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Scale control in heat exchangers

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ABSTRACT

Whenever natural water is used in a heat-exchanger, scale deposits tend to build up on heat transfer surfaces. This results mainly from the chemistry associated with the hardness and alkalinity of natural water. To ameliorate the problems created by scale deposition, a wide range of methods and processes are available.

This thesis investigates the efficiency of one of these methods, magnetic treatment. Two pilot plants were used to measure the effect of a magnetic field created by a commercial non-intrusive clamp-on device on scale formation. The first pilot plant consisted of four domestic boilers, two treated and two controls, filled and operated four times daily with mains water dosed to specific hardness and alkalinity levels. This rig operated in single-pass mode, with the water contained in the boilers being flushed out after each heating cycle. The second rig was based on two loops, treated and control, filled with deionised water to which reagents were added to control hardness and alkalinity levels. Each loop consisted of a 75 litre tank feeding a scaling cell via a centrifugal pump. The scaling cells included a copper element, exposed on one side to a regulated flow of heating water (set temperature) and on the other side to the flow of scaling water.

The boiler rig results showed no significant influence of magnetic treatment on the scaling of the boilers' heating elements. On the recirculating rig, no significant effect of the magnetic devices on the amount of scale formed was observed. However, magnetic treatment appeared to have reduced by 50 % the thickness of the hard scale layer on the copper elements. The reproducibility of the experiments was significantly improved by precoating the copper element with a scale layer to overcome discrepancies introduced by the induction process.

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NOTATIONS AND ABBREVIATIONS

A	Crystal growth surface	m^2
A_1	Empirical constant	homogeneous to k_r
DI	Deionised water	
E	Activation energy	$\text{kg.m}^2.\text{s}^{-2}$
GR	Growth rate	
k_r	Rate constant of chemical reaction	homogeneous to A_1
K_1	Equilibrium constant for Equation 3	(-)
K_2	Equilibrium constant for Equation 4	(-)
K_d	Equilibrium constant for Equation 2 and 3	(-)
K^1	Constant	$\text{kg.m}^{-2}.\text{s}^{-1}$
LSI	Langelier scaling index	(-)
m	Mass of scale sample	mg
MTD	Magnetic treatment device	
M_{sa}	Mass of aragonite scale layer	mg
M_{sc}	Mass of calcite scale layer	mg
M_t	Total mass of scale layer	mg
n	number of degrees of freedom in a t-test	(-)
pH_s	Calcium carbonate saturation pH	(-)
P	Sticking probability	(-)
R	Universal gas constant	$\text{kg.m}^2.\text{s}^{-2}.\text{°C}^{-1}$
R_f	Fouling resistance	$\text{s}^3.\text{°C.kg}^{-1}$
$R_{f\infty}$	Asymptotic value of fouling resistance	$\text{s}^3.\text{°C.kg}^{-1}$

RSI	Ryznar scaling index	(-)
SEM	Scanning electron microscopy	
s	Surface of scale sample	m ²
S _s	Scaled surface	m ²
t	Time	s
t _c	Measure of deposit's tenacity	s
t _d	Induction time	s
t _n	Value of t-test performed on a sample with n degrees of freedom	(-)
T	Temperature	°C
T _s	Surface temperature of heat exchanger	°C
U	Overall heat transfer coefficient (t=0)	kg.s ⁻³ .°C ⁻¹
U ₀	Overall heat transfer coefficient (t>0)	kg.s ⁻³ .°C ⁻¹
ΔT	Temperature difference	°C
Ω	Empirical factor (in scaling models)	(-)

Chapter 1: INTRODUCTION

The build up of scale deposits is a common and costly problem in many industrial processes using natural water supplies. In Britain alone the formation of scales in industrial process plant where water is heated or used as a coolant is estimated to cost £1 billion per year [1]. Such costs can be attributed to the cleaning of the scaled surfaces or to the increase in operating costs due to the poor conductivity of scale. For example, a 2.0 mm scale layer can induce a 47% decrease in overall heat transfer for a heat exchanger with a heat transfer coefficient of $1000 \text{ W.m}^{-2}.\text{°C}^{-1}$ [2]. Moreover, scale deposits narrow the inner diameter of piping, increasing the amount of energy required to pump the cooling fluid through the system.

Scaling is defined as the deposition of sparingly soluble salts present in water [2]. In the case of calcium carbonate (CaCO_3), the most common scalant in heated systems, this occurs as a result of temperature or pH changes, influencing the carbonate/bicarbonate chemistry. Other common scale-forming compounds include calcium sulphate, barium sulphate, calcium phosphate, magnesium hydroxide, zinc phosphate, iron hydroxides and silica, all of which occur naturally in raw water supplies.

Chapter 2 comprises a literature review on the problem of scaling in heat exchanger: Section 2.1 explains the concepts of hardness and alkalinity and the units in which they are usually expressed. Section 2.2 reviews the chemistry of calcium carbonate precipitation and crystallisation, and its application to scaling models and predictive indices. In Section 2.3, the consequences of scaling on the operation of heat exchangers are examined. This leads to Section 2.4 in which the scale controlling methods currently available are described, classified according to their mode of action. In this section, the emphasis is put on magnetic treatment, the scale controlling method assessed in this thesis.

In Chapter 3, the experimental equipment used to investigate the effects of magnetic treatment on scale formation is described: Section 3.2 and 3.3 present the two rigs on which the scaling tests were performed. Chemicals, equipment and analytical techniques used are presented in Section 3.4.

Chapter 4 includes all the results obtained on the experimental rigs. The discussion is separated between Section 4.1, concerning the boiler rig results, and Section 4.2 which deals with the recirculating rig. In addition, an extensive study of the composition of the scale layer is provided in Section 4.2.6.

Finally Chapter 5 gives the general conclusions that can be drawn from the experimental results obtained.

Appendices A and B include all the raw data obtained on the experimental rigs.

Chapter 2: LITERATURE REVIEW

2.1 *HARDNESS AND ALKALINITY*

The concepts of hardness and alkalinity are closely related to the description of scaling systems. The following sections review these two important parameters as well as the units used to express them.

2.1.1 *Hardness*

Hardness is defined as “the ability to form a scum with soap” [3]. In practice, that means that hardness is in fact a measure of the water’s content of Ca^{2+} and Mg^{2+} , both of which tend to form insoluble salts with organic anions from detergent. The natural hardness of water is a consequence of the presence in the ground of CaCO_3 which dissolves under the action of percolating rainwater into Ca^{2+} and CO_3^{2-} . CaCO_3 is the main constituent of chalk or limestone and in that respect is a major constituent of the earth’s minerals.

When natural water is boiled, calcium and magnesium bicarbonates decompose to carbonates, which have a low solubility in water. The amount of hardness which precipitates in this way is called the *temporary hardness* [4]. It is the amount of hardness or bicarbonate in the analysis, whichever is the lower [3]. After all the ions responsible for the temporary hardness have precipitated, the hardness which is left is called *permanent hardness*. This comprises the salts of calcium and magnesium, such as sulphates and chlorides, that are not affected by boiling. It is also sometimes referred to as *non-carbonate hardness*.

2.1.2 Alkalinity

Alkalinity is a measure of the water's ability to neutralise acids [3]. In natural water, it can be considered as a measure of the water's content in HCO_3^- . As it is the case for hardness, alkalinity is the consequence of the presence in earth's ground of CaCO_3 . In addition to that, CO_2 under Henry's law tends to dissolve in water, dissociating into the species responsible for alkalinity.

2.1.3 Units of measure for alkalinity and hardness

A common unit of measure for both alkalinity and hardness is "ppm as CaCO_3 " which is roughly the same as "mg as CaCO_3 " at low concentrations. The main interest of this unit is that it allows the hardness and the alkalinity of a water to be expressed in the same unit.

