Myth or fact?* 33 rd Convention of the SA Chemical Institute, Cape Town, January 1996

## Conclusions

Results from this project confirmed that certain types of PWT device could have antiscaling effects. These types include magnets, catalytic converters and electric devices where the feed water is in direct contact with inner surfaces of the device. Their effect is ostensibly related to the emission of certain impurities from inner surfaces coming into contact with feed water. In our opinion small amounts of metals could be introduced into the feed water in a cheaper and far more efficient manner through controlled electrolysis instead of magnetic or electric devices. We have not proven that no other mechanism related to the electromagnetic fields exists which could influence scale formation. If such effects do exist, our test methods were not able to measure any.

## Recommendations

It was not possible to make any final recommendation with respect to the practical viability of physical water treatment. We therefore recommend that further work be undertaken to address the following important aspects:

- long term experiments running on simulated industrial scale test equipment as was developed during this project
- the application of new analytical technology to measure effects of electromagnetic fields on water and scale forming components in water. Recent results from Japan have indicated that atomic force microscopy might provide a means of measuring the small direct effects that could arise from physical water treatment.
- the further development of the metal ion scale inhibitor patented in 1996 and based on initial work done under WRC contract no. K5/612
- application tests on commercial systems
- systematic investigation of new PWT technology not covered under this WRC contract. PWT devices based on RF(radio frequency) fields are prime candidates for inclusion in further work because of promising reports coming from industrial applications of these systems.

These aspects will be addressed in a new contract between Rand Afrikaans University and the WRC, which commenced in January 1997.

# 1. INTRODUCTION

The formation of scale in practically all systems where water is transported through conduits or treated in containers at temperatures even slightly above ambient, is a major problem around the world. The problems range from reduction in heat transfer efficiency, and blocked systems, to wastage of large volumes of coolant tower make-up due to limited cycles of concentration. There are two methods of reducing the impact of these problems. The first option is ***chemical treatment***, where the scale formation characteristics of water are inhibited by the addition of chemicals, for instance scale inhibitors like polyphosphates or polyacrylates. These chemicals are expensive, require sophisticated dosing and dosing control equipment with concomitant supervision, and also end up in the environment through the blowdown water. The second option is ***physical water treatment (PWT)*** which consists of a simple flow-through system in which the water is exposed to some form of electromagnetic field. It is then claimed that the properties of water are changed and/or dissolved or suspended solids present in the water undergo physical changes leading to a range of effects. An influence on scale and scale forming salts is only one, albeit predominant effect. This treatment, if successful, then circumvents the problem of chemicals, dosing control and environmental pollution. PWT is especially attractive at the thousands of small-scale heat exchange systems where the cooling water circuit is a small, minor component of the operation. It has also found application in large industrial installations such as power stations and paper mills. In a recent survey [51] it was reported that during 1990 alone more than 2 500 domestic and more than 1 000 industrial units, electro- or permanent magnets, were sold in the Netherlands. In a random test survey it was found that out of 65 cases, 55 had shown positive results.

Physical water treatment, however, despite its potential benefits, is currently met with scepticism by the broader technical community. The first reason is that there is no plausible, commonly accepted fundamental mechanism by which the results of physical treatment can be explained. In the absence of such a mechanism, manufacturers frequently revert to extraordinary claims and hypotheses which, without supporting scientific data, do more harm than good. The second reason is that the units do not always have the same degree of success in all installations, and in some cases do not succeed at all. These cases, often highly publicized, lead to even greater scepticism. Physical water treatment has been around since the last century, but there is continuing doubt as to whether the process works at all. The literature abounds with reports, both from full-scale practical installations as well as research laboratories, which are in direct conflict. Some report substantial effects, others no effects at all. Also from South Africa, local suppliers of PWT equipment offer a number of well documented case histories of successful industrial application.

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## 2. LITERATURE REVIEW

Physical water treatment for the prevention of scale has been actively promoted as an alternative for the chemical treatment of water since the first physical water treatment (PWT) patent was registered in 1945 [52]. This patent was for magnetic water treatment. Other PWT techniques include methods based on electric or electrostatic fields, "catalytic conversion" and ultrasonic vibration. Despite numerous laboratory and field studies [7,8,11,18,19,22,28,40] to prove the effectiveness of these methods, no conclusive evidence can be presented to date. Many theories have been proposed but none is able to provide a satisfactory foundation for a mechanistic explanation of the claimed effects.

It is claimed in reviews [3,51] that PWT leads to:

- a decreased **rate of scale formation** on heat exchanger surfaces
- the formation of a **soft scale** with a different morphology and **crystal structure** characterised by weaker **adhesive properties**
- **descaling** i.e. dissolution of existing scale
- increased **wetting capacity**
- lowering of **surface tension** and **viscosity** of water and changes in the **infrared spectrum** of water
- **degassing** of solutions
- increased **capacity of ion exchangers**
- increased efficiency of **flotation**

- a **memory effect** which can last up to 72 h
- the formation of **smaller crystallization particles**
- increases in **solubility** of slightly soluble compounds
- a decrease in **zeta potentials**
- inhibition of **bacterial and algal growth**
- an increase in **crop yields**
- intensification of **coagulation** processes
- reduction in **corrosion**
- and various other related effects

The literature on this subject ranges from the totally negative to the totally positive, the totally sublime to the totally ridiculous. It is an extremely difficult task to sort out the true from the false since many reports do not provide enough information to reconstruct the experiments. More often than not, experimental design and data interpretation tend to be inadequate. A short discussion of the literature is included in this report under the headings: the basic claims and effects, functional types and operating conditions, industrial experiments, and mechanistic explanations.

## The basic claims and effects

### *Crystal morphology*

PWT leads to the formation of less scale on heat exchanger surfaces [13,24] and the scale that does form is softer with lower adhesion properties. This is described as sludge that does not adhere to the surfaces of the heat exchanger, or alternatively scale with a low mechanical strength [19]. This suggests a change in the morphology of the scale. Claims are made that PWT changes the crystal structure of calcium carbonate scale from a predominantly calcite precipitate to a predominantly aragonite precipitate [14,22]. It has been suggested that aragonite is the main factor contributing to the formation of soft scale, i.e., the aragonite has less adhesion properties than calcite. Duffy [17] concluded from his results that the morphology changes were as a result of the corrosion of iron from the pipe as induced by the magnet placed over the pipe. Particles are formed in the solution which encourage the scale to precipitate in the bulk of the solution and not on the heat exchanger surfaces. This can be seen as an increase in precipitation of salts (eg. $CaCO_3$) from a saturated solution.

### *Particle size*

In the case of calcium carbonate scale, Donaldson and Grimes [22], have shown that the particle size of the precipitate obtained from hard water passed through a magnetic field, was increased. For calcium sulphate, laser scattering results showed an increase in particle size by the magnetic treatment while optical micrographs showed small crystals that had agglomerated. Zinc phosphate particles were found to be smaller after magnetic treatment while barium sulphate particles were found to be larger.

### *Rate of crystallization*

The rate of precipitation is dependent on field strength, i.e., the rate of precipitation increases with an increasing magnetic field strength [19]. Claims are made that PWT accelerates the formation of crystals in supersaturated salt solutions [26] due to the fact that the mobility of ferromagnetic particles, such as hydrated forms of iron oxides present in the water, is influenced by magnetic fields [4,11].

### *Descaling*

PWT removes existing scale from heat exchanger surfaces. It is suggested that existing scale becomes suspended in the water, i.e., as if it has broken off the surface as a result of PWT [15,32,42]. Manufacturers have claimed that the "activated" water created by PWT, "activates" the layer of scale with which it first makes contact and causes a microscopic swelling of these layers. The enlarged layer caused by this swelling process is then subjected to a process of dispersion and gradually "depolymerizes" into the flow of the water [18].

### *Water structure*

An idea that occurs frequently is that PWT actually changes the structure of water. In this paragraph effects that could be related to changes in the properties of water are summarised. The basic theory is that water tends to form clusters through hydrogen bonds, designated as $(H_2O)_n$ where n could be as large as 100. It is suggested that the magnetic field reduces the average binding energy of the hydrogen bonds, probably through a resonance effect [5,30]. This results in either a breaking up of the existing water clusters into smaller clusters which constitutes an alteration in the structure of the water. The implications of this are that the water, by breaking up, releases nucleation crystals [30] and/or leads to a change in physical properties of the water such as viscosity and surface tension. Another implication is changes in the wettability of solids by "magnetised" water [12], which would enhance the thickening or de-watering of sludge [38]. It is also suggested by a manufacturer that the increased wettability of the magnetised water promotes plant growth. Magnetic units are reported to reduce the saturation levels of oxygen by approximately 10 to 15 %. It has been demonstrated that magnetic treatment can enhance the effectiveness of deaeration equipment. The effectiveness appears to be a function of dissolved solids [43]. Electromagnetic pretreatment of a solution containing up to 100 ppm $Ni^{2+}$ increases the capacity of a type KU-2 cationic exchanger [47]. It is claimed that as a rule, magnetic treatment of water brings about an increase in pH, but this pH change is more perceptible for acidic solutions than for alkaline solutions [41,52].

### *Flocculation*

Under certain conditions, a deep secondary minimum of the interaction potential of a paramagnetic colloidal particle is formed which substantially affects the stability of the colloidal suspension placed in a magnetic field. The result is that flocculation can be induced by magnetic treatment [39,48]. It was further claimed that flocculation is induced when a colloidal suspension was stationary or flowing through a magnetic field [49,29].

### *Impurities*

Duffy (1977) [17] claimed that there is no effect of the magnetic field, but rather an effect of $Fe^{3+}$ and $Fe^{2+}$ given off by the magnetic devices as a result of galvanic and/or magnetic effects. Busch

(1986) [7] also suggested that even though these corrosion products are small, their possible role in the prevention of scale formation cannot be neglected. Meyer (1984) [37] found that trace amounts of impurities reduced the crystal growth rate of calcite crystals. The concentrations of impurities needed to reduce this growth rate by at least 20 % are as low as $1 \times 10^{-8}$ M $Fe^{2+}$, $5 \times 10^{-8}$ M $Zn^{2+}$, $6 \times 10^{-9}$ M adenosine triphosphate, $1 \times 10^{-8}$ M tripolyphosphate, etc. He listed 32 different impurities that reduce the crystal growth rate of calcite crystals.

### *Biological effects*

Manufacturers claim that the electronic water treater utilizes the oxygen in the water to achieve the destruction of iron reducing bacteria and other scale forming bacteria in piping systems [2]. Algae that normally grow on coolers and in swimming pools, die rapidly under the effect of magnetic treatment, probably due to the increase in the pH as induced by the magnetic treatment [52]. It is even claimed that a rotating magnetic field has been proven to destroy numerous bacteriophages and the polio virus, among other things [50]. On the other hand, researchers in Israel claim milk yield from cows is more, there is a gain in mass on calves, faster growth on geese is achieved, increased yield in fruit size with higher sugar content is achieved, etc, all as a result of using magnetically treated water for irrigation and drinking purposes [33,34].

### *Memory effect*

The ability of treated water to retain its antiscaling properties for some time following magnetic treatment has been reported by a number of authors, with this memory effect being given as ten minutes [20] to 143 hours [3]. An explanation was given by Evdokimov [21] that it is a problem of generalised diffusion, "the anisotropic coefficient of diffusion resulting from the action of the magnetic field is preserved for a certain time only because of the coagulation of the deformed macromolecules of colloidal iron which is always present in water."

### *Zeta Potential*

Means (1981) [10] indicated that the electrostatic device he was studying, caused an increase in the zeta potential whereas Krylov *et al.* (1986) [31] found that the magnetic field decreases the zeta potential. Krylov passed a suspension of calcium carbonate (in the form of calcite) through a closed system. After 1.75 hours, an electromagnet was switched on. Samples were extracted throughout the experiment and the zeta potential measured using the technique of streaming potential. The sedimentation of these samples were studied at the same time. It was found that the zeta potential drops as soon as the electromagnet was switched on, and the calcium carbonate particles settle faster after the electromagnet was switched on. Superficially the results look very impressive, but it seems very unlikely that changes in zeta potential of 0.5 mV and even less than 0.1 mV could be given the significance awarded to it in this article. Such small decreases could be seen even though there was no indication of any control over pH. A zeta potential measurement is not worth much if there is no indication of variation of pH. Zhai (1992) [55] used a suspension of calcium sulphate in his investigations. The suspension was exposed to an NMR (nuclear magnetic resonance) magnet while rotating in a test tube, with the control being a test tube rotated by a drill. The temperature and pH were stringently regulated. He found that the zeta potential drops with exposure to the magnetic field by 22.7 %. The zeta potential drops from 18.89 mV to 14.60 mV. The error is ± 1.86 mV. The fact that with all the care this researcher took and still got an error of ± 1.86 mV, places more doubt on the previous authors' results.

### *Infra-red (IR) Absorbance of Water*

Morozov and Klassen [27] found experimentally that the magnetic treatment of double distilled water "'under optimal conditions" resulted in a change in the rotation spectra of its vapours in the infra-red range. At the same time, the magnetic susceptibility of the double distilled water also varied, this effect intensified with oxygen saturation. They note that poor reproducibility is a noticeable feature of these experiments. It was pointed out that the structural relaxation time of water is $10^{-10}$ to $10^{-12}$ seconds and theoretically has no structural memory. In the course of about a day, the absorption returned to its original value. Bruns *et al.* (1966) [3] found that the IR absorbance of water (at 3300 - 3600 $cm^{-1}$) was changed by 30 % upon application of a 0.15 T magnetic field. Duffy (1977) [17] also investigated this matter and found no effect of the magnetic field on the IR absorption of doubly distilled water. He found that the similarities of the shape of the graph of absorption versus wavelength, he obtained, were similar to the graph by Bruns *et al* [3]. He suggests that the changes seen by other authors could be as a result of impurities which dissolved in the water during the magnetic treatment. Kronenberg (1985) [30] stated, as did many other authors, that the interaction between magnetic fields and the hydrogen bonds between the water molecules is orders of magnitude too weak for direct effects. The weak interaction between the magnetic field and the hydrogen bonds could, however, be amplified to the breaking point by a resonance effect.

### *Solubility of Minerals*

Donaldson (1988) [15] found that magnetically treated fluids retain more calcium phosphate in solution. He also found that the solubility of zinc phosphate increases. In his opinion, the only feasible explanation is that the magnetic field modifies the crystal nuclei, thus changing the rate of precipitation that would result from changes in the rate of growth of crystals on these nuclei.

### *Surface Tension and Viscosity*

Verification of the breaking up of hydrogen bonds between the water molecules would be a reduction in viscosity and surface tension. Kronenberg (1985) [30] forced waters containing various minerals, to flow through a number of magnetic fields. He observed a reduction of surface tension and viscosity of up to 2 %. It seems improbable, however, that he would be able to measure such small differences with any degree of significance.

### *Hydration of Diamagnetic Ions*

Klassen [27] claimed that magnetic treatment reduced the hydration of diamagnetic ions, particularly those which stabilised the structure of water (lithium, magnesium, calcium, copper and others).

## PWT Functional Types

PWT devices may be classified under four categories of functional types: These are magnetic, electrostatic, catalytic, and HF or RF electric field. Various subclasses and variants also exist. One article lists 40 different PWT devices [8].

*Design Details*

The literature gives a some design details for PWT devices, some of which are crucial for the successful functioning of the device. In **Table 2.1** a list of the various PWT devices, encountered in this investigation , are listed, with some of their details.

**Table 2.1** List of the PWT devices encountered in this investigation

| Name | Type | Coating | Company |
|---|---|---|---|
| Polar | Magnetic field | None | Polar International (Sandefjord Norway) |
| Aquasal | High frequency electric field | None | Aquasal (PTY) LTD (Randburg South Africa) |
| HDL | Magnetic field | "Teflon" (on magnets) | HDL Fluid Dynamics Limited (Amersham England) |
| CEPI | Magnetic field | "Epoxy-Type" | N.V. CEPI-CO (Antwerp Belgium) |
| SGA | Ozone Generator and Electrostatic Field | None | Source Gas Analysers, Inc. |
| PTH | Catalytic Converter | None | HOP Engineering Ltd. (Tel Aviv Israel) |
| Superior | Magnetic field | None | Kemtune, Inc. (Fort Wayne USA.) |

- One magnetic field device extensively studied, i.e., the HDL (or Hydrodynamics, Bogalusa, Louisiana, USA) unit consists of Alnico magnets of composition 24 % Co, 14 % Ni, 8 % Al, 3 % Cu and the balance Fe. An array of these magnets are "Teflon" coated to prevent corrosion of these magnets, and mounted within a stainless steel tube. Flow is in the direction along the horizontal pole pieces of the magnets. A typical unit has a field strength of between $2.5 \times 10^{-3}$ to 2.5 tesla [16].

- Another design is described as the following. The water requiring treatment passes through the working gaps formed between the ends of adjacent ring magnets. The ring magnets with like poles on one face. This results in the water flowing through the unit, experiencing a large number of magnetic fields in parallel and series, and a field strength varying from point to point.

- Many authors state that the arrangement of magnets must be with like poles facing each other, so that the unit will have no measurable loss in power [50].

- Other designs can be as simple as placing two magnets with opposing poles across a pipe.

- The Aquasal is a high frequency electric field device that produces high frequency alternating electrical impulses between stainless steel tube and rod electrodes. It has design details stating that the impulse frequency is proportional to the water flow rate and the impulse field strength is proportional to the conductivity of the water. It is stated that this alternating electric field has a much more powerful effect than the magnetic field. There is also an advantage in that there is no galvanic corrosion of the device, thus giving the device a longer life expectancy.

- The P.T.H. unit which is stated to be a "catalytic converter", is built in two parts: a cylinder and inner core with canals which by virtue of their shape cause a Venturi (negative pressure) flow and intense friction of the water with metal. The device is made of alloys of noble and semi-noble metals.

What all the designs have in common is that the water must flow through the field, and in most designs, the flow is perpendicular to the field, be it magnetic, electrostatic or electric in nature. There are some exceptions where no field is present, i.e., the P.T.H. unit.

*Operating conditions*

- The solution should be saturated to such an extent, that it reaches supersaturation at the instant it passes through the magnetic field, so that it forms "primers", i.e., crystallisation centres. If the number of "primers" is sufficiently large, further precipitation would occur in the bulk of the solution and not on the heat exchanger surfaces [36]. Others claim that the efficiency of PWT devices is reduced, if saturation occurs [9].

- When a conducting fluid flows through a magnetic field, the force, **F**, experienced by charged particles is given by the equation:

  $$\mathbf{F} = q(\mathbf{v} \times \mathbf{B})$$

  Where q is the charge of the particle or ion, **v** is the fluid velocity and **B** the magnetic field with v perpendicular to **B**. This equation is the basis for most theories [12], and the need for the fluid to flow through the magnetic field. Linear flow rates vary from 0.1 $m.s^{-1}$ [36] to 2 $m.s^{-1}$ [20]. The fluid must obviously be conducting based on the 4 principles of magneto hydrodynamics [10]. When a conductive fluid flows perpendicularly to a magnetic field, a force is created that act on the moving charged particles in the fluid, to separate the negative and positive charged particles in the fluid. This force is called the Lorentz force [12].

- Iron colloids present in the water have an effect on the performance of PWT [24]. Hydrated forms of iron oxide have ferromagnetic properties, and the magnetic field forces them to move about intensely, causing crystallisation of scaling salts on these particles [4].

Some researchers in the Soviet Union have shown that the best result for the inhibition of scale formation in a power plant was a combination of magnetic treatment and the removal of the iron content either before or after the magnetic treatment [5]. The last statement clearly contradicts the first two statements.

- Reimers *et al.* [44] and Boichenko and Sapogin [6] have noted the influence of the water quality on the performance of electrostatic treatment.
  *Constituents that improve electrostatic treatment*: Hardness, alkalinity, TDS (total dissolved solids), oxidants, calcium, bicarbonate, nitrate and magnesium.
  *Constituents that inhibit electrostatic treatment:* Suspended solids, organics, reduced nitrogen compounds, silicates, reduced constituents and sulfhydril organic compounds. The pH can be changed by the magnetic field. Treatment is most effective where the pH is below 6. There is hardly any effect if the pH is above 7.5 [52].

- The manufacturers of the Polar unit have stated that turbulent flow must prevail during a very brief magnetic contact while the manufacturers of CEPI devices claim that turbulence downstream of treatment causes destructive perturbations to the magnetic treatment [3].

- The manufacturers of the Polar unit state that there must be a minimum distance of 2 metres of pipe between the Polar outlet and the first tap or machine to be protected from scale.

- Ellingsen *et al.* [20] found that when solutions are treated initially by a magnetic field, there are cases where little influence is measured, but if there is a storage time before treatment, an improvement of the influence by the field may occur.

- Aerated water is prejudicial to the efficiency of the treatment, probably because of the fact that oxygen being a paramagnetic, absorbs part of the energy which has been imparted to the liquid [52].

## Industrial investigations

The efficiency of PWT had been determined in a number of reported full-scale investigations. In this section, the a) efficacy of the units will be discussed, and b) a summary will be made of the measurement methods used.

### *Reported case studies*

A number of studies showed that PWT indeed had a positive effect:

- A case study conducted by Raisen [42], on several air conditioner condensers, a sugar mill, a chemical process cooling system, a boiler system and a steam generator showed that PWT is effective in scale prevention. The author evaluated the performance of PWT devices by observing the tenacity and nature of scale formation, by monitoring the heat transfer efficiency, by calculating the thickness of scale formation and by visual inspection of the system.

- It has also been reported Kvajic [[32] that the PWT devices do not only prevent scale formation, but also cause the existing scale to dissolve over an extended period of time, usually two to three weeks. The author reported accumulation of scale in the form of muddy sediment which is usually disposed of by a regular blow-down.

Opposed to these positive results, there are negative results on the efficacy of PWT devices from industrial applications of these devices:

- A case study conducted by Eliassen *et al.* [18] showed that the PWT did not affect the rate of corrosion of steel pipes over a four month period and no scale reduction was observed.
- In a field study performed by Caplan and Stegmayer [8] on the use of PWT device, for a boiler feedwater treatment in Ontario, Canada, no descaling was observed during the test period. The assessment was based on routine analysis of deposit samples and photographic documentation. At the end of a four month trial period boiler failure occurred and for most of the tubes replacement was necessitated.
- Kochmarsky (Appendix A of this report) from numerous investigations he carried out is confident that currently there is no convincing data on the efficiency of these devices.

From the literature, the efficacy of PWT for scale prevention with respect to specific applications remains unclear.

*Measurements*

A number of different methods were used by different researchers to quantify the effects of PWT. In the reported studies the evaluation of PWT for scale prevention in industrial investigations were made in two different ways;

- direct measurement of scale formation and
- indirect measurement of scale formation.

Direct measurements were done by measuring;

- mass of scale formed
- determining the thickness by measuring the diameter of the pipes
- visual inspection
- photographic documentation

Indirect measurements used to evaluate the PWT devices can be summarized as follows:

- changes in chemical water composition
- changes in the heat transfer efficiency
- nature and composition of scale deposits.

No conclusions can be drawn from the literature on whether some methods have been found to be superior to others.

## Mechanistic explanations

Many different mechanistic explanations, showing largely diverting approaches, are found in the literature. We have categorised them in two main groups of theories or models:

Model 1: The nucleation and crystal growth model
Model 2: The water structure model

### *Model 1: The nucleation and crystal growth model*

According to this model the physical field causes a charge distribution or polarisation around colloidal particles or hydrated ions present in the water giving rise to enhanced nucleation of $CaCO_3$ embryo crystals or nuclei in water supersaturated in calcium carbonate. This leads to more particles forming in the bulk of the solution which reduces the chance of scale forming reactions occurring on surfaces. Various approaches to this theme are found in the literature.

a) Sinhezuk *et al.* [45] stated that in saturated or sufficiently close to saturated solutions, there are always micro-regions of supersaturated states, in which crystallisation nuclei of precritical size may appear with a definite degree of probability. Before the solution reaches a certain level of supersaturation, however, the micro-nuclei with subcritical radius, i.e. $< r_{cr}$ are redissolved. By activation of the particles by an energy effect (magnetic, electric or ultrasonic), the energy can be adequate to overcome the potential barrier for the appearance of a nucleus of size greater than $r_{cr}$, at the same supersaturation levels as before. By sufficient magnetic treatment, conditions for the appearance of micro regions are increased. There are adequate fluctuations in these regions so that the change in concentration exceeds the critical concentration leading to the formation of particles with a size greater than $r_{cr}$. $r_{cr}$ is given as the critical particle size.

b) Wagner (1989) [53] stated that slow nucleation and slow crystal growth meant that large numbers of seed crystals must be formed in order to explain the effects of PWT.

c) Tombácz *et al.* (1991) [49] explains the aggregation of haematite colloids in terms of the Lorentz force, which may result in an asymmetric distribution of surface charge on colloid particles which does not relax after the particles leave the field. The ensuing dipolar interaction may enhance aggregation. Alternatively, the diffuse portion of the electrical double layer may become polarised, disturbing the symmetry of the double layer, deforming the ionic atmosphere and introducing a dipolar character. In addition, an oscillating ionic atmosphere may form when the Lorentz force is abruptly ended when the particles leave the field. This could cause fluctuating dipoles, also enhancing aggregation.

d) The PWT device may act as sacrificial anode, releasing ions such as iron and aluminium which could act as seed crystals for calcium carbonate. Busch *et al.* [7] postulated that iron released by the housing of a magnetic unit, due to the production of currents when conducting solutions are made to flow through a magnetic device, may serve as seed crystals promoting heterogeneous crystallisation centres for calcium carbonate, or may play a role in inhibiting homogeneous nucleation. Herzog (1989) [23] found that $Fe^{2+}$ and $Fe^{3+}$ inhibited the growth of calcite, but not that of aragonite. The concentration of the $Fe^{2+}$ was 5.6 ppm.

e) According to findings by Meyer (1984) [37], small amounts of certain inorganic and organic impurities have a marked slow-down effect on the crystal growth rate of calcite. By using the pH-stat method and working at a pH of 8.23 and temperature of 20 °C, he obtained quantitative values for 34 ionic additives. He assumed that the inhibition of crystal growth occurs by the blocking of surface growth sites by adsorbed molecules or ions of the additive. The adsorption may be described by the Langmuir-Volmer isotherm:

$$f/(1-f) = Kc_{add}$$

Where:

$f$ is the fraction of occupied adsorption sites which may be terrace, ledge or kink sites,
$c_{add}$ is the concentration of the additive in solution, and
$K$ is a constant.

Anionic Additives - Large inhibitory efficiencies are found for the condensed phosphates. The concentrations of certain phosphates needed to inhibit the growth rate of calcite by 80 %, were between $8 \times 10^{-8}$ and $6 \times 10^{-9}$ M, which is very low.
Cationic Additives - Concentrations of some metal ions needed to inhibit the growth of calcite by 80 %, were extremely low, for example:

$Fe^{2+} = 6 \times 10^{-8}$ M (3.35 μg/l)
$Zn^{2+} = 2 \times 10^{-7}$ M (13 μg/l)
$Ce^{3+} = 4 \times 10^{-7}$ M (56 μg/l)
$Pb^{2+} = 8 \times 10^{-7}$ M (165 μg/l)

*Organic Additives* - Some organic additives also had inhibitory effects on the growth of calcite, for example, "tris" (tris-(hydroxymethyl)-aminomethane) and citrate (citric acid neutralised with NaOH) with concentrations on the order of $5 \times 10^{-5}$ and $5 \times 10^{-7}$ M, respectively.

Meyer [37] pointed out that only $10^{-8}$ M $Fe^{2+}$ is needed to halve the growth rate of calcite with an initial growth rate of 0.26 monolayers per minute. Even if the $Fe^{2+}$ was totally adsorbed onto the surface of the crystallites, only about 0.6 % of the $5 \times 10^{14}$ $cm^{-2}$ surface sites would be covered. Therefore growth inhibition by "blocking" the terrace cites can be ruled out. Calculations reveal that complete blocking of the growth steps and kinks by adsorbed $Fe^{2+}$ ions would, however, be possible. Impurity ions are more strongly bound to these sites than at terrace sites. The different efficiencies of the different additives in inhibiting calcite growth is explained in the literature by the different adsorption strengths of the additives. Meyer, however, found no systematic correlation for cations. From the above explanation given by Meyer, some of the effects seen by other authors could be explained in terms of trace amounts of impurities being released by the PWT devices.

### *Model 2: The water structure model*

It is proposed by several authors that the effect of Lorentz forces is the predominant reason for the changes observed when scale forming solutions are exposed to electromagnetic fields. The main objection to this assumption is that the energy imparted to the system due to the magnetic field is negligibly small in comparison to the H-bond energy of 4,5 kcal/mol. According to Belova [5] this critique does not take into consideration the fact that the bond does not have to be destroyed completely, but could also be changed or weakened, thus requiring less energy. The author theorized that since charged particles moving in a plane perpendicular to the magnetic flux will execute circular motion and those parallel to the field, helical motion, the motion will not be uniform if the field is not uniform. This will result in a reduction of freedom of motion, increase in collisions and therefore an increase in nucleation. The prerequisite for this theory is of course that the field must have either a gradient or be of an alternating sort.

Boichenko [6] stated that since the water molecule exists partly as $OH^-$ and $H_3O^+$ ions due to the ionization of the molecule , these charged particles will move in a circular trajectory, called a cycloid. The hydroxide and hydronium ions are combined with water molecules in an annular association, by means of collective H-bonds. The arc length of this cycloid is proportional to the ratio of the flow velocity and the magnetic field strength. Thus a change in the structure of the water molecule is expected after treatment with a magnetic field. These associations will then have the effect that fewer water molecules are available, therefore decreasing the hydration surfaces of particles ( negative hydration according to Samoilov), which will influence the electrical double layer. This will evidently result in the coagulation of hydrophobic particles and the precipitation in the bulk of the solution will be promoted. .

Srebrenik [46] proposed a quantum mechanical model. The formation of eigenstate water clusters in the presence of a magnetic field due to the action of Lorentz forces, jolting the water molecules surrounding the calcium ion, is predicted. The spins of the clusters align during treatment. The magnetic field influences the clusters, causing re-phasing. These clusters do not dissociate or exchange water molecules to the rest of the solution, thus serving as homogeneous nuclei.

### **Summary**

In summary then, there are many claims put forward and just as many effects observed. Some of the claims and effects are obviously impossible and far fetched while others seem plausible, if only on paper. The methods used by some of the researchers to verify claims are clearly inadequate and many interpretations would not survive scientific scrutiny.

# 3. LABORATORY INVESTIGATIONS

## Experimental criteria and design

Experiments were designed such that complete control over all the important physical and chemical parameters was assured. Any differences in the measured parameters between treated solution and its control could then confidently be attributed to the treatment. Only glassware was used to avoid any metal contamination from the experimental system.

*Parameters that were controlled:*

- all factors related to the test solution e.g. preparation procedure, storage procedure and age of solutions, using steam-cleaned glassware, etc.
- factors related to the treatment e.g. the use of an exactly replicated control (without electromagnetic component) devices, flow rates, temperatures,

*Parameters that were tested:*

The test parameters were selected based on various claims and effects ascribed to the interaction of electromagnetic fields with scale forming waters. The claims and effects were grouped according to the physico-chemical principle underlying the phenomenon and one or more parameters selected to test these particular claims or effects. The main groups identified were:

- Effects that could be attributed to a change in water structure. Analytical techniques used to probe possible effects on water structure included NMR (Nuclear Magnetic Resonance), FTIR (Fourier Transform Infrared) and surface tension measurements.
- Effects that could be attributed to a change in the charge distribution around particles. Analytical techniques to probe possible effects of charge distribution include particle size and zeta potential measurements, XRD (X-ray Diffraction) , SEM (Scanning Electron Microscopy).
- Effects that could be attributed to impurities, such as listed in Table 3.3, released from the device which could interfere with the nucleation and crystal growth processes.

*Experimental procedures:*

Experimental procedures were developed to ensure that test solutions could be prepared with the required degree of reproducibility. The most important laboratory methods developed for this study are summarised below. These are: i) cleaning procedures (ii) procedures to prepare metastable supersaturated $CaCO_3$ solutions.