The correspondence with the more specific units "ppm of Ca^{2+} " used for hardness and "ppm of CO_3^{2-} " used for alkalinity is based on the relative molecular masses of Ca, CO_3 and CaCO_3 , that is 40, 60 and 100 $\text{mg}\cdot\text{mol}^{-1}$. As an example:

$$\begin{aligned} 150 \text{ ppm hardness as } \text{CaCO}_3 &= (150/100 \times 40) \text{ ppm hardness as } \text{Ca}^{2+} \\ &= 60 \text{ ppm hardness as } \text{Ca}^{2+} \end{aligned}$$

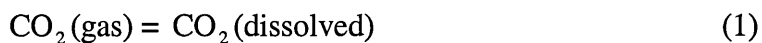
$$\begin{aligned} 300 \text{ ppm alkalinity as } \text{CaCO}_3 &= (150/100 \times 60) \text{ ppm alkalinity as } \text{CO}_3^{2-} \\ &= 90 \text{ ppm hardness as } \text{CO}_3^{2-} \end{aligned}$$

2.2 CALCIUM CARBONATE

The chemistry and crystallisation of calcium carbonate is presented below. The crystallisation process in particular is described together with its application to scaling models and predictive scaling indices.

2.2.1 Carbonate chemistry

Carbonate chemistry refers to the series of chemical reactions leading to the equilibria between CO_2 , HCO_3^- and CO_3^{2-} . These chemical reactions can be listed as follows:



The species involved react accordingly to the following laws of Mass Action:

$$K_d = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (5)$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (6)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (7)$$

with (5) being the product of the Laws of Mass Action of Equations (2) and (3). This common simplification is based on the assumption of equivalence of concentrations and activities at low concentrations and by the fact that H_2CO_3 is unstable, effectively existing as “dissolved CO_2 ” in water. All equilibria are pH dependant according to the above equations, which may be depicted graphically (Figure 1).

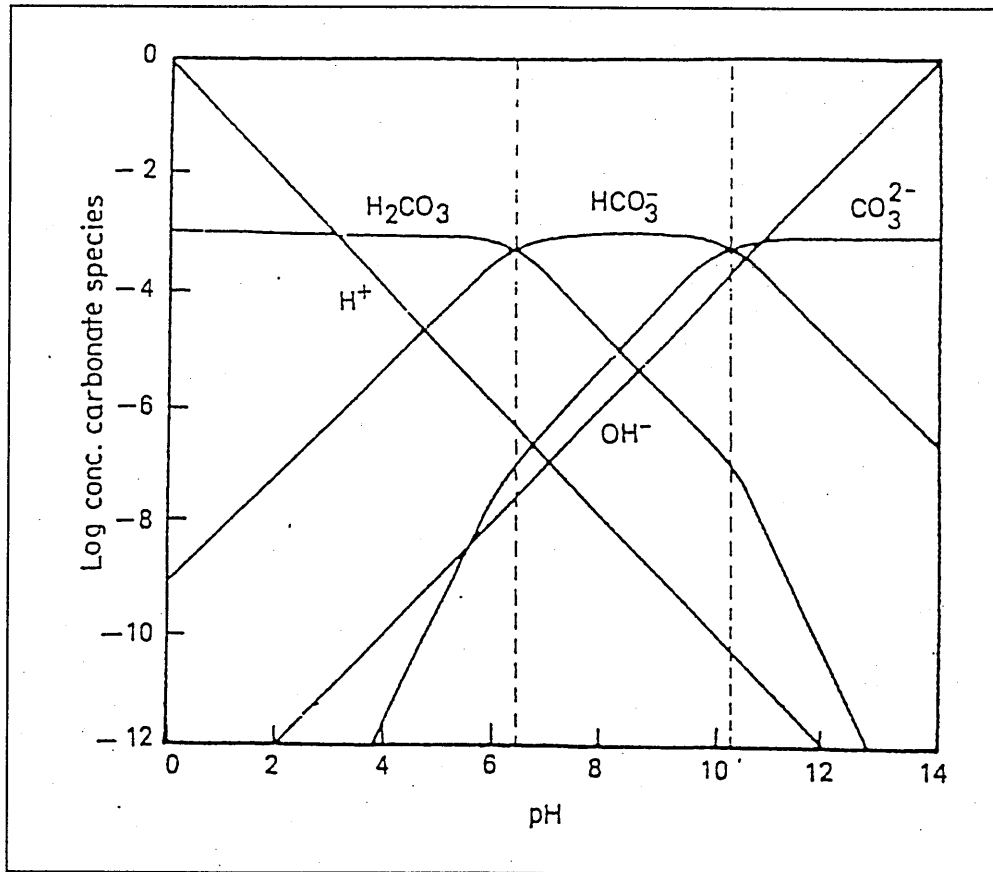
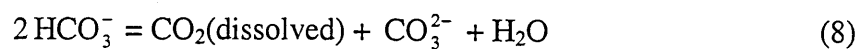


Figure 1: Concentration distribution for carbonate species [3]

The main consequence of the carbonate equilibria is that at a pH of 3.8, it can be considered that no HCO_3^- is present [3]. In same way, it is a reasonable simplification to say that at a pH of 8.3, no CO_3^{2-} is present.

The precipitation of calcium carbonate in heated solutions is ruled by the following two equations [5]:



When the solution is heated, CO_2 escapes, favouring the bicarbonate decomposition reaction followed by $CaCO_3$ precipitation.

2.2.2 Scaling prediction methods

The scaling potential of a water is often assessed by empirical indices. The two most commonly used are [6]:

- the *Langelier* index (or saturation)
- the *Ryznar* index (or stability)

To determine any of these, the pH of saturation (pH_s) for calcium carbonate is first calculated using Equations (5) through (7). This calculation has been simplified by the development of graphs and slide-rules. The scaling index is then evaluated and compared to a reference table. This indicates to which extent the solution has a potential for scaling (or corrosion) [6].

In addition, more sophisticated methods for the prediction of calcium carbonate scaling rates are available such as Hasson's model [7][8].

2.2.2.1 Langelier index

The Langelier index is the most commonly used index, and is particularly used for brackish waters and tap water [9]. It is defined as being the difference between the pH of the water and the saturation pH value in the conditions of CaCO_3 chemical equilibrium [9]:

$$\text{LSI} = \text{pH} - \text{pH}_s \quad (10)$$

where LSI is the Langelier index
 pH is the measured or calculated pH value
 pH_s is the saturation or equilibrium pH value

It is a common simplification to assume that if the LSI is positive, calcium carbonate scale will form whereas if it is negative, scale will dissolve [6].

2.2.2.2 Ryznar index

The LSI only shows the direction of the scaling driving force but do not indicates if the supersaturation is high enough to initiate crystallisation. Ryznar suggested an index, which can be considered to be a quantitative as well as a qualitative measure of the solution's scaling potential. It is defined as [8]:

$$RSI = 2pH_s - pH \quad (11)$$

where RSI is the Ryznar index
 pH is the measured or calculated pH value
 pH_s is the saturation or equilibrium pH value

Ryznar has shown experimentally that if the RSI is less than 6, calcium carbonate scale will tend to form whereas if it is greater than 6, scale will tend to dissolve [6].

The following table keys the scaling potential of water to the Langelier and Ryznar scaling indeces.

Table 1: Scaling severity keyed of water keyed to the Langelier index [6]

LSI	RSI	Scaling Conditions
3.0	3.0	extremely severe
2.0	4.0	very severe
1.0	5.0	severe
0.5	5.5	moderate
0.2	5.8	slight
0.0	6.0	stable
- 0.2	6.5	very slight tendency to dissolve scale
- 0.5	7.0	slight tendency to dissolve scale
- 1.0	8.0	moderate tendency to dissolve scale
- 2.0	9.0	strong tendency to dissolve scale
- 3.0	10.0	very strong tendency to dissolve scale

2.2.3 Calcium carbonate crystallisation

The sequence of events that leads to the crystallisation of a salt may be defined as [10]:

SUPERSATURATION → CRYSTAL NUCLEI FORMATION → CRYSTAL GROWTH

A solution is said to be supersaturated when it contains species in concentration such that the corresponding salt's solubility as defined by thermodynamic equilibria, is

exceeded. This situation arises if, for instance, a solution temperature is modified. Supersaturation is then a consequence of sluggish crystallisation kinetics caused by a high activation energy barrier. The formation of crystals (also called nucleation) usually follows and either occur spontaneously (homogeneous nucleation) or can be aided by the presence of suitable nuclei, which may be either solid impurities in suspension in the solution or sites on the heat exchanger surface (heterogeneous nucleation). Crystal growth by incorporation of ions into the crystal lattice follows the formation of stable nuclei within the region where super-saturation occurs [11].