(i) Cleaning procedures

Due to the fact that premature nucleation of $CaCO_3$ had to be avoided at all cost, extreme care was taken with the cleaning of equipment. Efficient cleaning minimised the possibility of any foreign particle matter which could induce heterogeneous nucleation at an inopportune moment during the experiments. Equipment, including test rig components, was soaked in 10% $HNO_3$ for 12 hours, rinsed with deionised water until free from traces of acid and then steam cleaned. In the steam cleaning procedure a jet of steam was projected onto the inner surfaces of equipment that would come into contact with the test solutions. It proved to be the only way to ensure a satisfactory removal of particles adhering to surfaces.

(ii) Preparation of test solutions

High quality deionised water ( conductivity 0.06 µS $cm^{-1}$ ) freshly extracted from a Millipore deionising system consisting of an active carbon filter, two mixed-bed resins and a diaphragm filter, was used to prepare test solutions. Two procedures were used to prepare metastable supersaturated $CaCO_3$ solutions:

The $CO_2$ method

A sufficiently stable supersaturated $CaCO_3$ solution with suitable scale forming potential was prepared by bubbling $CO_2(g)$ using a glass frit as dispersing nozzle, through a suspension of 3.8 g of $CaCO_3$ (Merck analar) in 5 l of water for 1 hour. The suspension was suction filtered rapidly through 0.45 µ Millipore cellulose acetate membrane filters to remove undissolved calcium carbonate and the calcium concentration determined by ICP-OES. Deionised water and tap water with a typical composition summarized in Table 3.1 were used. The required final concentration for calcium bicarbonate solutions was obtained by dilution of the ca 300 mg/l Ca stock solution with deionised water.

**Table 3.1** Chemical analysis of typical tap water (All concentrations in mg/l except when indicated otherwise).

| Parameter | Quantity | Parameter | Quantity | Parameter | Quantity |
|---|---|---|---|---|---|
| conductivity (μS/cm) | 125 | boron | <0.1 | selenium (μg/l) | <0.1 |
| turbidity (NTU) | 0.7 | cobalt | <0.1 | active silica | 2.6 |
| pH | 7.96 | copper | <0.1 | total silica | 4.0 |
| alkalinity ($CaCO_3$) | 76 | iron | <0.05 | ammonia as N | 0.12 |
| hardness ($CaCO_3$) | 78 | manganese | <0.03 | orthophosphate as P | 0.03 |
| calcium | 19 | lead | <0.03 | nitrate as N | 0.23 |
| magnesium | 7.6 | zinc * | <0.1 | nitrite as N | 0.11 |
| sodium | 17 | nickel | <0.1 | chloride | 14 |
| potassium | 4 | aluminium | 0.15 | fluoride | 0.28 |
| cadmium (μg/l) | <30 | mercury (μg/l) | <0.1 | sulphate | 16 |
| chromium | <0.05 | arsenic (μg/l) | <0.1 | phenol (μg/l) | 1.1 |

* Zinc concentrations were found to vary from day to day between 40 and 60 μg/l

The mixture method

Due to the fact that the $CO_2$ method resulted in a labile system with an unknown amount of $CO_2$ escaping from the prepared solution, it was decided to use mixtures of calcium and bicarbonate salts to prepare a calcium bicarbonate solution. The $CaCl_2$ and $NaHCO_3$ salts were tried first. With some precipitation experiments ( calcium bicarbonate solution spiked with Zn ) using the BATCH method (see (iii) following page), the results seemed to be not as evident as when the $CO_2$ method was used. Due to the possible complexation reactions of Zn with chloride ( $ZnCl_3^{1-}$ (aq), $ZnCl_2$ (aq) ) it was then decided to change the calcium salt to the nitrate.
$Ca(NO_3)_2.4H_2O$ (Unilab from SAARCHEM) and $NaHCO_3$ ( AR from SAARCHEM) were then used. The solution was prepared by making the two solutions separately in acid cleaned glass containers and then mixing the two solutions with magnetic stirring. It was found, however, that the pH of the resulting bicarbonate solution was already at 7.5 - 7.6 and an induction time was not observed at all, because nucleation had already started . After investigating the lowering of the initial pH with carbon dioxide gas, it was decided that the best control would be obtained if the pH was lowered by the addition of acid. The acid chosen was nitric acid (AR from Merck) since

the anion was already a common ion. The acid was added to the bicarbonate solution in concentrated form in order to reduce dilution errors. The solution was allowed to equilibrate for at least 30 minutes. The calcium solution was then added and allowed to equilibrate for another 10 minutes. The pH was controlled continuously to ensure that it would not increase to a point where possible nucleation could start. The pH of the solution was controlled to be between 7.2 and 7.4. A fresh solution was prepared for every experiment.

### (iii) The batch method for determining crystallization kinetics

Kinetics of calcium carbonate crystallization from supersaturated calcium carbonate solutions were studied by using a batch method in which a test and control could be run simultaneously in triplicate. $CaCO_3$ solutions were always supersaturated. The concentration was, however, chosen in such a way that the solution was metastable with regard to precipitation. This means that the precipitation could take place thermodynamically but kinetically the nucleation rate was too slow to produce precipitation for the duration of the experiment if kept at ambient temperature. Precipitation thus only started after prolonged heating at 37°C. Extreme care was taken to ensure that all experimental conditions were exactly the same for test and control run. These included the parameters: temperature, concentration, age of solution, condition of glassware, and pH.

Calcium carbonate solutions, made up with deionised water or tap water, typically 150 mg/l Ca, were circulated in the test loop with or without device for 10 min. Aliquots from the same stock solution were used for test and control runs. 200-ml samples in triplicate of the treated solutions were transferred to 250 ml glass beakers, covered with Parafilm and placed on a multi-point magnetic stirrer assembly (the rate of stirring was exactly the same at all stirring positions) in a waterbath at 37 °C after a predetermined waiting time, typically 15 min. The pH of six solutions, three tests and three controls, were followed simultaneously as a function of time for up to 6 h. The same pH probe was used to monitor all six solutions to ensure comparability of the measurements.

### (iv) Determination of crystal morphology and crystal structure

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

### *Physical water treatment devices*

Type: Permanent magnet

The Polar Model PD15 illustrated in Figure 3.1 was obtained from Polar International, Sandefjord

, Norway. It consists of a steel cup which houses a well-type magnet. The size of the magnetic gaps on two sides is only 1.5 mm across which enables concentration of the magnetic field in the active region to a value of 0.7 tesla. The unit is as also provided with a stainless steel strainer fitted with a central rod which acts as a collector for magnetic particles that might be present in the water to be treated. This prevents the accumulation of magnetic particles in the magnet and clogging the magnetic gaps. A 1.5 cm zinc sleeve is fitted to the rod for corrosion protection. The composition of the special alloy used in the magnet material was not disclosed by the manufacturer. The unit is specified to operate at a linear flow rate of 2 m $s^{-1}$.

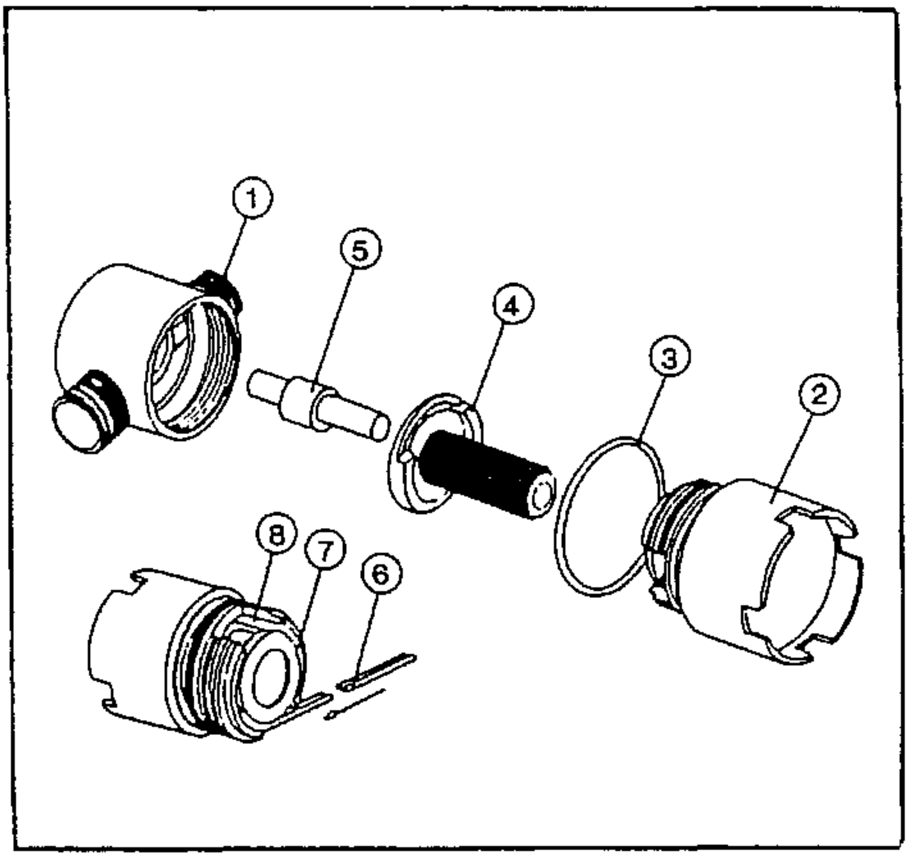

**Figure 3.1** Diagramme of Polar Model PD15 magnetic water treatment device. 1) base cup 2) treatment unit 3) O-ring seal 4) strainer basket 5) magnetic rod with zinc anode 6) plastic strips for flow rate control 7) steel pole shoe ring 8) ring shaped magnet

Type: High frequency electric field

The Aquasal Type 90-2 illustrated in Figure 3.2 was obtained from Arndt Weber & Associates, Johannesburg, South Africa. It consists of a 38 mm diameter stainless steel tube outer electrode and a 10 mm diameter stainless steel rod (225 mm long) inner electrode mounted in a concentric fashion. The high frequency field (ca 6 000 Hz) across the electrodes consists of square wave pulses, 14 volt positive and 18 volt negative. The relative values of the positive and negative signals changed slightly with the conductivity of the feed water. Currents increased with conductivity and values up to 1 amp were measured at conductivities of 1 000 $\mu S.cm^{-1}$. No minimum flow rates are specified for this unit.

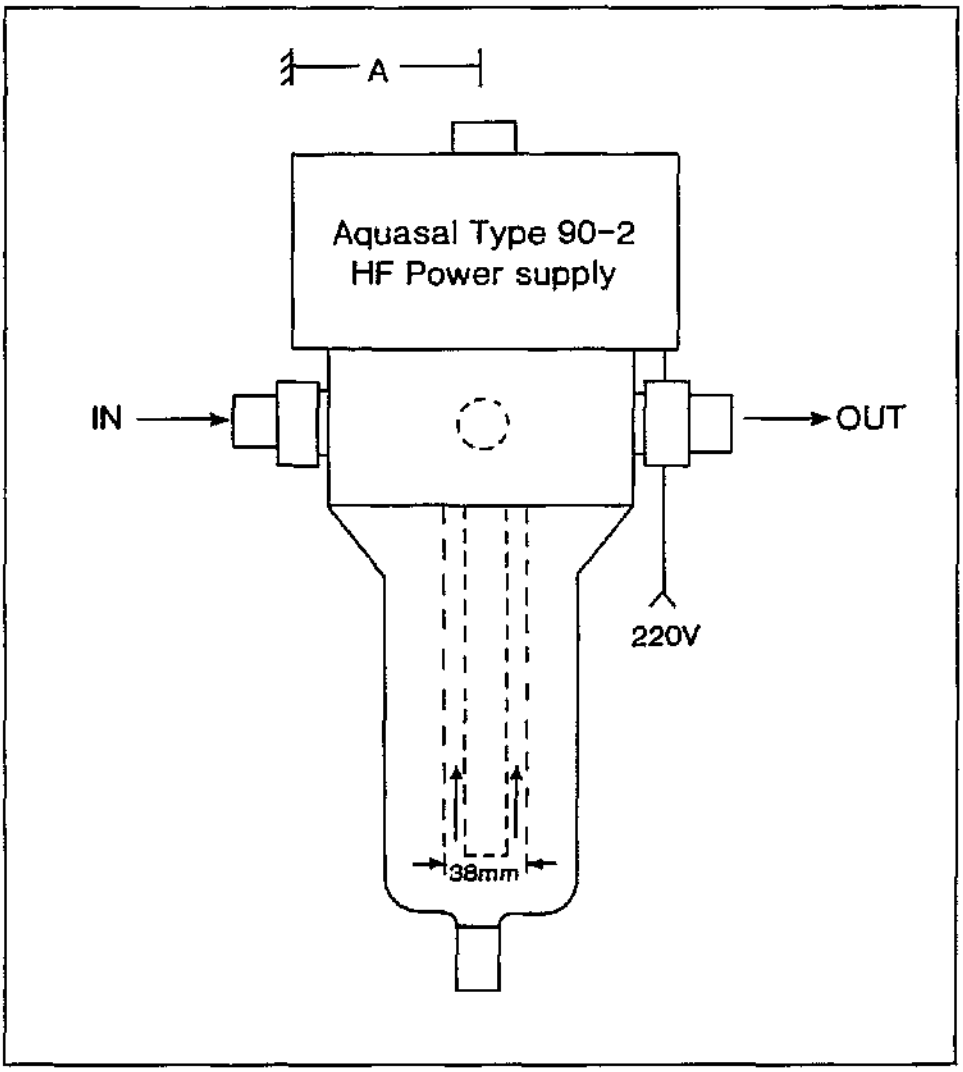

**Figure 3.2** Diagramme of Aquasal high frequency electric field water treatment device.

Type: Catalytic converter

The PTH Model PTH 20A was obtained from PTH, Haifa, Israel. It consists of an alloy grid made out of an unspecified selection of base and noble metals mounted in a stainless steel tube. The manufacturer specifies that the unit must be earthed when in use. Minimum flow rates of 10 *l*/min are required.

Type: Permanent magnet with inert coating

The CEPI model was obtained from CEPI, Brussels, Belgium. The permanent magnet is coated with an inert epoxy layer. Specified minimum flow rate is 35 l $\mathrm{min}^{-1}$.

*Typical laboratory test loops*

The test loops made out of 20 mm PVC piping and used for testing the devices, are depicted in Fig.3.3(a) for the Polar and Fig.3.3(b) for the Aquasal and PTH units. In the case of the Polar device, an exact replica made out of PVC was used for control runs. In the case of the Aquasal and PTH units, a piece of PVC tubing was inserted in place of the device when dummy runs were performed. Different test loops were used to allow for the substantially different minimum flow rates required by the different devices.

- The flow rate for the Aquasal was 6 *l*/min. For a typical 3 *l* sample the exposure rate was two times per minute in a 2.5 m circuit.
- The flow rate in the 4 m long test loop for the Polar was 2 *l*/min. For a typical sample of 1*l* the exposure rate was also two times per minute.
- The flow rate for the PTH unit was 35 *l*/min. For a typical sample of 10 *l* the exposure rate was 3.5 times per minute.

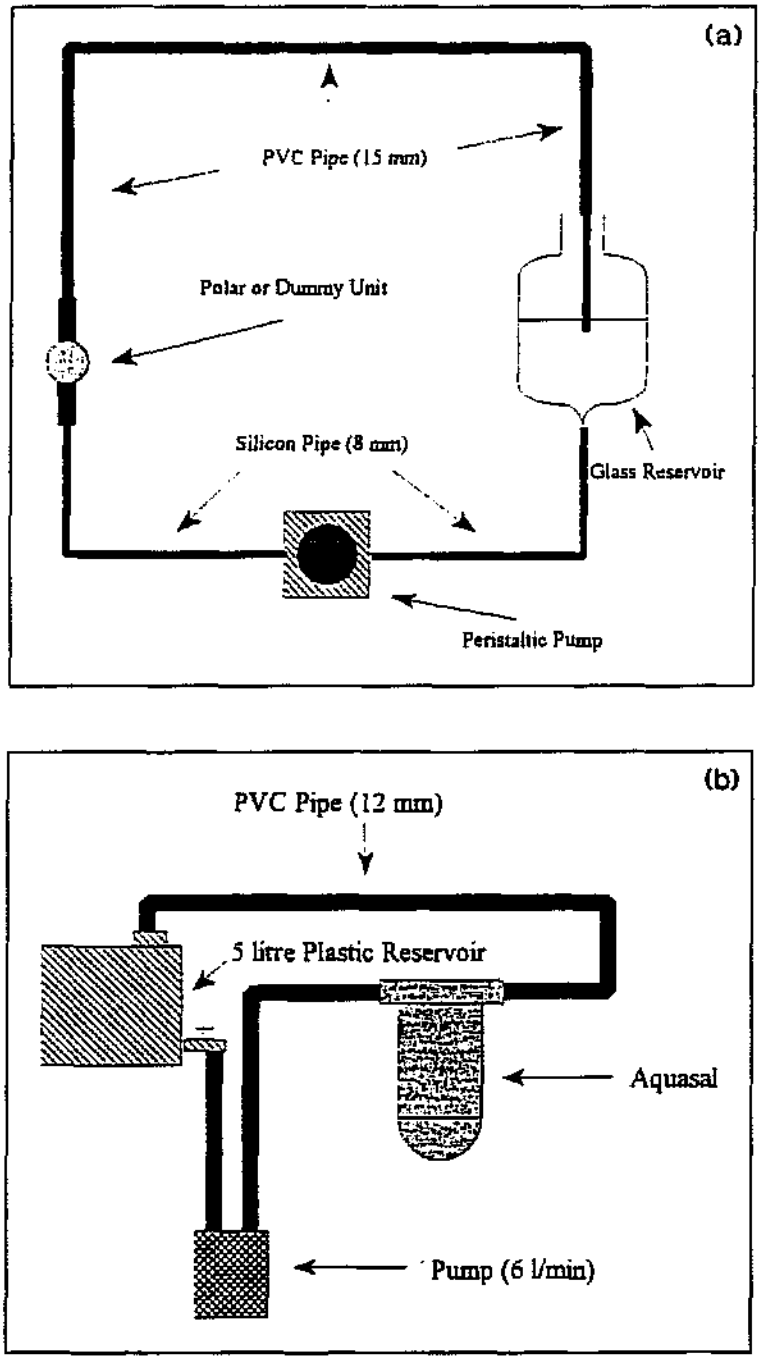

**Figure 3.3(a)** Test loop for Polar antiscaling device
**(b)** Test loop for Aquasal and PTH antiscaling devices

## Results and discussion

*Precipitation chemistry of $CaCO_3$*

A brief review of the basic precipitation chemistry of $CaCO_3$ would facilitate the interpretation of results obtained in the crystallization kinetic experiments and is given below. A fundamental aspect of scale formation involving $CaCO_3$ is the relationship between $CO_2(aq)$ concentration in the solution and the solubility of $CaCO_3$ and the effect of temperature on this solubility. The solubility of $CaCO_3$ varies inversely with temperature. On heating $CO_2$ escapes, favouring the bicarbonate decomposition reaction followed by calcium carbonate precipitation:

$$\begin{array}{lcccccccc} 2HCO_3^- & & & = & CO_2(aq) & + & CO_3^{2-} & + & H_2O \\ Ca^{2+} & + & CO_3^{2-} & = & CaCO_3(s) & & & & \\ \hline Ca^{2+} & + & 2HCO_3^- & = & CaCO_3(s) & + & CO_2(aq) & + & H_20 \end{array}$$

At temperatures < 50°C calcite is the preferred crystal structure and at temperatures > 60°C aragonite predominates [54]. In the region between 50° and 60 °C both forms can occur. It must also be kept in mind that aragonite ($K_{sp} = 4.6\times10^{-9}$) is slightly more soluble than calcite ($K_{sp} = 3.3\times10^{-9}$). A third form, vaterite, which is unstable and transforms into calcite especially at high temperatures, also occurs occasionally. It is very rare and for all practical purposes does not exist in nature [35].

The metastable region for $CaCO_3$ is exceptionally large. This region is characterised by the non-precipitation of calcium carbonate despite the fact that the solution is supersaturated. The phenomenon is caused by the fact that nucleation is limited by the relatively high solubility of microscopically small crystals initially formed during nucleation. The width of the metastable region is given thermodynamically by the free energy of formation of a nucleus in homogeneous nucleation. This energy can be lowered by metal surfaces or the presence of colloidal particles that might act as seed crystals whereby the width of the metastable region is decreased. This is called heterogeneous nucleation and is the dominant mechanism during scale formation. This phenomenon made it possible to prepare supersaturated metastable solutions which could be used in time-dependence experiments without danger of premature precipitation occurring.

*Crystallization kinetics*

The crystallization reaction of calcium carbonate can conveniently be studied by following the pH of the precipitating solution as a function of time. The data from these experiments can then be presented graphically as precipitation curves, which are plots of pH vs time. Precipitation curves obtained for the three antiscaling devices are shown in Fig. 3.4 (top) for the (a) Polar, (b) PTH, and (c) Aquasal devices. The equivalent curves for the controls are included in each case.

The curves can be interpreted by referring to the abovementioned chemical equilibria. The initial rise in pH with time is caused by the removal of $CO_2$ from the solution as the temperature is increased from ambient to 37 °C. Typically the experimental temperature of 37 °C was obtained in the test solution within 5 minutes after introducing the test solutions to the waterbath. The sharp downward adjustment of the pH marks the onset of the precipitation of solid $CaCO_3$. It was also possible to confirm this by the visible appearance of a slight turbidity in the solutions. The time interval required for the precipitation to start, the induction period, could be determined in this way.

Investigation of the crystal morphology of the precipitates by scanning electron microscopy provided another experimental parameter to obtain information with regard to possible effects on the precipitation process.
The measurable effects caused by the three units on the crystallization process of $CaCO_3$ were compared to that observed for the controls and are summarized in Table 3.2.
These effects were:

- increase in induction time i.e. the time needed for the precipitation reaction to begin
- formation of calcium carbonate in the aragonite form rather than calcite.

**Table 3.2** Observed delay times, Δt, and crystal form of precipitates for different PWT devices.

| Device | Δt min | Crystal form | µg/l of Zn released/10 min |
|---|---|---|---|
| Polar | 35±4 | 80-100% aragonite | 100 |
| Polar coated | 0 | 100% calcite | 0 |
| Aquasal | 6±2 | 50-80% aragonite | 14 |
| Aquasal coated | 0 | 100% calcite | 0 |
| PTH | 20±1 | 50-80% aragonite | 20 |
| PTH coated | 0 | 100% calcite | 0 |
| Control | 0 | 100% calcite | 0 |
| Zn added to control | 33±4 | 100% aragonite | 100 |

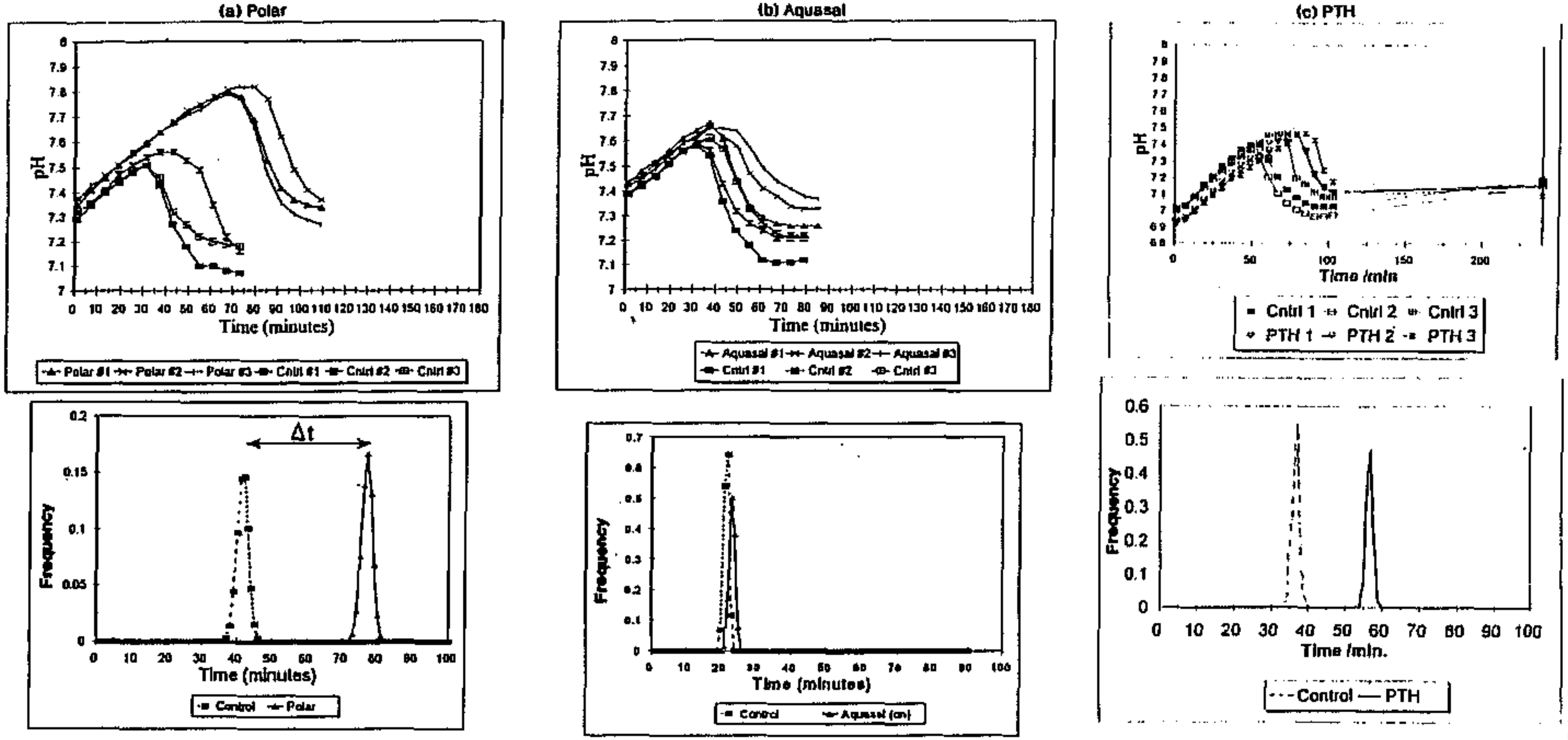

**Figure 3.4** **Top:** Typical precipitation curves for $CaCO_3$ from $Ca(HCO_3)_2$ solutions that were exposed to an antiscaling device and its control
(a) Polar (b) Aquasal (c) PTH

**Bottom:** Guassian distributions of induction times for $CaCO_3$ precipitation for treated and non-treated $Ca(HCO_3)_2$ solutions showing the average delay time.
(a) Polar (b) Aquasal (c) PTH

The effective delay time, $\Delta t$, was determined from the difference between the average induction time observed for the device and that of the control. The standard deviation for each set was used to calculate a Gaussian distribution for the measured induction times. Graphical representations of these distributions, which illustrate the statistical significance of the delay time are shown in Fig.3.4 (bottom) for a) Polar,(b) Aquasal and c) PTH.
In subsequent experiments all internal surfaces that came into contact with the test solution were coated with a silicone based liquid polymer (Dow Corning R43117) in order to determine whether contact of the solution with the internal surfaces was of any consequence. Results showed that by eliminating direct contact with internal surfaces the delay times for all devices were essentially reduced to zero, i.e. the precipitation modification effect disappeared That means no observable difference in induction times was evident when compared with the controls. A typical result is given in Fig.3.5. This result obviously pointed to an effect caused by some surface reaction or the release of species from the surface which might increase the nucleation time of calcium carbonate solutions. The magnitude of the delay time was taken as an indication of the scale inhibition potential of the treatment.

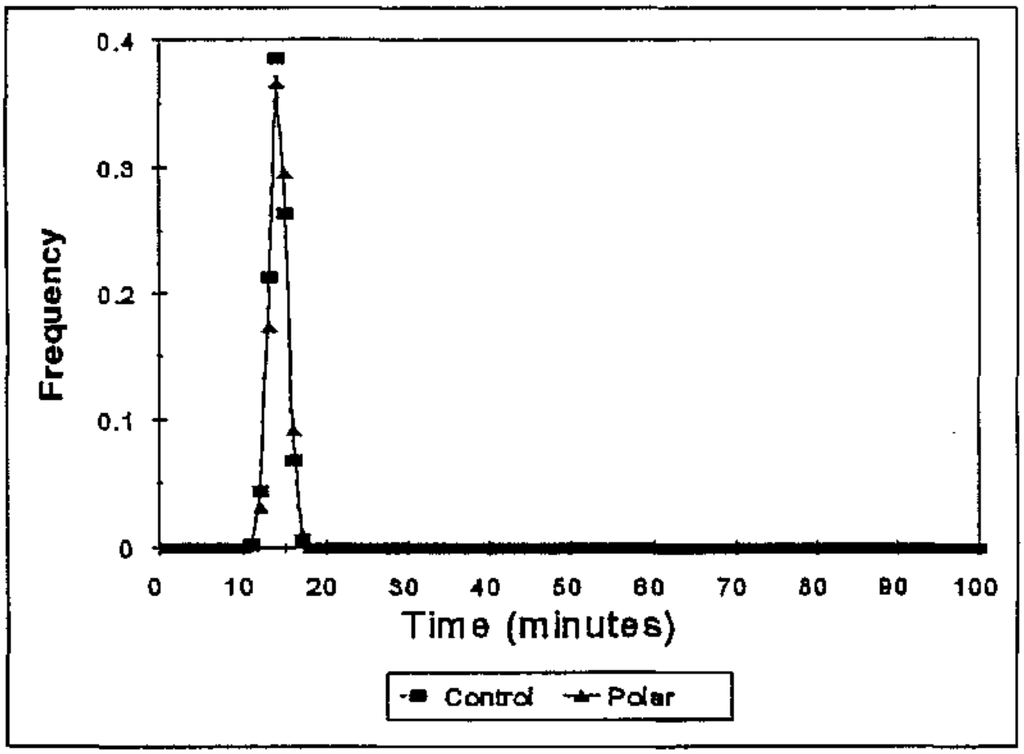

**Figure 3.5** Gaussian distributions of induction times for coated Polar unit showing zero delay time between control and treated solution

The amount of impurities introduced into the solution was determined for each device by circulating a known volume of 0.001 M KCl solution in deionised water at a constant flow rate for one hour. The metal concentrations were determined by ICP-MS and the results are summarized in Table 3.3. The POLAR, PTH, and AQUASAL units released substantial quantities of zinc while for the PTH unit other metals like copper and nickel were also found. In subsequent experiments the release rate of metals was found to be linear with time.

**Table 3.3** Amount of metal released (µg/l per hour) into a 0.001 M KCl solution at constant flow rates as required by each device ( see Experimental criteria and design).

| Element | Polar | Polar blank | Aquasal | Aquasal blank | PTH | PTH blank |
|---|---|---|---|---|---|---|
| Al | 10 | <10 | <10 | <10 | <10 | <0 |
| Ba | <10 | <10 | <10 | <10 | <10 | <10 |
| Co | 54 | <5 | <5 | <5 | <5 | <5 |
| Cr | <5 | <5 | <5 | <5 | <5 | <5 |
| Cu | <5 | <5 | <5 | <5 | 24 | <5 |
| Fe | <100 | <100 | <100 | <100 | <100 | <100 |
| Nd | <10 | <10 | <10 | <10 | <10 | <10 |
| Ni | 10 | <10 | <10 | <10 | 78 | <10 |
| Zn | 589 | 8 | 124 | 15 | 118 | 8 |

It was found that the effectiveness of the devices tended to deteriorate with time during frequent use. This was caused by scale build-up on the internal surfaces effectively reducing the amount of metal ions released into the feed stream. After cleaning the surfaces with dilute acetic acid the emission values recovered and the same delay times as before were observed. In the case of the Polar, Zn emissions from the magnet and the Zn sleeve in the strainer were of similar magnitude. The amount of zinc released per cycle ranged from 5 µg/l for the Polar, 0.5 µg/l for the PTH and 0.4 µg/l for the Aquasal. The rate of metal release is strongly dependent on the conductivity of the circulating solution. The rate in deionised water was approximately 10 times lower than for 0.001 M KCl.