One of the characteristics of calcium carbonate is that it possesses an “inverse solubility”, that is to say that the solubility of CaCO_3 decreases with temperature. The main consequence of this property is that calcium carbonate will precipitate preferably in areas of high temperature. Heaters are thus particularly exposed to the scaling of their surfaces [5].

When calcium carbonate precipitates it can form crystals of various defined allotropic structure, or form an amorphous deposit. There are three allotropic forms for CaCO_3 crystals: aragonite, calcite and vaterite. Their formation depends mainly on the conditions under which the precipitation occurs, mainly the solution's temperature, and subsequent transformation, particularly in the case of vaterite, can occur. Each allotropic form is easily recognised by the shape of the crystals it forms: needle-shaped for aragonite, cubic for calcite and spherically-shaped for vaterite. Figures 2 and 3 show pictures taken by Scanning Electron Microscopy (SEM) of calcite and aragonite crystals.

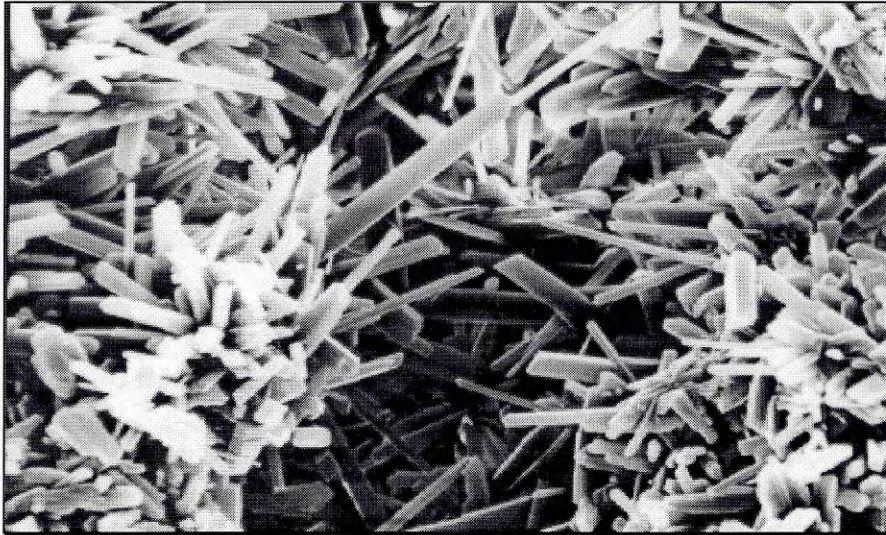


Figure 2: Picture of clusters of CaCO_3 aragonite crystals taken by SEM

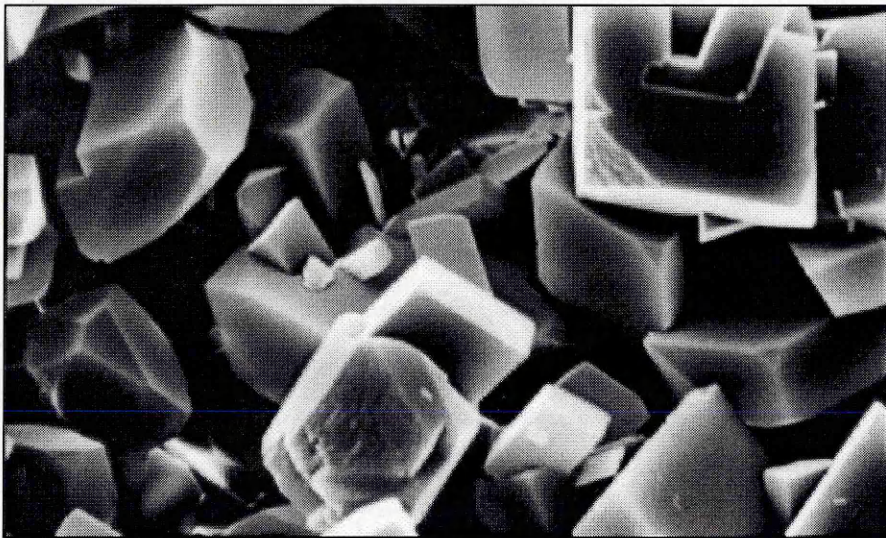


Figure 3: Picture of clusters of CaCO_3 calcite crystals taken by SEM

2.2.4 Crystallisation fouling models

Mathematical analysis of chemical reactions can provide a first intuitive model of crystallisation fouling, since the incorporation of ions into the crystal lattice on a heat transfer surface may be regarded as a chemical reaction [10]. If the rate of deposit formation is assumed to be some function of A and k_r , where A is the crystal growth area and k_r is the rate constant of the assumed overall chemical reaction describing the chemical process, then k_r can then be expressed according to an Arrhenius model [10]:

$$k_r = A_1 \cdot e^{-\frac{E}{RT}} \quad (12)$$

where A_1 is an empirical constant
 E is the activation energy
 R is the universal gas constant
 T is the absolute temperature

The difficulty in this approach is in assigning values to A_1 and E .

An early practical model was developed by Kern and Seaton in 1959 [12]. This model is based on an exponential relationship that takes into account a number of interacting factors, principally the relation between deposition and removal forces. It has been used as the basis for many models applied to particular fouling processes [10].

$$R_f = R_{f\infty} \cdot \left(1 - e^{-\frac{t-t_D}{t_c}} \right) \quad (13)$$

where R_f is the fouling resistance at time t
 $R_{f\infty}$ is the asymptotic value of the fouling resistance
 t_D is the induction time
 t_c is a measure of the tenacity of the deposit

R_f can be equated to a measure of the level of fouling [13]:

$$R_f = \frac{1}{U} - \frac{1}{U_0} \quad (14)$$

where U is the overall heat transfer coefficient at $t=0$

U_0 is the overall heat transfer coefficient at $t>0$

In order to take into account the effect of supersaturation, Hasson (1981) quoted a simplified model [7]:

$$\frac{dm_f}{dt} = K^1 A P \Omega^{\frac{-E}{RT_s}} \quad (15)$$

where m_f is the mass of deposit

K^1 is a constant

A is the area on which the fouling occurs

P is a “sticking probability”

Ω is an empirical factor

T_s is the surface temperature

E is the activation energy

R is the universal gas constant

This model is empirical and can only be applied to conditions under which the conditions were obtained [10].

2.3 SCALING IN HEAT EXCHANGERS

To appreciate the full extent of the problem represented by scaling in heat exchangers, one only has to turn to data provided by industry. It has been estimated that fouling can cost a typical American refinery as much as \$1 million a year in terms of increase in capital and operating costs [14]. The market for scaling-control methods is thus of considerable size.

The problem caused by fouling of a heat exchanger fall into two broad categories: operating difficulties and additional costs [15]. The following table lists the usual consequences of fouling:

Table 2: Problems caused by fouling

Category of problems	Problem identification
Operating difficulties	<ul style="list-style-type: none">• loss of heat transfer efficiency (Figure 4)• increased pressure drop• reduced flow rate• uneven flow distribution
Sources of additional costs	<ul style="list-style-type: none">• corrosion• additional heat exchange surface• operation and maintenance• loss of production• additional pumping power

The complexity of the phenomena involved and their mutual interaction makes fouling reduction a difficult problem. In the particular case of scale reduction, it should be noted that crystallisation in general, and crystallisation of calcium carbonate in particular is a process that is not yet fully understood, and even today is subject to

speculation [16]. The scale-control market thus incorporates a broad range of methods based on a variety of fundamental mechanisms, some of which have little scientific credibility. However, scale controlling methods are generally based on either prevention or inhibition of scale. Prevention of scale is achieved by eliminating the scale-forming cations (i.e. the ions contributing to the “hardness”) from the water. In the case of inhibition, the aim of the technique is to retard as much as possible the appearance of scale.