*Crystal morphology*

Scanning electron microscopy of the precipitated crystals revealed a consistent pattern for all three devices and is summarised in Table 3.2. Treated solutions consistently produced calcium carbonate in the aragonite form whereas the controls gave calcite. Occasionally treated and untreated solutions gave rise to $CaCO_3$ precipitating in the vaterite form. This seemed to appear at random and no correlation between its formation and experimental conditions could be established. When the internal surfaces were coated, the crystal morphology reverted to calcite. It should be pointed out that calcite would be the preferred crystal form under the experimental conditions used. It is known that trace impurities present in a solution during precipitation can alter the crystallographic form because $CaCO_3$ precipitates in the calcite form at temperatures below 40 °C . It is also known that trace impurities inhibit the crystal growth rate of calcium carbonate [37]. Both these facts point to the role of metal impurities, especially zinc, in explaining the observed effects of three different physical water treatment devices.

*The Zn hypothesis*

In order to prove this hypothesis a number of experiments were conducted in which small amounts of $Zn^{2+}$ ions were added to supersaturated calcium carbonate solutions containing 150 μg/l Ca. The crystallisation reaction was then followed as before at 37°C and the precipitation curves compared.

The concentration of Zn generated in a calcium carbonate solution, 150 μg Ca/l, and which was exposed to the Polar device for 10 min, was ca 100 μg/l. The average delay time measured for this solution was 35±3 min. By adding 100 μg/l of Zn as freshly prepared $ZnSO_4$ to a calcium carbonate solution containing 150 μg/l Ca, an average delay time of 33±4 min was obtained. Actual precipitation curves for $Ca(HCO_3)_2$ solutions containing 50 μg/l Zn are shown in Fig.3.6. Further support came from the fact that the crystal morphology was aragonite rather than calcite. These results were repeated consistently for different Zn concentrations and different Ca concentrations.

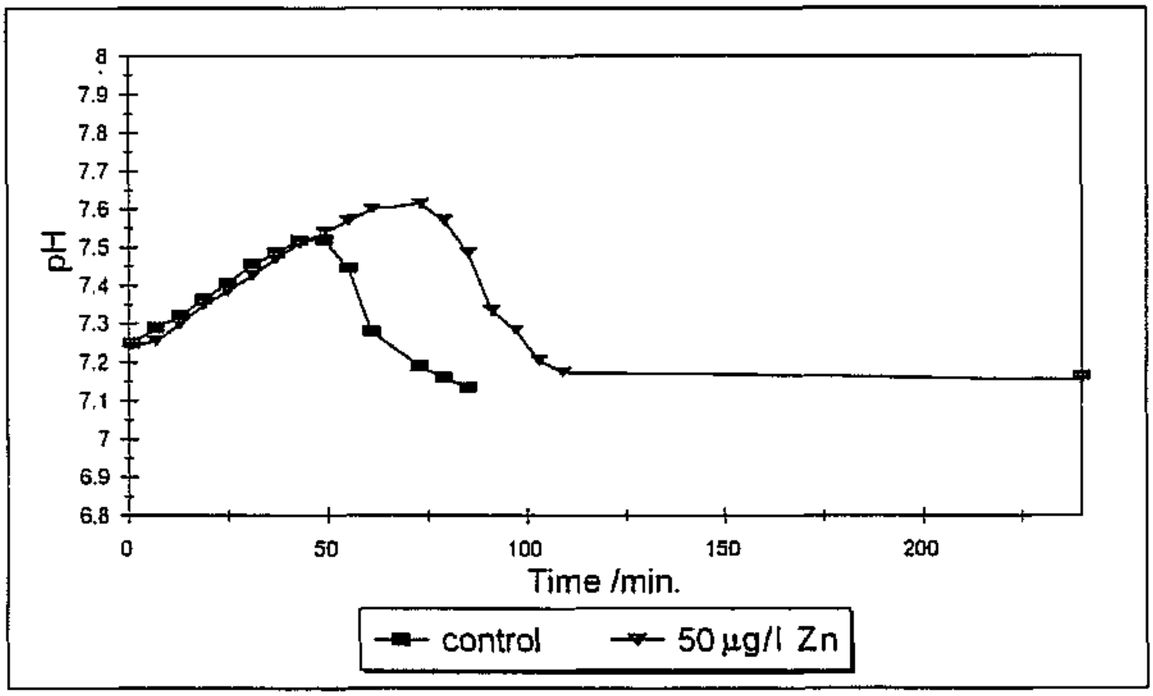

**Figure 3.6** Typical precipitation curves for calcium carbonate from calcium bicarbonate solutions containing 50 μg/l Zn vs. the control containing no Zn

*Memory effect*

It is claimed by manufacturers that the effects of PWT devices are still noticeable for periods up to 72 h after treatment. In a series of experiments, 50 µg/l of freshly prepared $ZnSO_4$ solution was added to four supersaturated calcium carbonate solutions . These solutions were then equilibrated for different waiting periods ranging from 1 minute to 24 h after which precipitation reactions were induced as before. Delay times gradually decreased with time, from 35 min at 1 minute, to 7 min after 24 h.

Polarographic results obtained by following the height of the zinc polarographic peak after introducing 50 µg/l of freshly prepared $ZnSO_4$ into a 0.001 M $NaHCO_3$ solution revealed a slow decrease in peak height over time. This indicated the transformation of free zinc into polarographically inactive species. By implication these species could also be less effective in influencing the $CaCO_3$ crystallization reaction. Adsorption of zinc species could also have been responsible for the observed reduction in peak heights. However, a similar experiment using a 0.001 M KCl solution to which 50 µg/l zinc was added produced no change in zinc peak height over a 24-hour period. The speciation in such a solution is, however, different with chloro complexes of zinc predominating.

Speciation calculations for the zinc/bicarbonate system using Minteqa2 [1] produced the distribution diagramme in the pH range 6.5 to 9 shown in Fig. 3.7.

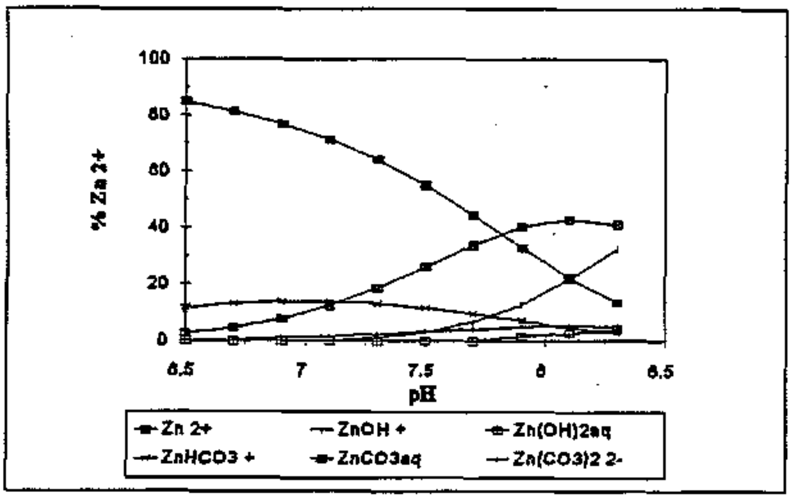

**Figure 3.7** Species distribution for the $ZnSO_4/NaHCO_3$ system, $[Zn]_{tot}$ = 50µg/l and $[HCO_3]$=0.001 M

At pH above 7.5, which was typical for the solutions studied, the zinc carbonate complex species, $ZnCO_3(aq)$ and $Zn(CO_3)_2(aq)$ were predominant. These complexes are relatively stable, effectively preventing the hydrolysis of $Zn^{2+}$ to $Zn(OH)_2(s)$ which would normally occur at this pH.

One could speculate on the relative ineffectiveness of a neutral species like $ZnCO_3(aq)$ to block growth sites on $CaCO_3$ crystals if one assumes a surface adsorption mechanism as part of the scale forming process. It is, however, beyond the scope of this investigation to present a proper mechanistic explanation of the observed phenomena. Further work is in progress to study possible mechanisms

*Development of Zn process for scale prevention*

The efficiency of Zn to decrease the rate of $CaCO_3$ crystallization was tested by spiking 150 µg/l $CaCO_3$ solutions with decreasing amounts of zinc, ranging from 500 µg/l to 10 µg/l. Even at the 10 µg/l level an increase in the nucleation time was measured and aragonite crystals were formed in stead of calcite. It was shown that the smaller the supersaturation of $CaCO_3$ the smaller was the amount of zinc required to produce the same antiscaling effect. Organic ligands, like EDTA, which form strong coordination complexes with Ca destroy the effect of µg/l levels of zinc when present in mg/l levels. EDTA actually reduces the nucleation time. On the other hand, high concentrations of up to 1 000 µg/ml of inorganic anions like chloride and sulphate can be tolerated without interfering substantially with the zinc scale inhibition effect.

Two procedures of introducing controlled amounts of zinc to feed water were considered and briefly tested on laboratory scale: 1) Dosage of a concentrated solution of $ZnSO_4$ via a peristaltic pump 2) Dosage via controlled electrolysis using a Zn electrode and pulsed DC power supply.

In once-through type experiments, 300 mg/l $Ca(HCO_3)_2$ solutions spiked with 150 µg/l $ZnSO_4$ ( Zn concentration equals 1/2000 of the Ca concentration) by either dosage method, was pumped through glass coil heat exchangers ( 5 mm i.d. x 1 m ) submerged in a waterbath held at constant temperature of 53 °C. The amount of scale formed after 1 hour was determined by dissolving it in 5% $HNO_3$ and measuring the Ca concentration by atomic absorption spectrometry. The percentage reduction in scale formed relative to a control without zinc, ranged between 50 and 80 %.

*Effects of fields on the physical and chemical properties of water*

- NMR and Infrared spectra of water

It was reported (Kochmarsky 1995, private communication) that changes in the NMR spectra of magnetically treated water were observed by scientists at the University of Kiev, Ukraine. Although such an effect was unlikely to be measured we nevertheless repeated a similar experiment using tap water spiked with $D_2O$. No differences were found between water exposed to a magnetic device ( Hydrodynamics unit) and a control.

Various references reporting changes in infrared spectra of water exposed to magnetic fields are found in the literature. In our experiments where extreme care was taken to avoid any form of contamination no discernable differences were found in the spectral region 400 to 4000 $cm^{-1}$.

- Conductivity

Following up reports [16,31] of increased solubility of various slightly soluble salts on exposure to magnetic water treatment devices we repeated some conductivity based experiments. The results reported in the literature could not be confirmed by our meticulously controlled experiments.

- Surface tension

In carefully designed and detailed experiments using sophisticated surface tension instrumentation (Dynamic contact angle apparatus, Cahn DCA 3220) we discovered some very interesting artifactual phenomena which could easily mislead the inexperienced observer. When all these effects were accounted for, the differences which do crop up from time to time, could be attributed to factors other than the electromagnetic field.

- Concluding remarks

These results indicated that electromagnetic fields did not induce lasting structural changes in water. It is, however, important to emphasise that these results do not prove beyond any doubt that no structural changes can occur at all. It only stresses that the particular methods used were oblivious of any effect. Recent developments in analytical science and its application to this topic produced results [25] that could be interpreted as possible structural changes to water. Investigation of this matter was, however, beyond the scope of this project.

# 4. SIMULATED FULL-SCALE INVESTIGATIONS

## Objectives of simulated full-scale investigations

The overall objective of the full-scale investigations was to study the effect of PWT on prevention of scale formation. Due to the lack of a suitable measurement method, a measurement method for the evaluation of the devices had to be developed and reproducibility experiments had to be conducted. The specific objectives of the full-scale investigations can be summarized as follows:

- Develop a method to measure scale formation
- Conduct reproducibility tests on the system
- Evaluate the effects caused by PWT devices on scale formation

## Description of test loops

A simulated full-scale heat exchanger system with control and test systems was constructed (Figure 4.1), in order to evaluate the possible effects of PWT devices on scale formation.

The system consisted of two identical but separate test loops, one as control with a dummy unit and the other one with a PWT unit. Each of the test loops consisted of five main components as follows:

- Reservoir and the distributor pump
- PWT unit or the dummy
- Heat exchanger circuit
- Heating circuit
- Cooling tower

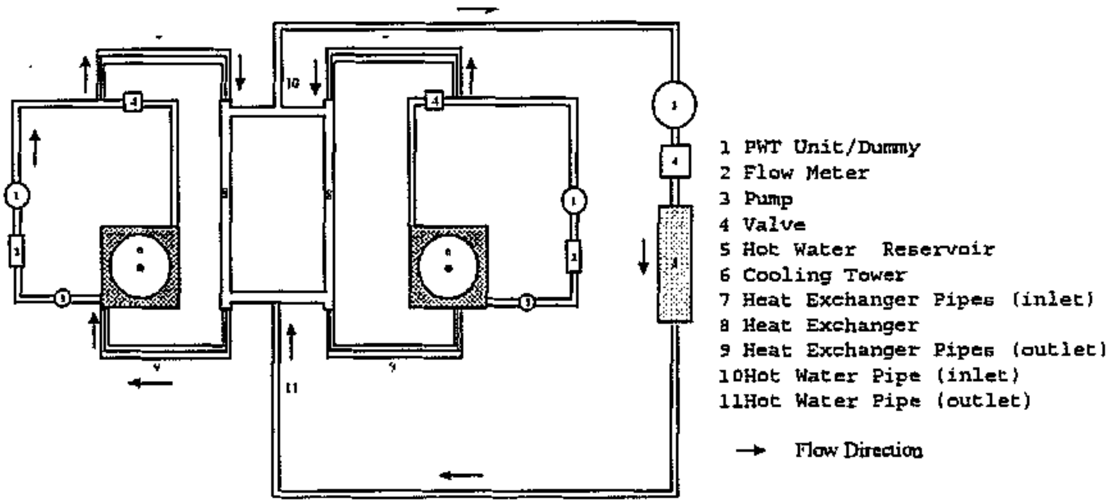

**Figure 4.1** Schematic Presentation of the Test System

*Reservoir and the distributor pump*

Reservoirs consisted of galvanized steel tanks of dimensions 640×800×300 mm and they were coated with a tough rubber coating to prevent metallic contamination of the system. An external pump (DAB by Italy, model K40/200T), flow control valves and flow meters (KENT-PSM KM3) were used to maintain a constant flow rate of 20-30 ℓ/min through the system.

The water in the reservoir was continuously recirculated through the system. The water level in the tanks was kept constant by an automatic flow of make-up water into the reservoir. The storage capacity of these plastic make-up water tanks was 140ℓ each.

### *PWT unit or the control*

The unit was placed between two removable pipe segments. The system was able to accommodate the hydraulic requirements of four different PWT devices (Polar, Aquasal, PTH, Cepi). The unit and the dummy were interchangeable and they were replaceable with a pipe segment and a cap to enable consistency tests between two loops. The PWT tested was manufactured by Polar International Norway (model PD15). The unit and the dummy had both an inlet and an outlet. The incoming line was attached to the reservoir via pump and the outlet was attached to the heat exchanger pipes.

### *Heat exchanger circuit*

The simulated full-scale tests were conducted on a shell-and-tube counterflow type heat exchanger. The shell-and-tube heat exchanger consisted of two parts: the annulus and the pipes. Galvanised steel pipe with outside diameter of 34.7 mm and 1.82 m length was used as annulus pipe. The cold water pipes were stainless steel. Outside and inside diameters were 6.4 and 4.0 mm, respectively, and the length of the pipes was 1.97 m. The rest of the loop consists of inside diameter of 32 mm PVC pipes.

Water coming from the reservoir after passing the PWT could be split to a by-pass pipe in order to reduce the flow rates in the heat exchanger pipes. The quantity of the by-passed water could be adjusted to the desired amount by a valve.

Each heat exchanger pipe was connected to the cold water circuit with the aid of copper pipes and copper connection parts. Small valves were used to adjust the flow rates individually. The outlet of each pipe was connected to plastic tubes of inside diameter 6.4 mm. The heated water returns to the cooling tower through these plastic tubes and the by-passed water is sprayed directly from the top part of the cooling tower to the packing from there it returns back to the reservoir.

The measurement of the inlet and the outlet temperatures for each stream as well as the temperatures at the annulus were made by Aluminium Chrome (K-type) thermocouples to a precision of 0.1° C. Measurement points consisted of 12 fixed points for the heat exchanger pipes; 6 for the inlet and 6 for the outlet temperature measurements and at the annulus it consisted of 2 points; 1 for the inlet and 1 for the outlet temperature measurements.