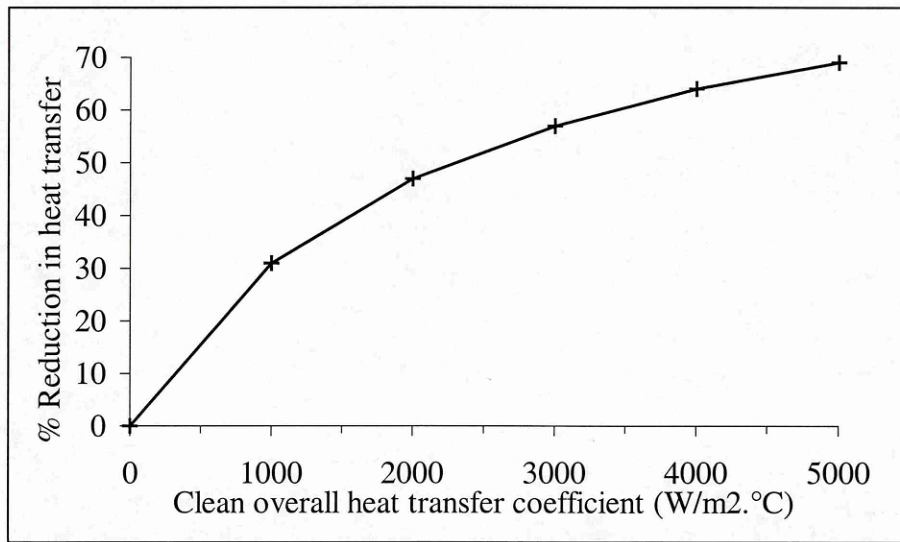


Figure 4: Reduction in Heat Transfer due to CaCO_3 Scaling (1.0 mm layer) [2]

2.4 SCALE CONTROLLING METHODS

The existing scale controlling methods can be classified as follow:

- processes accommodating the effects of scaling in the design of the system
- processes using chemical or physico-chemical treatment of the scaling water
- processes using physical treatment

The various methods used to remove existing scale belong in the first category. These include acid-washing of the surfaces as well as all the various mechanical methods in use, such as brushing and scraping. The following table gives a review of all the existing methods for the amelioration of scaling.

Table 3: Methods for amelioration of scaling

Approach	Generic method	Process
In-situ methods		
Design approach	Mechanical	fluidised media physical treatment of surfaces over-sizing
Scale removal	Chemical	acid wash
Ex-situ methods		
Batch-wise scale removal	Mechanical	scrapping, hydro-blasting etc.
	Chemical	acid wash
Pre-treatment methods		
Hardness removal	Physico-chemical	ion exchange precipitation by lime dosing pellet softening
	Chemical	precipitation
Decarbonation	Chemical	acid dosing + air stripping
pH control	Physico-chemical	acid dosing
Scale prevention	Chemical	threshold inhibitors (Zn, polyelectrolytes etc.)
	Physical	magnetic treatment ultrasonic treatment etc.

2.4.1 In-situ methods

In-situ methods are those which incorporate scale reduction within the heat exchanger design. For instance, heat exchangers may be over-sized to accommodate the loss of heat transfer efficiency due to scaling, which implies bigger initial investment cost [2].

The heat transfer surfaces can also be manufactured to deter the deposits from sticking [17]. Some specific designs have also been developed over the years to minimise scaling problems. An example is the fluidised bed heat exchanger (Figure 5). It contains particles that are agitated by an upward flow of fluid. Several designs have been developed over the years. They include the standard model as well as circulating fluidised beds, which are becoming increasingly popular because of their operational stability [18]. The success of this technology relies upon the abrasive effect the bed particles have on the heat-transfer surfaces. Particles between 1 and 5 mm in diameter can be manufactured from a wide variety of chemically and mechanically resistant materials. Examples range from glass beads [17] to stainless steel wire cuts [18].

The advantages of fluidised bed heat exchangers are [18]:

- completely scale-free heat-exchange surface by the abrasive effect of the particles
- excellent heat transfer coefficients at low superficial velocities
- pressure losses comparable to normal forced-convection tube-bundle heat exchangers
- negligible erosion of the tubes

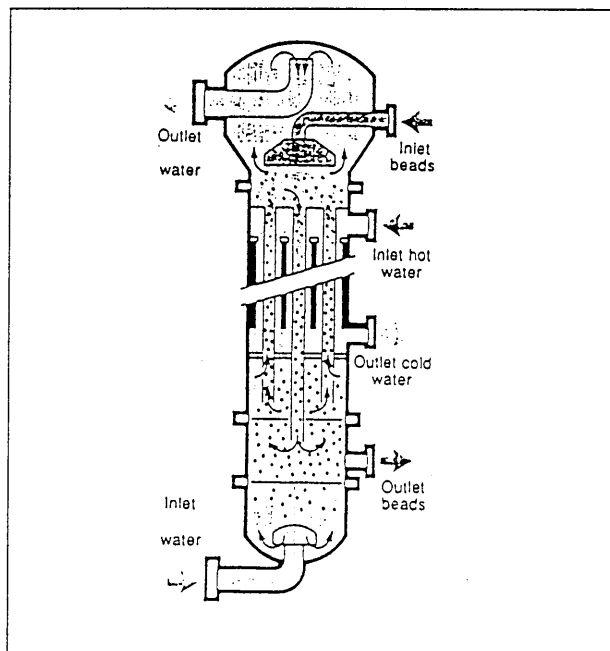


Figure 5: Typical design of a fluidised bed heat exchanger [17]

2.4.2 Ex-situ methods

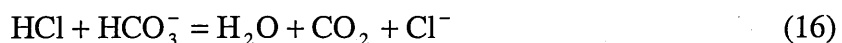
Physical removing of scale as a method of scale control can be accomplished using scraping, hydro-blasting, sand-blasting, metal or nylon brushing of the heat-transfer surfaces [19]. In some cases (shell and tube design), this entails taking apart the heat exchanger to gain access to the heat transfer surface.

All these operations are quite costly through the expenses related to down-time. Moreover, scrapping can prematurely age the heat exchanger surfaces. Great care must also be given to avoid roughening the surfaces, which would create preferential scaling sites.

2.4.3 Chemical conditioning of water

2.4.3.1 Processes altering the water chemistry

Scaling in cooling water can be controlled by maintaining a pH lower than 7, by acid feeding. The acids most commonly used for this purpose are sulphuric acid and hydrochloric acid [9]. Sulphuric acid however increases the content of sulphate ions in the feed water and consequently the risk of CaSO_4 precipitation [9]. Acid dosing acts by converting bicarbonate to carbon dioxide, accordingly to the following reaction (HCl acid dosing):



In any cases, corrosion inhibitors are required to avoid the severe problems that can occur at such pH levels [2][20].

Another chemical-based method is precipitation, using for instance soda. This involves separating the precipitates in an additional step using flocculation, sedimentation or filtration processes. This method require sophisticated process control since the process is highly sensitive to fluctuations of the operating parameters [9].

Additional methods include pre-treating the water to diminish its scaling potential, the most straight-forward way being softening the water using for instance ion exchange or reverse osmosis. In the case of ion exchange, synthetic resins with incorporated sulphonic acid groups such as styrene-based copolymers are commonly used [9]. Unfortunately, softening the water presents the major drawback of creating very favourable conditions for corrosion [21].

Pellet softening can also be used as a method of scale reduction. A pellet softener consists of a cylindrical vessel containing a fluidised bed of grains of seed material that provides a large surface on which the crystallisation of calcium carbonate takes place in a fast reaction. Softening chemicals such as caustic soda (NaOH), lime (Ca(OH)_2) or soda lime (Na_2CO_3) are used to instigate the crystallisation [22]. A typical design of a pellet softener is presented in Figure 6.