*Heating circuit*

One heating circuit was used for both testing loops. The heating was accomplished by 12 elements; each 1 kW. The elements were arranged in four groups of three elements each. Each group could be manually switched on/off. The elements were mounted in 31 mm diameter galvanised steel pipes.

The rest of the circuit consisted of a "Perspex" reservoir with capacity 15 litres which was filled with deionised water in order to prevent scale adhesion on the outside surfaces of the heat exchanger pipes. The flow rate through the elements could be adjusted with a valve.

*Cooling tower*

Cooling towers in the system were natural draft cooling towers 1.5 m in height and diameter of 600 mm, both with reservoirs of 150 litres. The packing height was 1 100 mm. All the water which moved through the heat exchanger was returned into the packing while the by-passed water out of the heat exchanger was distributed through the sprayers and then cooled down by flowing through the packing.

A stand was mounted at the top of the cooling towers to enable easy measurement of the flow rates through the tubes coming from the heat exchanger pipes.

### Scale deposition measurement method

The principle of the method developed during this project is based on the measurement of the mass of scale precipitated on the heat transfer surfaces by dissolving the scale with an acid solution. The method is quantitative and rapid.

Initial tests were devoted to the refinement of the technique used to strip the scale from the heat exchanger pipes. The final procedure defined below was followed in all the experiments reported in this report.

- The heat exchanger was taken apart
- Pipes were connected to a peristaltic pump via plastic tubes
- A solution of 400 mℓ 10 % acetic acid was prepared

- The scale precipitated during the experiment was stripped for 60 minutes (this time was determined after the initial tests with different stripping times, a typical result for these tests is shown in Table.4.1)
- 100 mℓ of samples were taken from each solution
- The samples were analysed for calcium.

During preliminary experiments, scale deposition was noticed on the sprayers used to distribute water to the top of the cooling tower. It was consequently decided to measure this scale as well. After each experiment these sprayers were removed and placed in 400 mℓ of 10 % acetic acid solution for 30 minutes, before the calcium concentration in the solution was measured.

**Table 4.1** Calcium Concentration Results (mg/l) of Preliminary Tests With Different Stripping Times

| | Stripping Time | |
|---|---|---|
| Tube Number | 30 minutes | 60 minutes |
| $t_1$ | 485.52 mg/l | 485.57 mg/l |
| $t_2$ | 963.83 mg/l | 950.93 mg/l |
| $t_3$ | 417.05 mg/l | 417.44 mg/l |

**Experimental procedure**

The experimental procedure to form a scale deposit on the heat exchanger surfaces was as follows:

- The system was cleaned and filled with tap water
- The calcium concentration was measured
- Chemicals ($Ca(NO_3)_2 4H_2O$ and $NaHCO_3$) were added to obtain the desired concentration and the pH of the solution was adjusted to approximately 7
- The calcium concentration was measured again
- Flow rate adjustments were made for the main circuit as well as the small pipes
- The system was started
- Temperature, flow rate and conductivity measurements were taken twice a day
- The experiment was stopped, the heat exchanger was taken apart and the mass of scale was measured.

*Preparation of the test solution*

It was the aim to prepare a solution that would cause scaling within an acceptably short time. Scaling usually develops over a long period of time which can take a number of weeks. For the purpose of the research, the experiments had to be carried out in a shorter time.

There are a number of ways to make such a solution and the simplest one was chosen and applied. This method involved adding a calcium salt (e.g. $Ca(NO_3)_2 4H_2O$) and bicarbonate salt (e.g. $NaHCO_3$) together in the right quantities to make up a calcium bicarbonate solution.

The solution was prepared by the following steps:

- Calcium concentration of the tap water was measured.
- Appropriate quantities of chemicals to be added were calculated and weighed to obtain a specific Ca goal, which was varied during the experiments.
- 2 ℓ of tap water was spiked with $Ca(NO_3)_2 4H_2O$.
- 2 ℓ of tap water was spiked with $NaHCO_3$.
- The pH of the $NaHCO_3$ solution was measured, which was usually found to be 8.0 to 8.3.
- The solution was titrated with nitric acid by continuous mixing, and measuring of the pH until it reached a value of approximately 7.
- The $Ca(NO_3)_2 4H_2O$ and $NaHCO_3$ solutions were added and mixed in the tanks

*Cleaning of the system*

The system was cleaned by flushing tap water at high pressure through the system. The tanks were emptied and rinsed with tap water. The scale on the heat exchanger surfaces were stripped with 10 % acetic acid solution and rinsed with tap water 3 times.
Complete cleaning of the system could not be achieved since only the scale in the heat exchanger pipes was removed after each experiment but the scale which was formed in other parts of the equipment was left as "it is". Because of the problems encountered caused by the blockage of the pipes, flow meters and the valves, 10 % acetic acid solution was circulated through the system to remove scale formed on these materials twice during the experimental period of 8 months. This procedure could not be used after each experiment because repeated acid washing could damage the equipment.

### Parameters that were monitored

Parameters such as the flow rates, the temperatures, the calcium concentration, and the conductivity were measured during the experiments. From the results of these parameters some other parameters could be calculated.

*Flow rates*

The flow rates had to be kept constant for two loops as well as within a loop between the pipes. Practical problems were encountered initially to control the flow rates accurately (an equal split between the three pipes in a loop) and they were eventually solved by changing the valves.

The flow rate in the main stream was kept at 20 ℓ/min and the flow rate in the three pipes was 2 ℓ/min for all the experiments. Before each experiment flow rates in the main stream and in the heat exchanger pipes were adjusted, measured and recorded twice a day. The flow in each heat exchanger pipe was measured volumetrically. The measurement of the flow rate for the main stream was made by using a municipal type flow meter.

### *Inlet and outlet temperatures*

At temperatures <50°C calcite is more likely to form, at temperatures >60°C aragonite predominates and between 50 and 60° C both forms can occur. For the experiments conducted on the system calcite formation was aimed for and the temperature was therefore kept around 37- 45° C.

Temperature measurements were made with 14 permanently installed thermocouples. A thermometer by Fluke (USA), model 52 K/J was used for the measurements. The heat exchanger inlet and outlet temperatures were measured for each pipe (3 pipes within one loop, 6 pipes in total) and the annulus pipe. Each temperature was measured at the beginning and at the end of the experiments and regularly two times a day. In an experimental run of 51 hours a total of 6 measurements were taken from each pipe. The ambient temperature in the laboratory was also considered to be an important factor and therefore it was followed during the experiments.

The heating circuit consisted of 4 series of elements as explained in the description of test loops. From the preliminary tests performed on the system, the use of two series was adequate to obtain the required temperature target. The temperature in the heat exchanger stabilised approximately one hour after the start.

### *Conductivity and Total Dissolved Solids*

In the current study, measurement of the conductivity was used to estimate total dissolved solids in the tank water. The conductivity was measured by a laboratory conductivity meter by Hanna Instruments, model HI 8633. This parameter was measured in the two reservoirs. Measurements were made at the beginning and at the end of each experiment and regularly two times a day.

TDS can be estimated by simply multiplying conductivity (in micromhos per centimetre) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components in the water and on the temperature of measurement. For this project it was assumed as 0.7. Conductivity was measured throughout the experiments and TDS was calculated for each measurement.

### *Calcium and zinc concentrations in the tanks*

Calcium concentration in the tanks was measured and recorded before the experiment (which is equal to tap water calcium concentration), and after spiking with $Ca(NO_3)_2 4H_2O$ and NaHCO3, at the end of each experiment. As the experiments progressed, the zinc concentration was also measured.

*Total water loss*

The loss in the system had two components; one was by evaporation of water from the system, and the second one was the loss from the sprayers to the wind.

A continuous flow of make-up water was fed to the system. The water addition from these tanks was measured and recorded regularly. Since the water level in the reservoirs was kept constant, this addition of make-up water was equal to the water loss from the system.

On average, the total water loss was 200 ℓ per loop in an experiment, which represents approximately a loss of 4 ℓ/hour from the system. The fractions of the total water loss was calculated by a mass balance using the Total Dissolved Solids in the system.

The calculation procedure used was as following:

$$TDS_b \times V_b + TDS_{ad} \times V_{ad} = TDS_e \times V_e - TDS_v \times V_v - TDS_s \times V_s$$

where;

| | |
|---|---|
| $TDS_b$ | TDS at the beginning of the experiments |
| $TDS_{ad}$ | TDS of the water added during the experiment |
| $TDS_e$ | TDS at the end of experiments |
| $TDS_v$ | TDS of the water evaporated |
| $TDS_s$ | TDS of the water lost from the sprayer |
| $V_b$ | Volume of water in the tank at the beginning of the experiment (ℓ) |
| $V_{ad}$ | Volume of water added during the experiment (ℓ) |
| $V_e$ | Volume of water left at the end of the experiment (ℓ) |
| $V_v$ | Volume of water evaporated (ℓ) |
| $V_s$ | Volume of water lost from the sprayer (ℓ) |

The TDS of water lost from the sprayer was considered to be the average TDS during the experiment:

$$TDS_s = TDS_a$$

where;

| | |
|---|---|
| $TDS_a$ | Average TDS during the experiments |

The TDS of the water added to the system was equal to the initial TDS of water:

$$TDS_{ad} = TDS_b$$

Theoretically, the TDS of the water evaporated should be zero, since only the water evaporates living the salts behind.

$$TDS_v = 0$$

Therefore, mass balance equation could be reduced to the following form:

$$TDS_b \times (V_b + V_{ad}) = TDS_e \times V_e - TDS_a \times V_s$$

Then the volume of water lost from the sprayers could be calculated:

$$V_s = \frac{TDS_b \times (V_b V_{ad}) - TDS_e \times V_e}{TDS_a}$$

Finally, the water loss through evaporation was calculated as follows:

$$V_v = Total\ \ Loss - V_s$$

*Heat transfer rate*

The heat transfer rate is a parameter useful to determine the performance of the heat exchanger. The heat transfer rate was calculated for each of the six heat exchanger pipes and for the annulus according to the following equation:

$$q = \dot{m}\, C_p \left(T_o - T_i\right)$$

where;

| | |
|---|---|
| $q$ | heat transfer rate (W) |
| $\dot{m}$ | mass flow rate (kg/s) |
| $C_p$ | specific heat of water at concerned temperature (J/kg.K) |
| $T_o$ | outlet temperature (°C) |
| $T_i$ | inlet temperature (°C) |

*Cycles of concentration*

This ratio was calculated to determine the salt balance in the system. For its calculation TDS at the beginning of the experiment and at the end was measured, and the ratio was expressed as follows:

$$COC = \frac{TDS_e}{TDS_b}$$

Where;

| | |
|---|---|
| COC | Cycles of concentration |
| $TDS_e$ | Total Dissolved Solids at the end of the experiment |
| $TDS_b$ | Total Dissolved Solids at the beginning of the experiment |

*Total scale and scale fractions*

Scale deposition in the heat exchanger pipes and on the sprayers were measured and analysed. However there are other components of scale deposition in the system. Scale deposition had occurred on the cooling towers, on the valves, flow meters, pumps etc. The total mass of scale deposited is calculated from a mass balance applied to calcium in the system.

The calculation of the scale deposition in the rest of the system is shown as following:

$$Ca(t) = Ca(b) + Ca(a) - Ca(e) - Ca(d) - Ca(s)$$

where;

| | |
|---|---|
| Ca(t) | Total calcium deposited in the rest of the system (mg) |
| Ca(b) | Mass of calcium at the beginning of the experiment (mg) |
| Ca(a) | Mass of calcium added during the experiment (mg) |
| Ca(e) | Mass of calcium in the water at the end of the experiment (mg) |
| Ca(d) | Total mass of scale deposited in the pipes and the sprayers (mg) |
| Ca(s) | Mass of calcium lost by the sprayers (mg) |

## Results and Discussion

A total of 16 experiments was performed. The first five of these experiments were used to refine the experimental procedure and to solve the practical problems encountered. This left 11 experiments to consider for the purposes of this project.

- Seven of the tests were performed without any treatment. Both test loops were operated under identical conditions to test the reproducibility.

- In two experiments, the Polar magnetic treatment unit was tested against a dummy control unit.
- Two tests were performed with zinc addition achieved by an electrode, against a control.

*Experimental approach and summary of runs*

The operational parameters were kept constant apart from the calcium concentration, which was increased after the sixth experiment, and the treatment technique used, either zinc addition or Polar magnetic treatment.

A summary of the experimental matrix is shown in Table 4.2

**Table 4.2** Summary of Experimental Runs

| Experiment No | Date | Side123 | Side456 | Ca | Comment |
|---|---|---|---|---|---|
| 1 | 9-11/1/96 | Polar | | spiked (75 mg/l) | Ca not measured |
| 2 | 17-19/1/96 | Polar | | spiked (75 mg/l) | Ca not measured |
| 3 | 24-26/1/96 | | | spiked (75 mg/l) | |
| 4 | 31/1-2/2/96 | | | spiked (75 mg/l) | |
| 5 | 7-9/2/96 | | | spiked (75 mg/l) | |
| 6 | 21-23/2/96 | | | spiked (100 mg/l) Tank | Bulk precipitation |
| 7 | 6-8/3/96 | | | spiked (100 mg/l) MW+Tank | pH adjustment |
| 8 | 18-20/3/96 | | Zinc | spiked (100 mg/l) MW+Tank | pH adjustment |
| 9 | 27-29/3/96 | | | spiked (100 mg/l) MW+Tank | pH adjustment |
| 10 | 9-11/4/96 | Zinc | | spiked (100 mg/l) MW+Tank | pH adjustment |
| 11 | 17-19/4/96 | | | spiked (100 mg/l) MW+Tank | pH adjustment |

*MW :Make-up Water

(Side123 is the side which consist of heat exchanger pipes 1,2 and 3, the side 456 is the side which consist of the heat exchanger pipes 4, 5 and 6.)

*Operational parameters*

- The temperature in the heat exchanger for the total of 11 experiments was kept constant as far as possible within an experiment amongst the pipes as well as for different experiments. Small temperature changes in both inlet and outlet of the heat exchanger were attributed to the changes in the ambient temperature. The temperature was measured to be approximately 38° C for the inlet and 48° C for the outlet with 2 series of elements switched on, for all the 11 tests and for each of the six tubes. Consequently, a temperature increase of 9-10° C was attained in the heat exchanger pipes during each pass.

- The heat transfer rate and the heat transfer coefficients were calculated for every measurement for each of the 11 experiments. The heat transfer rate for each of the 6 tubes was calculated to be between 884 W and 1292 W.

- Preliminary experiments were conducted with tap water without addition of the chemicals. From the 11 experiments, the first 5 was to obtain a final solution of 75 mg/l of calcium. In the next 6 experiments it was aimed to obtain an end solution of 100 mg/l of calcium. Calculation of appropriate chemicals to obtain the aimed concentration was done taking the already existing calcium concentration in the tap water into account. The tap water calcium concentration varied between 35-50 mg/l. In the sixth experiment it was aimed to obtain 100 mg/l of calcium for the first time. But premature nucleation was observed before the experiment started due to the high pH of the solution. To avoid this in the next 5 experiments, the pH of the solution was controlled before the experiments started.

- Calcium concentrations were not measured for the first two experiments. From the third to the fifth experiment, only calcium in the tanks at the beginning and at the end of experiments was measured. From the fifth experiment tap water calcium concentration was also measured. After experiment 7, make-up water calcium concentration and, from experiment 10, calcium after 24 hours running time were also measured. Therefore, the calcium data for the experiments contain some gaps.

- The zinc concentration data was incomplete for the experiments since its possible effect on scale formation was noticed later. The available data on zinc concentration during the experiments in the tanks and in the make-up water as well as the concentration in the tap water are only limited to three experiments which are experiments 8, 10 and 11. The values of zinc increased in the tanks, therefore a possible zinc leaching to the system was investigated. A solution of tap water with a known zinc concentration was circulated in the system for 2 days and the zinc concentration was measured periodically. The results of this test are shown in Figure 4.2. According to the results of this test the zinc concentration was less than 50 μg/l at the beginning of the experiment, and it immediately increased to 120-150 μg/l in the tanks and reached approximately 500 μg/l in two days. The zinc in the heat exchanger pipes increased to 300 μg/l in this period.

- The COC increased from 1.5 to approximately 2.0 and the TDS from 250 to 650 mg/l with a rise in calcium concentration from the sixth experiment onwards.

- The total water loss in the system was measured to be 4 ℓ/h of which approximately 2.5 ℓ/h was calculated to be the evaporation losses. The spray losses were initially higher in the first experiments but are reduced by a relatively better control over the system.

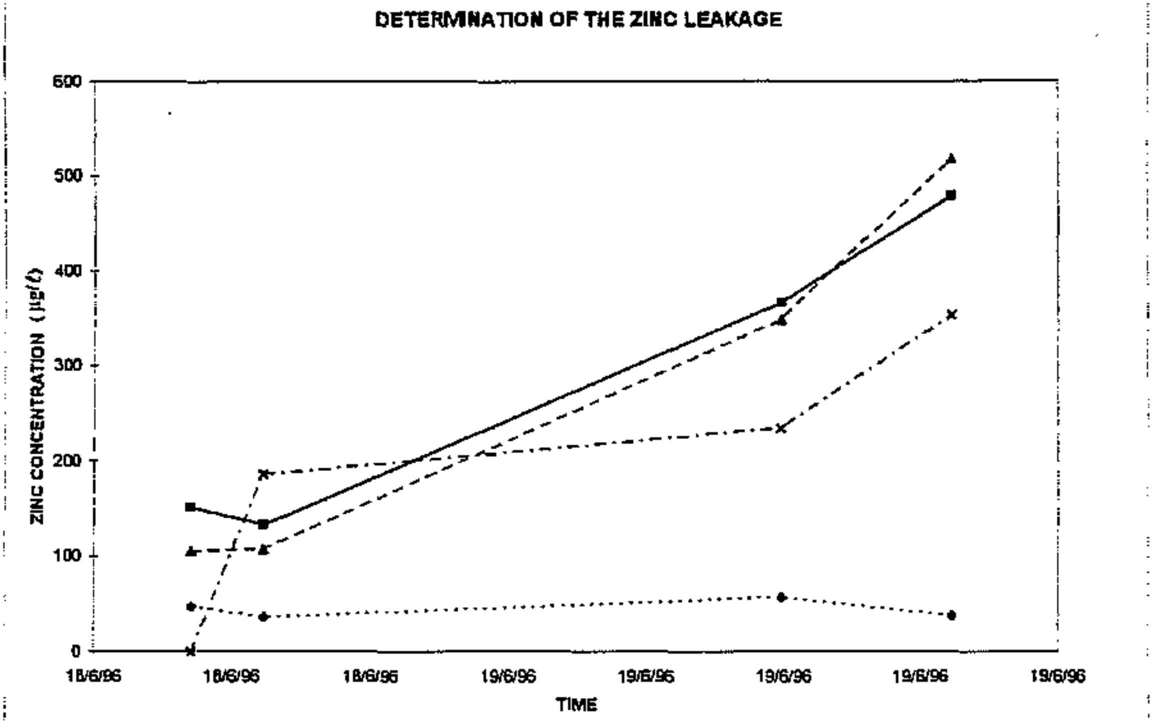

Figure 4.2 Results of the Test to Determine the Source of Zinc Leakage (µg/l)

*Measurements of scale and scale fractions*

The scale deposition had three components:

- The scale deposition in the heat exchanger pipes, was the major concern since this part of scale usually creates heat transfer losses and flow restrictions. In 4 reproducibility tests out of 7 where neither Polar nor zinc was used, the scale deposition in the test and control pipes were equal. In 2 tests, performed with zinc addition, in 1 case zinc decreased the deposition and in the other case increased it. In 2 tests, performed with Polar unit, in one case the unit decreased the scale deposition, in the other case deposition was increased.
- With regard to the scale deposition in the sprayers, from 7 reproducibility tests where neither Polar unit nor zinc addition was used, the results of scale deposition in the two

side sprayers were not consistent. In two tests performed with zinc addition, scale deposition in the sprayers was decreased. In two tests performed with Polar unit, scale deposition in the sprayers decreased.

- The scale deposition in the rest of the system reached values of up to 10 000 mg.

*Statistical results and interpretation*

The data were analized statistically. The four independent variables are: heat transfer rate ($i_1$), TDS ($i_2$), COC ($i_3$) and calcium concentration ($i_4$). The dependent variables are the scale deposited in the heat exchanger pipes ($d_1$), the scale deposited in the sprayers ($d_2$), the total of the scale deposited in this two ($d_4=d_1+d_2$), the scale deposited in the rest of the system ($d_3$) and the ratio of the scale deposited in the heat exchanger pipes to the total scale in the pipes and the sprayers ($d_5=d_1/(d_1+d_2)$) (Table 4.3).

**Table 4.3** Summary Table of Independent and Dependent Variables

| Experiment No | $i_1$ | $i_2$ | $i_3$ | $i_4$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 side 123 | 1183 | 248 | 1.45 | | 15.53 | 75.80 | | 89.34 | 0.15 |
| side 456 | 972 | 241 | 1.34 | | 140.41 | 79.88 | | 220.28 | 0.64 |
| 2 side 123 | 1230 | 252 | 1.48 | | 749.31 | 56.89 | | 806.20 | 0.93 |
| side 456 | 1022 | 254 | 1.49 | | 88.07 | 101.51 | | 189.58 | 0.46 |
| 3 side 123 | 1039 | 217 | 1.26 | 55 | 223.35 | 83.14 | | 306.48 | 0.73 |
| side 456 | 982 | 261 | 1.53 | 54 | 37.82 | 56.53 | | 94.34 | 0.40 |
| 4 side 123 | 1101 | 252 | 1.49 | 30 | 23.32 | 55.96 | | 79.28 | 0.29 |
| side 456 | 1020 | 255 | 1.49 | 42 | 17.56 | 28.48 | | 46.04 | 0.38 |
| 5 side 123 | 1060 | 250 | 1.57 | 56 | 15.96 | 59.46 | 1541 | 75.42 | 0.21 |
| side 456 | 1125 | 256 | 1.62 | 52 | 14.70 | 41.23 | 1704 | 55.92 | 0.26 |
| 6 side 123 | 1114 | 399 | 1.24 | 69 | 174.77 | 60.09 | | 234.86 | 0.74 |
| side 456 | 1082 | 424 | 1.33 | 40 | 7.64 | 43.97 | | 51.61 | 0.15 |
| 7 side 123 | 1004 | 636 | 1.75 | 85 | 678.84 | 124.96 | 8591 | 803.81 | 0.84 |
| side 456 | 1137 | 656 | 1.83 | 92 | 715.51 | 74.87 | 7097 | 790.38 | 0.91 |
| 8 side 123 | 1099 | 621 | 2.03 | 74 | 943.04 | 116.16 | 9973 | 1059.20 | 0.89 |
| side 456 | 919 | 620 | 2.08 | 73 | 651.01 | 84.63 | 10060 | 735.64 | 0.88 |
| 9 side 123 | 1114 | 619 | 1.75 | 70 | 16.46 | 49.62 | 9167 | 66.08 | 0.25 |
| side 456 | 936 | 648 | 1.81 | 66 | 15.01 | 30.14 | 11390 | 45.16 | 0.33 |
| 10 side 123 | 1202 | 611 | 1.78 | 68 | 39.74 | 83.08 | 9864 | 122.82 | 0.32 |
| side 456 | 1121 | 626 | 1.92 | 65 | 21.77 | 90.24 | 10021 | 112.01 | 0.19 |
| 11 side 123 | 1031 | 576 | 1.69 | 72 | 48.46 | 61.43 | 10852 | 109.89 | 0.44 |
| side 456 | 1122 | 598 | 1.76 | 73 | 20.26 | 76.70 | 10315 | 96.96 | 0.21 |

where;

| | |
|---|---|
| $i_1$ | heat transfer rate |
| $i_2$ | total dissolved solids |
| $i_3$ | cycles of concentration |
| $i_4$ | calcium concentration |
| $d_1$ | scale deposited in the heat exchanger pipes |
| $d_2$ | scale deposited in the sprayers |
| $d_3$ | scale deposited in the rest o the system |
| $d_4$ | total scale deposition in the heat exchanger pipes and the sprayers |
| $d_5$ | ratio of the scale deposited in the heat exchanger pipes to the total scale in the pipes and the sprayers |

From the total of 22 data points the regression analysis was applied to 14 data points. The data points which corresponds to the experiments conducted by using zinc and Polar, experiment 6 in which bulk precipitation occurred before the experiment, and experiments 1and 2 which contain gaps in the calcium concentration data were discarded for this analysis.

First a linear relationship was investigated between the dependent and independent variables. As seen from Table 4.4, the values of the correlation coefficients ($R^2$) for each case were low. The best correlation coefficients ($R^2$) are shown in bold. The degrees of freedom are indicated for each of the cases. The calcium concentration, therefore had the strongest influence on each of the dependent variables.

**Table 4.4** Linear Regression Results, Using only One Independent Variable at a Time

| | $d_1$ | | $d_2$ | | $d_3$ | | $d_4$ | | $d_5$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** |
| $i_1$ | 0.02 | 12 | 0.04 | 12 | 0.08 | 8 | 0.02 | 12 | 0.00 | 12 |
| $i_2$ | 0.18 | 12 | 0.17 | 12 | **0.83** | **8** | 0.19 | 12 | 0.07 | 12 |
| $i_3$ | 0.21 | 12 | 0.15 | 12 | 0.42 | 8 | 0.22 | 12 | 0.02 | 12 |
| $i_4$ | **0.38** | **12** | **0.30** | **12** | 0.23 | 8 | **0.39** | **12** | **0.28** | **12** |

- df is the degrees of freedom

(see Table 4.3 for a description of the variables( i and d))

The equations of the best fit lines for this analysis are as follows:

$d_1 = -558.22 + 11.99426 i_4$

$d_2 = 7.82 + 0.9421 i_4$

$d_3 = -3338.92 + 20.7919 i_2$

$d_4 = -550.399 + 12.94347 i_4$

$d_5 = -0.08866 + 0.08579 i_4$

As can be seen from these equations the scale formation increased with increasing calcium concentration in four cases, as expected. However, the scale formation in the rest of the system increased with increasing TDS. This can be explained as the bulk of the scale precipitation is more dependent on TDS than calcium concentration.

As a next step, two independent variables were used simultaneously. The first was the calcium concentration $i_4$, the best single predictor and the remaining three independent variables were tried in turn as the second (Table 4.5).

Table 4.5 Multiple Linear Regression Results, Using the Data in Untransformed Form (Therefore Assuming an Additive Model)

| | $d_1$&Ca | | $d_2$&Ca | | $d_3$&TDS | | $d_4$&Ca | | $d_5$&Ca | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** |
| $i_1$ | 0.38 | 11 | **0.32** | **11** | 0.84 | 7 | 0.39 | 11 | 0.30 | 11 |
| $i_2$ | **0.40** | **11** | 0.30 | 11 | - | - | **0.41** | **11** | **0.38** | **11** |
| $i_3$ | 0.38 | 11 | 0.30 | 11 | 0.82 | 7 | 0.39 | 11 | 0.35 | 11 |
| $i_4$ | - | - | - | - | **0.91** | 7 | - | - | - | - |

(see Table 4.3 for a description of the variables( i and d))

Equations of the best fit lines are shown as follows:

$d_1 = -623.497 - 0.44659 i_2 + 16.29427 i_4$

$d_2 = -64.6372 + 0.069816 i_1 + 0.920775 i_4$

$d_3 = 1979.601 + 28.70449 i_2 - 137.148 i_4$

$d_4 = -618.655 - 0.46697 i_2 + 17.43966 i_4$

$d_5 = -0.2044 - 0.00079 i_2 + 0.016203 i_4$

It can be seen from the equations presented above, the multiple linear regression analyses also show a similar trend as obtained from the linear regression data with single independent.

Lastly a logarithmic relationship between the variables was studied (Table 4.6).

**Table 4.6** Multiple Linear Regression Results, Using the Data in Log-transformed Form (Therefore Assuming a Multiplicative Model)

| | $d_1$&Ca | | $d_2$&Ca | | $d_3$&TDS | | $d_4$&Ca | | $d_5$&Ca | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** | **$R^2$** | **df** |
| $\log i_1$ | 0.27 | 11 | **0.32** | **11** | 0.95 | 7 | **0.34** | **11** | 0.19 | 11 |
| $\log i_2$ | **0.30** | **11** | 0.24 | 11 | - | - | 0.33 | 11 | 0.19 | 11 |
| $\log i_3$ | 0.29 | 11 | 0.23 | 11 | 0.94 | 7 | 0.32 | 11 | **0.23** | **11** |
| $\log i_4$ | - | - | - | - | **0.97** | **7** | - | - | - | - |

(see Table 4.3 for a description of the variables( i and d))

Equations or the best correlations are as follows:

$$d_1 = -2.97039\, i_2^{-0.88579}\, i_4^{3.938899}$$

$$d_2 = -6.1703\, i_1^{2.217372}\, i_4^{0.702502}$$

$$d_3 = -40.629\, i_2^{2.369979}\, i_4^{1.39571}$$

$$d_4 = -10.0358\, i_1^{2.806747}\, i_4^{2.066402}$$

$$d_5 = -2.12004\, i_3^{-1.68984}\, i_4^{1.168708}$$

The statistical analysis of the data is not conclusive. On average, only 30-40 % of the inconsistency in the results can be explained by the differences in the calcium concentration and the TDS.

# 5. CONCLUSIONS

## Summary of the work done

The aim of this project as set out in the introduction, was to test the claims and effects made concerning physical water treatment for scale inhibition, critically evaluate the theories put forward to explain these phenomena and then make recommendations with regard to the practical implementation of PWT.
To achieve this aim we used a two-pronged approach, namely
(i) simulated full-scale investigations and
(ii) laboratory investigations where the problem was studied at the molecular level.

The main thrust of the laboratory investigations can be summarised as follows:

- **to develop laboratory test methods** to verify the effects of physical water treatment in as short as possible experimental run times. The batch method based on measuring the rate of $CaCO_3$ precipitation ( pH vs time), was developed for this purpose. Tests were run on 5 commercially available PWT devices, 3 magnetic, 1 electric and 1 catalytic converter, and a 2 tesla variable laboratory electromagnet, using the above methods.
- **to verify experimentally under controlled conditions the occurrence of some effects** listed in the literature. The effect of PWT on the rate of crystallisation (by implication scale formation), crystal morphology (by implication adhesion properties of scale), and the effect of impurities released by the devices were studied in detail.
- **to evaluate the two main mechanistic models**, namely the water structure model and the nucleation model.

The focus of the simulated full-scale investigations can be summarized as follows:

- **to design, construct and optimize a full-scale testing system** to measure scale formation in heat exchanger pipes rapidly and quantitatively.

- **to evaluate selected PWT devices for industrial applications.**

## Summary of results

- **Verification of effects.** We have shown that the emission of metal ions, in particular zinc ions from three different types of PWT device can affect the rate of crystallisation of $CaCO_3$ and can cause changes to the crystal morphology of precipitates. Nucleation rates are decreased and the morphology of the scale changes from calcite rhombohedrons to aragonite needles. Presumably the adhesion properties differ between these two crystallographic forms of $CaCO_3$. Scale inhibition effects shown by these devices could therefore be attributed to these phenomena. Where devices released no measurable amounts of impurities, no effects were observed.

- **Proposed mechanistic model.** Results from experiments designed to test the water structure model, proved negative. The devices had no measurable effect on surface tension, infrared spectra or NMR of water which would have indicated structural changes to water . The fact that after coating the inner surfaces of the devices with an impenetrable thin layer of polymer, the effects on nucleation rate and crystal morphology disappeared, indicated that the release of impurities from inner surfaces were responsible for the observed effects. In view of these results, a mechanistic model based on the substoichiometric blocking of crystal surface growth sites, is proposed. This means that metal ions, in particular free metal ions with the right stereochemistry are preferentially adsorbed at "kinks" and "steps" in the growing crystal. This blocks the preferred growth pattern of calcite, converting to an aragonite growth pattern at a slower rate.

- **Full-scale investigations.**
  A quick, method was developed to determine the rate of scale formation in a full-scale test rig. The method comprised of stripping the scale from straight pipes with 10% acetic acid and determining the Ca content after acid stripping. The reproducibility amongst different pipes, and amongst different experiments, was not as good as expected. Further work should be conducted to improve the reproducibility of the test rig before meaningful verification of PWT could be done on this rig.