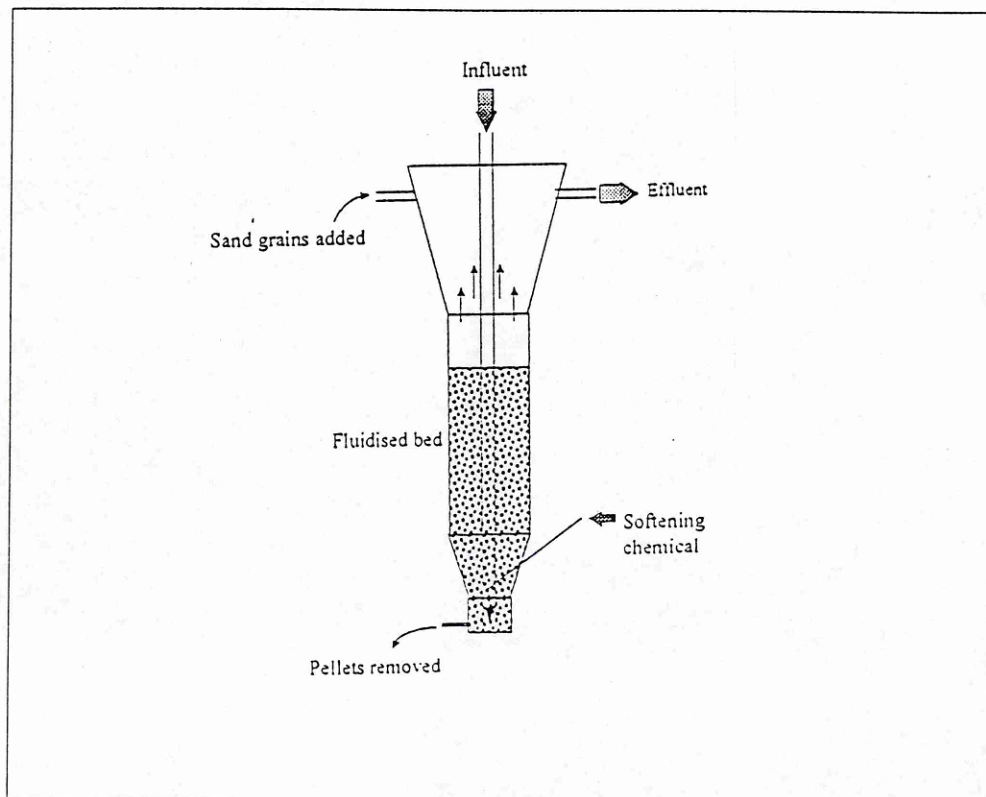


Figure 6: Example of Pellet Softener (Blackpool design) [22]

Pellet softening technology presents the advantage of generating recyclable products, solid grains of calcium carbonate, which have uses in industry and agriculture. However, calcium and bicarbonate cannot be removed to the low concentration produced by conventional softening and the crystallisation process only proceeds for as long as the solubility product of calcium carbonate is exceeded. Also, hardly any magnesium is removed [22].

2.4.3.2 Processes inhibiting the crystallisation process

A widely used technique for controlling scaling problems is by dosing trace amounts (0.5 to 10 ppm) of chemical additives that are able to inhibit growth of a scale layer and tend to weaken its adherence to a flow surface. The mode of action of these chemicals are listed below [15]:

- sequestering action: forms a chemical complex with the fouling substance to keep it in solution or suspension
- threshold inhibition: retards precipitation of scale forming salts while they remain in the system, prevents the growth of crystal nuclei
- dispersing action: imparts like charges to both the heat exchanger surface and particles in order to maintain the particles in suspension
- chelating action: forms a strong chemical complex with scale forming cations
- crystal modifier: changes the crystal habit to prevent the formation of large crystals in suspension or on the heat exchanger surface

The following table lists some common chemical additives used to control scaling in heat-exchanger using water as a cooling liquid:

Table 4: Some common additives used for scaling treatment [2] [15][20][23][24]

Chemicals type	Mode of action	Advantages	Drawbacks
Zinc chromate <i>Being replaced by phosphates</i>	•crystal distortion	•well known by its wide usage	•hazardous to health •requires cleaning of settled scale sludge
Polyphosphates Most popular additive <i>(sodium tripolyphosphate)</i>	•threshold inhibition	•successfully used for years	•sensitive to pH and T° •easily oxidised •used as nutrients by micro-organisms •reacts badly to shock loads
Phosphonates	•threshold inhibition	•excellent threshold inhibition •excellent crystal distortion •stable over a wide range of pH and T°	•costly •environmental impact
Water soluble polymers <i>(ex: polymaleic acid)</i>	•sequestering action •threshold inhibition	•low-cost treatment	•requires cleaning of settled scale sludge •requires dispersing agents on heavy loads

The most important parameters determining the effectiveness of scale inhibition are the chemical composition of the scaling water, the chemical nature of the inhibiting species and its dosage level. Recent work has indicated that the flow configuration may also be of major importance, both in scale inhibition and in scale suppression[25].

The use of chemical inhibitors does not involve major initial capital investment. However, in once-through systems, the cost of treatment may be high [15]. The large number of chemical formulations available makes the choice of an additive very difficult. Moreover, theoretical aspects of crystal growth are, at best, inadequately understood and the literature provides very little guidance on the expected performance of a specific additive in a given scaling situation [25]. Last but not least, whichever type of threshold inhibitor is used, occasional de-scaling is needed after a period of time depending on the application and the conditions of use (one year for sea-water evaporators) [4].

2.4.4 Physical conditioning of water

Physical conditioning can be based on electric, magnetic or ultrasonic treatment. Such treatment does not modify the mineral content of water but acts on the morphology of the precipitate which is then mainly made up of fine particles [26]. Moreover, by their very nature, these methods do not generally add to the chemical content of the water.

2.4.4.1 Electronic treatment

Electronic anti-fouling technology (EAF) is based on the use of an induced electrical field that fluctuates with time. An EAF device is usually composed of one or several wires wrapped around a feed pipe to a heat exchanger, forming a solenoid (Figure 7). The two ends of each wire are connected to the EAF control unit, which produces a pulsing current to create time-varying magnetic fields inside the pipe. Subsequently, the time-varying magnetic field creates an induced electric field, a phenomenon that can be described by Faraday's law. In order to maximise the induction, a pulsing current having a square-wave signal is used. The frequency of the signal has to be adapted in order to minimise the self-induction caused by the solenoid coil [19].

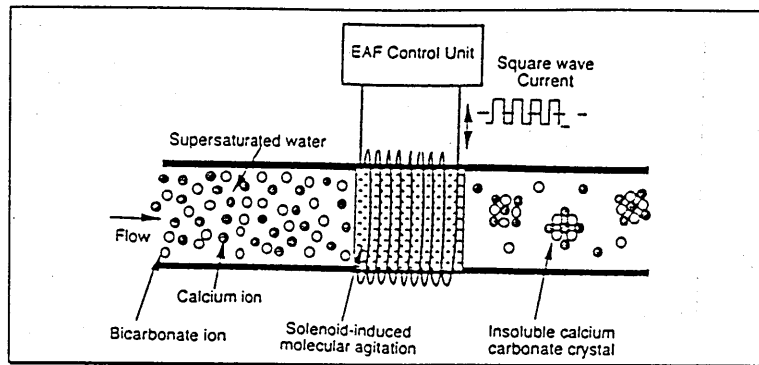


Figure 7: Schematic diagram of an EAF device [19]

Cho et al. proposed the following mechanism describing the action of EAF. The effect of the induced electric field, which oscillates with time, is to provide the necessary molecular agitation to charged mineral ions such as calcium and bicarbonate so that they collide and precipitate. The precipitated nuclei and the heat-exchanger surface compete for dissolved mineral ions. Since the combined surface area of the nuclei can be greater by several orders of magnitude than the surface area of the heat-exchanger, the fouling at the heat exchanger surface is prevented [27]. By its action, EAF creates a sludge compose of suspended calcium carbonate crystals, such that the devices must either be coupled with a filtration unit [19] or the sludge must be manually removed [26].

Claims about EAF technology include effective scale prevention [19], reduced speed of scale formation [26], scale reduction [16] and preferential formation of a less adherent scale, which is then more easily removed [27].

2.4.4.2 Ultrasonic treatment

Ultrasonic treatment is based on a generator which produces electrical impulses at high frequency, which are transmitted via a coaxial cable to transducers mounted externally. Each transducer contains piezoelectric ceramic crystals which, when excited by the electrical impulses, generate an ultrasonic beam [28].

As with others physical conditioning methods, ultrasonic devices are non-invasive such that possible contamination is avoided. Very few scientific publications can be found concerning this technology, evidence of its efficiency is rather anecdotal.