**Research products**

- *Free metal ion scale inhibitor.*
  In view of the results obtained, a scale inhibition procedure was proposed based on the controlled addition of metal ions, such as zinc, to scale forming water. Broad operating guidelines were established. In experiments done with tap water and deionised water both spiked with $CaCO_3$ at concentrations up to 500 mg/l, scale reduction of between 50 and 80% was achieved. Strong ligands for Ca complexation, such as EDTA, when present in mg/l quantities, will destroy the beneficial effect of µg/l levels of active zinc. High concentrations of inorganic ions, such as, chloride and sulphate may, however, be tolerated. The addition of free metal ions to feed water may be achieved by controlled electrolysis via a pulsed DC power supply. This has the advantage of controlling the concentration of free $Zn^{2+}$ ions and preventing the zinc anode of becoming deactivated by formation of a protective ZnO coating or deposition of scale.

- *Dissertations*

1. M. YACOBY M.Sc.(Chemistry)(RAU)1996, with distinction:
   The effect of magnetic and constant electric field antiscaling devices on the mechanism of $CaCO_3$ scale formation.

2. S.S. HOWELL M.Sc.(Chemistry)(RAU) 1996, with distinction:
   A critical evaluation of physical water treatment for the prevention of scale

3. S.G. CANBULAT M.Eng (Civil Egineering) (RAU) 1997
   Measurement of scale formation in an experimental heat exchanger circuit.

- *Research papers*

1. PP COETZEE, M YACOBY and SS HOWELL (1996) The role of zinc in magnetic and other physical water treatment methods for scale prevention. *Water SA* **22(4)** 319-326

2. V KOCHMARSKY (1996) Magnetic treatment of water: Mechanisms and conditions for applications. *Magnetic and Electrical Separation* 7(2) 77-107

- *Patent*

  PP COETZEE, Process for treatment of water: Prevention of scale deposits *SA Patent* No. 95/6807

- *Conference contributions*

1. PP COETZEE, The role of metal surfaces in antiscale physical water treatment. Plenary lecture at the International symposium: *Antiscale Magnetic Treatment: How does it work?* Cranfield University, Bedford, UK, 14 March 1996.

2. PP COETZEE, M YACOBY, SS HOWELL, Magnetic water treatment for prevention of scale. Myth or fact? *33 rd Convention of the SA Chemical Institute*, Cape Town, January 1996

## 6. RECOMMENDATIONS

It was not possible to make any final recommendation with respect to the practical viability of physical water treatment. We therefore recommend that further work be undertaken to address the following important aspects:

- long term experiments running on simulated industrial scale test equipment as was developed during this project
- the application of new analytical technology to measure effects of electromagnetic fields on water and scale forming components in water. Recent results from Japan have indicated that atomic force microscopy might provide a means of measuring the small direct effects that could arise from physical water treatment.
- the further development of the metal ion scale inhibitor patented in 1996 and based on initial work done under WRC contract no. K5/612
- application tests on commercial systems
- systematic investigation of new PWT technology not covered under this WRC contract. PWT devices based on RF(radio frequency) fields are prime candidates for inclusion in further work because of promising reports coming from industrial applications of these systems.

These aspects will be addressed in a new contract between Rand Afrikaans University and the WRC, which commenced in January 1997.

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## APPENDIX A PWT INFORMATION OBTAINED FROM DR. V. KOCHMARSKY

## Background

Dr Volodymyr Kochmarsky of the Ukranian Institute of Water Engineers, Rivne, UKRAINE was invited to give a series of seminars and on magnetic water treatment during May 1995. The seminars were held in the Department of Chemistry, Rand Afrikaans University and published under the title "Magnetic Treatment of Water: Mechanisms and conditions for applications" in *Magnetic and Electrical Separation* 1996 7(2) 77-107. Dr. Kochmarsky is an expert in the field of magnetic water treatment and was the coordinating scientist in the old Soviet Union for this research field, over a period of 10 years. As part of his consultation on this project the following questions were put to him by Proff: Coetzee and Haarhoff:

*Question 1: Many researchers claim that zeta potentials in collodial suspensions change during exposure to a magnetic field. Do you know of any convincing experimental evidence for this effect? Can you suggest a theoretical model that could support such an observation? What theoretical basis is there to predict the effect of H on diamagnetic collodial particles? (Eg. the polarization of surfaces or the electrical double layer around particles in ionic solutions).*

**Answer 1:** A possible reason for a change in zeta-potential of colloidal particles is a change in the concentration of opposite ions of micelles. The mechanism of the influence of magnetic field on the water medium, proposed by us during the seminar, does not exclude such an effect.

Studies are known to us (Mikhel'son M.L. The solution of the DeBye-Huckel equation for the magnetized particles present in solutions. 1973, DAN SSSR (Doklady Akademii Nauk USSR), vol. 212, no.4, p. 911-914), which give the theoretical basis and some experimental observation of the effects related to the changes of zeta-potential. Our attempt to reproduce the kinetic experiments regarding the zeta-potential under the influence of magnetic field was unsuccessful.

Regarding the changes in the structure of the electric double layer around the micelle, as a result of its dia- or para-magnetism and corresponding properties of ions, in our opinion, the induced magnetic dipole infraction is considerably less (by several orders of magnitude) than that of electric dipole. This is why the magnetic effects of this type are not likely to be observed under ordinary conditions.

*Question 2: Klassen and others claim a reduction in the hydration sphere of diamagnetic ions during exposure to H. Could this point to a possible effect of the field on the destabilization of H bonds in water? What experimental methods can be developed to investigate changes in hydration sphere?*

*If destabilisation of H bonds occur one would expect a decrease in surface tension of water. The POLAR company in Norway claims that their unit causes a reduction in surface tension which returns to normal shortly after exposure, typically 56 to 72 dynes/cm within 5 minutes. Do you know of any reliable measurements on PWT's that could prove this point?*

*What is the expected life time of the destabilization of the H bond? Does this destabilization lead to a reduction in the average size of water clusters or an increase in the number of clusters?*

**Answer 2:** The ideas explained by me on the destabilization of H-bonds in water as a result of the influence of magnetic field can in principle change the statistical number of instantaneous clusters of molecules in water or their size. But this effect in clean water takes place only under influence of magnetic field. The period of relaxation of magneto-disturbed state is $\tau = 10^{-11}$-$10^{-13}$ s, if there are not some irreversible chemical reactions which would fix the disturbance.

How this can be related to the hydration of ions or the changes in the surface tension of water I do not know at this stage, and apart from general phrases, I cannot comment.

The effect of the change in surface tension is not explained in the study known to me (Kushenko A.D, Boguslavskii D.I. The surface tension and electric conductivity of so called magnetized water. 1967, Elekrokhimiya (Electrochemistry), vol.3, part 1, p.123-126). In our experiments with capillary phenomena and changes of contact angle we also did not observe any magnetic effects.

***Question 3:*** *The venturi effect might play an important role in the formation of crystal nuclei when water saturated with calcium carbonate passes through a PWT. For example in the PTH device manufactured in Israel no magnet or electrostatic field is used. The device seems to operate on the principle that pressure reduction decreases the solubility of* $CO_2$ *which in turn leads to an increase in pH followed by* $CaCO_3$ *nucleation. Is it possible to calculate the number of particles required to show an effect on the precipitation reaction? Can the venturi effect produce this number of particles in a saturated calcium carbonate solution?*

**Answer 3:** Yes, it is possible to estimate a number of particles and kinetics of the process of formation of crystal nuclei as a result of the venturi effect. However, the experimental work and physico-chemical models of the process are necessary to achieve this. Currently, we are working in this direction.

***Question 4:*** *What mechanism can be suggested to explain an increased release of metals from magnets in contact with water flowing at say more than 1 m/s?*

**Answer 4:** Apart from magnetostriction effects and mechanical shear stress, working from the side of the liquid, the electrochemical processes are also possible. They are related to the carbonic acid corrosion.

*Question 5: What mechanisms can be suggested to explain the memory effect?*

**Answer 5:** Regarding the "memory effect", I unfortunately do not have sufficiently reliable data about the existence of such an effect. All experiments performed and effects observed by us on magnetic phenomena in the water medium do not give fully reliable basis that these effects were caused specifically by the magnetic field. This also includes our recent kinetic experiments. This is why seriously discussing the "memory effect" is premature.

*Question 6: What mechanisms can be suggested to explain the descaling effect?*

**Answer 6:** Possible mechanisms of the descaling effect as a result of magnetic field were discussed by me in sufficient detail during the seminar. I have nothing more to add.

*Question 7: Some researchers claim that the solubility of slightly soluble salts is increased when exposed to H. How would you explain this phenomenon?*

**Answer 7:** I leave these statements up to the conscience of authors. We shall be performing this type of kinetic experiments, and I shall report the results.

*Question 8: Many reports mention the fact that water treated with PWT can reduce corrosion. Is this a marketing gimmick or do actual evidence exist?*

**Answer 8:** We have no reliable data in this respect.

*Question 9: What is your opinion on the NN-SS-NN-SS magnetic field configuration? Is a resonance effect on the water clusters possible?*

**Answer 9:** Till the time when the influence of magnetic field on the water media is well defined and determined, mainly concerning the changes in their ion-molecular kinetic and static properties, such as the effect on the kinetics of the $CaCO_3$ crystallization, any discussion of any configuration is premature.

*Question 10: Conditions: How dependent are the claimed effects on the field strength, flow speed, turbulence, design details of the magnet, water composition?*

**Answer 10:** This point was discussed in my presentation. In addition, I can refer to the answer as per question 9.

To conclude, I can only add that I share your interest in magneto-chemical effects in media that do not contain static radicals. I think that this is a very interesting field of scientific investigation. The problem is that it is necessary to design, if possible, series of experiments that would allow statistically reliable observation of magneto-chemical effects under the controlled conditions, or theoretical models that would reliably allow and predict such effects.

*Question 11: Make some remarks on the use of magnetic treatment devices for the prevention of scale formation in the former USSR, with regard to*

(1) *estimated number of installations*
(2) *typical applications, e.g. power stations, building heating systems, etc.*
(3) *range of sizes typically encountered, expressed in terms of the hydraulic treatment capacity*
(4) *other simultaneous methods of scale control, for example chemical scale inhibition*

**Answer 11:** In the former USSR the main producers of magnetic apparatus (MA) were as follows:

I. Cheboksarskii Energy maintenance plant producing units AMO-25, 50, 200 and 600 with a capacity of 25, 50, 200, and 600 $m^3/h$. The source of magnetic field in these units are electromagnets;
II. Moscow Voeykov Foundry producing MA on the basis of permanent magnets with a capacity of 5, 10, 15 and 20 $m^3/h$;
III. Sevastopol Municipal Industrial plant producing units designed by the Academy of Municipal Industry (AMI) with electromagnets series T-5, 10, 15, 25 and 50.

In total about 200000 of various MA were produced. These were used in the following applications:
I. to prevent deposits in the heating systems, boilers and water heating units;
II. to improve efficiency of water-treatment plants such as purification units and ion-exchange filters;
III. to improve efficiency of flotation processes in mineral beneficiation plants.

The production of magnetic units for domestic use started at the end of 80's (Type CO-1,2 with a capacity of 0,1-1,0 $m^3/h$). Developer and producer was "Magnetron of Novocherkassk. The MA were also applied in agriculture to improve growth of useful vegetables (tomatoes and cucumbers) and for desalination of soil during irrigation.

Besides the magnetic treatment (which is considered to be an auxiliary method) the following methods are used to prevent the deposits:

I. ion exchange and thermal desalination of water;
II. membrane desalination units;
III. chemical stabilization of water with phosphonates, sulphonates or acidification of water with $CO_2$ and $H_2SO_4$.

*Question 12: Since what time has this technology been in general use? Has the use of these units decreased since, has it stabilized, or is it still on the increase?*

**Answer 12:** Magnetic treatment of water to prevent scale was used in the 60's in the former USSR. The Novocherkassk's Polytechnic Institute (V.I.Minenko) were the pioneers of this work.

These authors used magnetic treatment of water mainly to prevent deposits in heat exchange

equipment. In addition, V.I. Klassen was using magnetic treatment to intensify flotation of minerals as well as for the intensification of chemical technology processes for the production of mineral products (work of VNIIGIAP).
Judging from the number of publications, the research in the magnetic treatment was at its best in the mid-70's and beginning of 80's.

Later on the number of articles started to diminish and its tendency continues still today.
It is possible to specify several fundamental applications of magnetic treatment:

I. Prevention of deposits in the heat exchangers;
II. mining and mineral processing industry-intensification of flotation
III. intensification of chemical technology processes - crystallization, precipitation, dissolution etc;
IV. petroleum industry-fight against salt deposits during the mining of oil;
V. agriculture and medicine.

Lately a boom can be observed in the medical applications of magnetic treatment

***Question 13:** Who designed and constructed these units? Were they all designed and built by the same people according to a standard type of design, or are there a great multiplicity of unit types and manufacturers?*

**Answer 13:** As a rule, the designers and the producers were different firms. The main designers of MA were GIGKHS of Lubercy (V.I. Klassen). Vnigiap of Moscow, Panfilv's AKKH of Moscow and KHIEI of Krakov. The producers of MA were already listed in Point 1.

Till today a standard type of units does not exist.

***Question 14:** The users of these units have provided some feedback on their efficiency. Please summarize this feedback.*

**Answer 14:** Reliable investigations of the efficiency of MA produced in the USSR and the imported units were not carried out. Starting from 1983 in the system of Minenergo of the USSR, such investigations are performed in our laboratory. We have examined all large magnetic apparatus installed to prevent deposits in the condensers of turbines (Kashirkaya Hydroelectric Power Station, Podmoskov'e; Zaiskaya Hydroelectric Power Station, Starobeshevskaya Hydroelectric Power Station, Zuevskaya Hydroelectric Power Station-2, Zmievskaya Hydroelectric Power Station, Rovenskaya Power Station), as well as magnetic units with lower capacity (up to 200 $m^3/h$). The MA are included in various lines of technological processes of the power stations.

As a result of these investigations I am confident that currently there are no convincing data on the efficiency and usefulness of these units.

There is a phenomenon of Saratov heating station - 1 where there is no chemical treatment of water and all the feed water passes through the MA. Currently we are investigating this heating station in order to explain which element of the water treatment system is essential for the normal performance of boilers in the heating station. Unfortunately, a year ago our laboratory had to interrupt the work due to the lack of funds.

*Question 15: Your laboratory did extensive field testing at many different applications. Please summarize your findings.*

**Answer 15:** Refer to answer 14.

*Question 16: According to your experience, both at laboratory scale and full-scale, does the efficiency of the magnetic units depend very much on the design details of the units themselves and the precise flow rate through these units? Or is it more dependent on the chemistry of the water and particles at a particular application?*

**Answer 16:** Before we try to determine how many devils can be placed on the sharp tip of a needle, we must determine if the devil really exists.

*Question 17: You have indicated that reproducible scale precipitation measurements are difficult to achieve. Please comment on the relative importance of precisely controlling:*

I. *the preparation of the surfaces on which precipitation will occur*
*II. the chemical composition of the water from which the scale is precipitated*

**Answer 17:** The amount of the deposits on the heated surface can be determined by the following groups of factors:

I. thermal hydrodynamic situation in the vicinity of the surface;
II. composition of the water medium both chemical and dispersion;
III. condition of the surface itself.

All these factors are equal importance. The control of the condition of the surface is the easiest to achieve. Use chemically passivated surface with even micro relief.

*Question 18: What is a good practical way of preparing metal surfaces prior to scale precipitation?*

**Answer 18:** I suggest etching of degreased surface with 3-8% solution of HCl or other strong acid.

*Question 19: Do you believe that there are essential differences between the efficiency of units at laboratory and full-scale? (small* versus *big) Or between units operating in a "real" environment with dust and impurities, or operating under laboratory conditions? (dirty* versus *clean)*

**Answer 19:** Refer to answer 6.

*Question 20: Finally, what is your personal opinion on the future of magnetic water*

*treatment within the next ten to twenty years? Will it be refined and improved to a consistent, robust form of scale control, or will it remain a rather unpredictably, unreliable method?*
**Answer 20:** I think that till the "magnetic phenomena" are not thoroughly investigated on a laboratory scale by independent qualified researchers, the future of magnetic units will remain uncertain and will depend on the trust of users and funds spent on advertising.