2.4.4.3 Magnetic treatment

2.4.4.3.1 Introduction

Magnetic treatment has an extensive history. Based on the application of magnetic fields to prevent scale, an early patent by Faunce and Cabel was registered in 1890. This patent was to prevent boiler encrustation. Many more patents have since been registered promoting a wide range of devices for the physical treatment of water. The technology has been most widely accepted by industry in the former Soviet Union, who have been employing devices in a variety of applications for many years and include some substantial installations to treat very large flows. As a result of this, most early research originates from Soviet laboratories, and a wide range of fundamental studies have since been translated into English. European interest in anti-scale magnetic treatment (AMT) first became evident with the works of Vermeiren (1958). The range of physical water treatment devices currently available is extremely varied and academic opinion is still divided as to its true efficacy. Recent level of research activity suggests that commercial interest remains high, however, and many institutions world-wide are currently engaged in further research into this area.

2.4.4.3.2 Industrial applications of commercial devices

Commercial magnetic treatment devices (MTD's) are available in various configurations from numerous manufacturers, some using electromagnets and others using single or arrays of permanent magnets with many different orientations of magnetic field. Some MTD's are intrusive (i.e. plumbed in, and therefore have to satisfy relevant legislation) or non intrusive (i.e. clamped on) and the cost of the unit varies with size up to

thousands of pounds [29]. Gruber and Carda (1981) classified MTD's using permanent magnets into four categories (Fig. 8), each employing different orientations of magnetic field. Some units employ a field that is orientated mostly orthogonal to the direction of flow (class II and class III) whilst others employ a mostly parallel field (class I and IV).

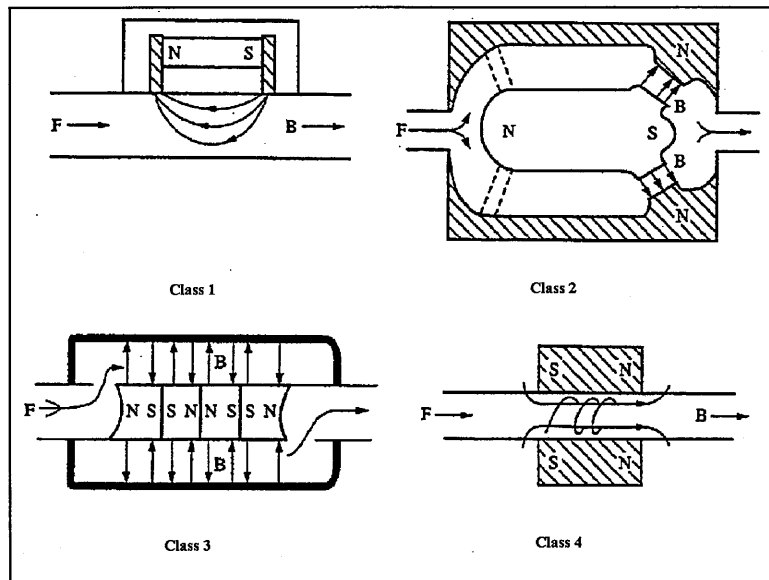


Figure 8: Classification of permanent magnet type MTD's [30]

The trade literature surrounding AMT contains abundant qualitative surveys of installed commercial apparatus. Details of positive effects regarding scale treatment have been documented many times in recent years [31][32][33][34]. AMT appears to have been most effective for scale suppression in systems with heated surfaces [29].

Results presented in literature normally take the form of photographic evidence. These suggest that magnetic treatment can not only reduce the scaling potential of the water but also cause the existing scale to dissolve over an extended period of time, normally between three to six months [35]. This action has been attributed to the ability of magnetic treatment to produce scale crystals which remain discrete, forming sludges or passing out of the system instead of adhering to surfaces [36]; the accumulation of easily removable flakes of scale in low points of the system has frequently been reported [37].

Whilst anecdotal evidence appears impressive, reports on specific applications often lack details of the conditions under which results were obtained. Critical design parameters of commercial magnetic conditioners are never revealed because the information is proprietary. It has also been reported [23] that improvements following installation of an MTD may have been due to an accompanying change in another process operating parameter, such as the increased blow down rate of a boiler.

2.4.4.3.3 Trials of commercial devices

Many impartial scientific studies attempting to quantify the magnetic effect on adhered scale, commissioned to test manufacturers' claims under repeatable conditions have failed to confirm that magnetic devices have an effect on either deposit growth or tenacity [23][30][38][39][40][41].

The abundant favourable anecdotal evidence, mostly presented in trade magazines, tends to suggest that most successful implementations result from continuously recirculating conditions. This is emphasised by analysis of the MTD sales of CEPI-Co., Belgium, 70% of which are destined for recirculating industrial cooling circuits. This could imply that continuous treatment of the water above a magnetic exposure threshold is necessary before any meaningful scale suppression can be exerted, or could otherwise imply that any effect is so small that a duration of 3 months or more is required before any positive effect can be manifested in quantitative experiments.

2.4.4.3.4 Effects on nucleation, growth and stability

The reported effects of magnetic treatment on the nature and size of precipitated particles vary widely. A large number of theoretical studies have been produced to support proposed mechanisms for magnetically affected crystallisation behaviour, usually with reference to crystallisation nuclei (CN's) formation in the bulk of the solution [42][43][44][45].

If the particle size can be influenced by magnetic treatment, then the solubility must also be slightly affected since larger particles have lower solubility than smaller ones due to their different surface energies[46].

2.4.4.3.5 Effects on crystallinity

Of the three calcium carbonate polymorphs of calcite, aragonite and vaterite, calcite is the most thermodynamically stable form at standard temperatures and pressures [47]. However at the surface temperatures commonly encountered in systems such as heat exchangers and boilers, aragonite is normally the first phase to be precipitated out of solution [48]. In this case, re-crystallisation of the aragonite into calcite over time could enhance the formation of a more tenacious encrustation [48][49]. The following table sums up the experimental data concerning the effects of magnetic treatment on calcium carbonate crystallisation published so far.

Table 5: Summary of experimental data concerning magnetic treatment

Reference	Observed effect	Comments
[50]	Suppressed nucleation with enhanced crystal growth	Used low strength, low frequency alternating field
[51]	Changes in the scaling tendencies of treated solutions	Accelerated scaling techniques, best effects with plastic-housed MTD
[52]	Enhanced nucleation with smaller crystals	Used CEPI devices
[35][49][53]	Suppressed nucleation and accelerated growth of nucleated CaCO ₃ particles (larger crystals).	Beneficial effects of AMT in many different scaling environments
[54][55]	Increased rate of precipitation, proportional to applied field; simpler crystal habit in treated water; increased CaCO ₃ solubility	Different effects recorded at different levels of supersaturation
[30]	No change reported in scale-forming tendency of hard water	Tested class I and III devices in once- through system
[40][41]	No effect on scale growth or tenacity of magnetically treated water	Tested class III devices in predominantly once-through systems under accelerated scaling conditions.

Magnetic treatment has been found to cause occasional differences in the precipitate crystal allotropic form, although authors come up with contradictory results. This can be attributed to a possible contamination by ions [5][47][56].

2.4.4.3.6 Effects on scaling kinetics and equilibria

Effects on CaCO_3 scaling rates have been noted in a number of studies conducted under diverse conditions. These have indicated that the magnetically induced change in the scaling rate can vary with field strength [54][57], the level of supersaturation or pH [54], the flow rate through the device [51] and the dissolved solids concentration [54].

Duffy (1977) concluded that the rate of CaCO_3 precipitation was unchanged by magnetic treatment. Other workers have found different results [54]. Dalas and Koutsoukos (1989) postulated that the magnetic field was probably merely influencing the kinetics of a single step in the crystal growth process, namely the dehydration step before growth units can diffuse to the active growth sites.

2.4.4.3.7 Influence of other physical and operating parameters

Many authors have found that the magnetic field's strength is an important variable, both in fundamental studies of magnetic fields on rates of crystallisation [55][57], the effects of MTD's on particle size [53] and on scaling rate in real installations [33]. Others have found that increases in magnetic flux density above a certain threshold produce no further effect [58][59]. It appears, both from the general design of MTD's and from the bulk of the scientific evidence, that an orthogonal field has the greatest effect.

There is evidence to suggest that AMT is also influenced by the concentration of supporting electrolytes, in much the same way as normal scaling is. Reports of AMT in such scenarios as cooling tower circuits and cooling water mains are often positive [31][60][61]. Under these instances the circulating water will certainly have a high ionic and suspended solids load. Koubikova (1969) demonstrated clear effects using a mineral water of conductivity 6.8 mS/cm.

2.4.4.3.8 Proposed Mechanisms

Assessment of the many proposed mechanisms for AMT is made difficult by the varied and often contradictory nature of the experimental results presented. The integrity of reported results and their interpretation are compromised by a number of factors such as irreproducibility of the experiments or unspecified chemical and physical conditions.

Proposed mechanisms can be broadly divided into four basic categories:

- intra-atomic effects (changes in electron configuration)
- contamination or 'seeding' effects (due to magnetically enhanced dissolution)
- inter-molecular/ionic effects (changes in co-ordination of water with ions)
- interfacial effects (distortion of the double layer)

Intra-atomic effects have been extensively discussed [57][62][63]. While some authors dismiss the intra-atomic hypothesis on the basis of energy calculation, other have come to the opposite conclusion [62].

Other workers have suggested that increased amounts of impurities may be introduced that can explain the results observed [5][23][48][64]. However, this cannot explain the results obtained using high purity solutions or results obtained using non-intrusive MTD's [57][59][65].

Lorentz forces have also been implicated in other proposed mechanisms based on different phenomena, including stabilisation of co-ordinated water [66], double layer distortion [50][67] and formation of stable or "frozen" complexes of calcium surrounded by co-ordinated water molecules [66].

Many authors have proposed that the magnetic effect is ostensibly interfacial, and some of the most credible experimental evidence would seem to support this view [49][50][58][63][65][67][68].

2.4.4.3.9 Summary

There is little doubt that in some cases AMT can exert a significant scale-inhibiting effect that cannot be attributed entirely to incidental factors such as solution chemistry, with specific reference to contamination, and temperature. However the efficacy of AMT with respect to specific applications, operating under particular physicochemical conditions, remains unclear. The majority of the reported evidence suggests that AMT is most effective when operating under conditions of:

- orthogonal fluid flow with respect to the magnetic field orientation
- recirculated solution and/or prolonged magnetic exposure

There is also much evidence pointing to an increased effect under conditions of enhanced supersaturation (i.e. higher temperatures, higher hardness and electrolyte concentrations, etc.).

Whilst some of the suggested mechanisms for AMT are plausible, many do not take full account of all the reported effects, and none are fully comprehensive.

Taken as a whole the reports on AMT and magnetically modified coagulation tend to support a mechanism based on the action of Lorentz forces in the electrical double layer causing a semi-permanent change in the charge at the shear (or outer Helmholtz) plane.

At this stage it is still uncertain whether magnetic suppression of scaling is a bona fide phenomenon. It is undoubtedly the case, however, that more widespread acceptance of AMT would result from a more comprehensive understanding of the mechanism by which the process may operate.

Chapter 3: EXPERIMENTAL PHASE

3.1 INTRODUCTION

Experiments were limited to the study of a commercial non-intrusive magnet, and conducted using the facilities available at the School of Water Sciences in Cranfield University. The first part of the study focused on the effect of permanent non-intrusive magnetic devices on scale formation in a single-pass rig. The second part of the study investigated the effects of the same magnets in recirculating conditions. Since it has been reported in numerous publications [5][69] that scale formation is extremely sensitive to physico-chemical conditions, each rig was run with both magnetically treated and control lines. Moreover, in view of the fact that changes in amounts of scale can be attributed to small differences in “identical” lines (i.e. the pipework, boilers and instruments), the magnetic devices were commutated between each run to account for these differences.

3.2 BOILER RIG

3.2.1 Introduction

The boiler rig was designed in order to simulate the conditions of use of a domestic boiler. It is located at the School of Water Sciences, Cranfield University.

3.2.2 Experimental set-up

The boiler rig consisted of four purpose-built 75-litre capacity rolled copper boilers fed by a 1500-litre polypropylene tank. This feed tank was mixed by means of a submersible pump which circulates water at approximately $4 \text{ m}^3 \cdot \text{h}^{-1}$. Each boiler is equipped with two heating elements having a combined power of 2 kW that regulated

the water temperature to the specified setting (70 °C). The piping was made out of 0.7 inches internal diameter normal-grade copper tubing.

Four GMX 800 devices were fitted on each test-boilers with two control-boilers left untreated. Each boiler was filled four times daily with tap-water pumped by four self-priming pumps. Each filling took about 150 seconds, using water pumped at a flowrate of 30 l.min⁻¹ and a velocity of 1.8 m.s⁻¹. The total daily throughput for each boiler was 300 l, checked by four combined cumulative/instantaneous flowmeters. Mains water was used throughout the experiments, dosed each day to the specified hardness and alkalinity levels using AnalaR grade CaCl₂(H₂O) and NaHCO₃ (BDH).

A flowsheet of the boiler rig is presented in Figure 9.

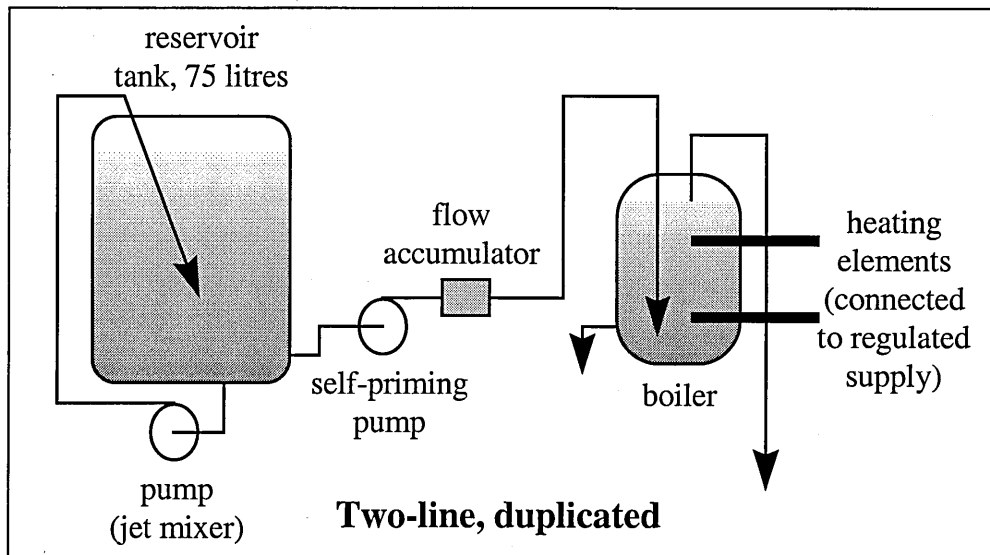


Figure 9: Experimental setup of the boiler rig

3.3 *RECIRCULATING RIG*

3.3.1 *Introduction*

The recirculating rig was designed to check the efficiency of magnetic treatment under the conditions that have been reported as being the most favourable, these being[70]:

- orthogonal fluid flow with respect to the magnetic field orientation
- recirculated solution
- accumulative exposure to the magnetic fields

The recirculating rig allows the control of most of the parameters that have been reported as having a critical influence on scaling. These parameters include flowrate, temperature of the heated surface and temperature in the feed tank, as well as control of the usual key water quality parameters of hardness, alkalinity and pH.

3.3.2 Experimental set-up

A flowsheet of the recirculating rig is presented in Figure 10:

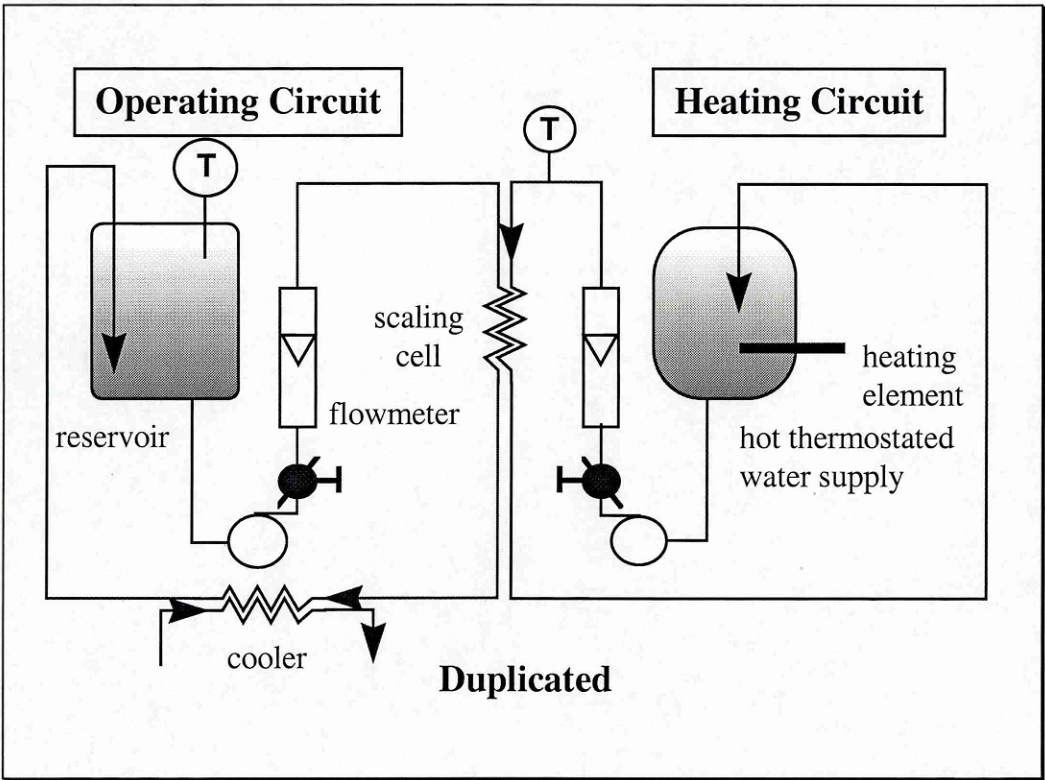


Figure 10: Experimental setup of the recirculating rig

The rig consists of two identical flow loops for direct comparison between treated and untreated systems. The operating conditions are chosen to promote scaling (pH range of 7.5-8.0, heated surface temperature between 60 and 65 °C, flow velocity ranging from 1.2 to 1.7 m.s⁻¹, Reynolds number between 12000 and 17000). The scaling cells design is based on the flat-cell type used previously at Cranfield and originally designed and

used by the Department of Chemical Engineering at Cambridge University. Figure 11 provides a schematic diagram of the device:

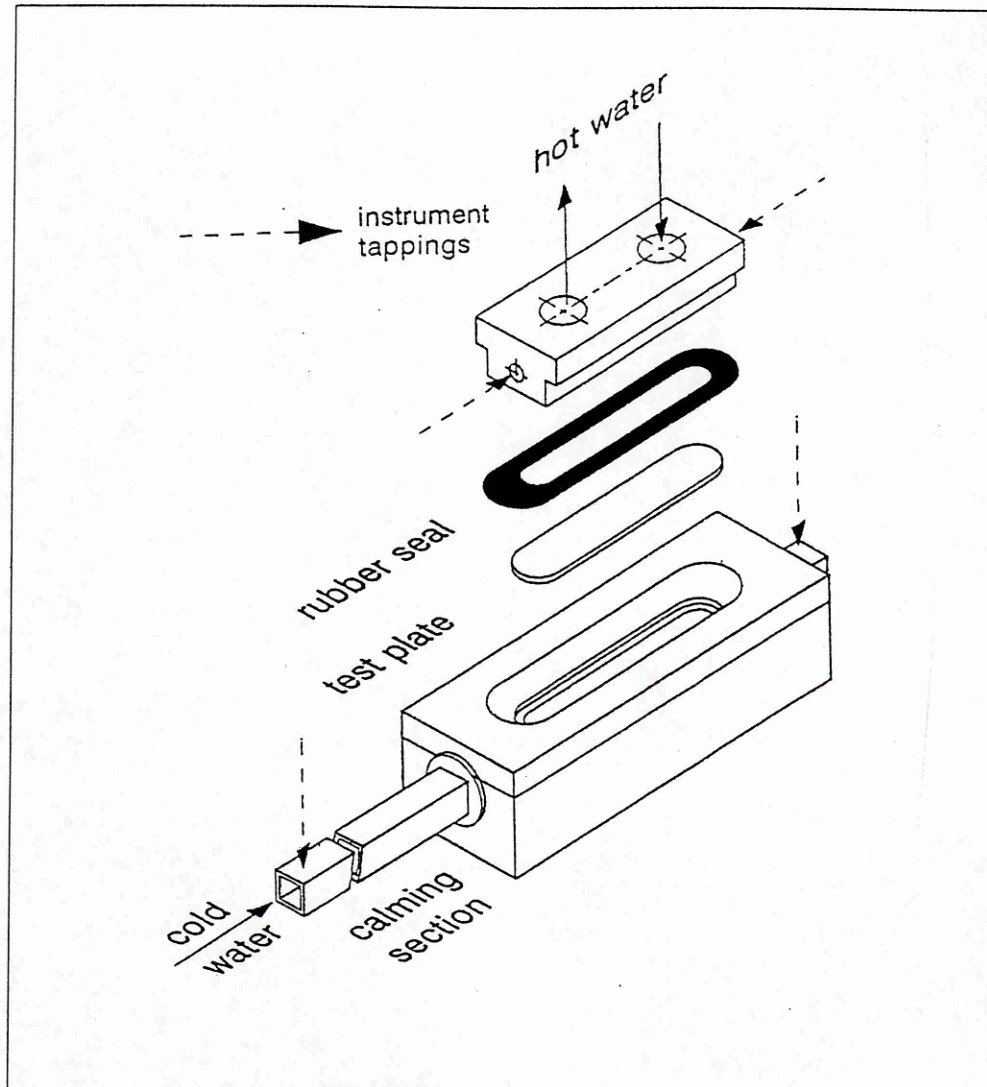


Figure 11: Schematic diagram of scaling cell [71]

Each loop includes the following elements:

- standard cylindrical PVC tank with a 90 litres capacity (FORBES)
- magnetic drive centrifugal pump (MARCH MAY)
- flowmeter
- Perspex™ scaling cell fitted with copper element and rubber seal
- cooler (copper-brazed / plate and gasket) (OCCO)

Two versions of this rig have been used throughout the experimental phase. The original design was used during the first two series of runs evaluating the efficiency of the GMX 800 elements (GMX trials 1 & 2) and on the commercial scale inhibitor runs (ATG trial). The new design was used on the subsequent runs (trials 3 and Calcat). Table 6 gives a detail summary of the organisation of the different trials.

The following improvements were made during the rebuilding of the rig:

- the inlet of the pump was brought to ¾” to increase the maximum flowrate
- the shape of the PVC feed tanks was modified to a cylindrico-conical shape to insure proper recirculation of the settled scale particles
- the two copper brazed coolers were changed to stainless steel plate and gasket models to get rid of possible contamination by Cu²⁺ ions.

Table 6: Detailed summary of the runs conducted on the recirculating rig

	Total runs carried out	Reproduci- bility runs	GMX 800 runs	Diagnostic runs	Calcat runs	ATG runs
GMX trial 1	11	4	7	-	-	-
GMX trial 2	10	5	5	-	-	-
ATG trial	10	2	-	-	-	8
Rebuilding of the rig (Section 3.3.2)						
GMX trial 3	12	1	10	1	-	-
Calcat trial	2	-	-	-	2	-
TOTAL	45	12	22	1	2	8

3.3.3 Protocol

The following list describes the typical operational procedure carried out between each runs on the recirculating rig:

1. **Physical and chemical conditioning of the copper element:** Each copper plate was cleaned with a 5 % HCl solution. The hydrochloric bath also removed the thin layer that tended to form when the elements were left under atmospheric conditions (probably copper oxide).
2. **Acid-washing of the rig:** Each tank was filled with 5 litres of a 2 % in weight HCl solution and left for 15 minutes. The tanks were then filled to capacity (75 litres) with DI water. Perspex™ cells were equipped with stainless steel elements that remained in place throughout the whole cleaning process. The rig was then flushed with the acid water to clean the rest of the pipes in the line.
3. **DI water cleaning of the rig:** This operation consisted in filling each tank with DI water and pumping it through the rig. After 15 minutes, the pumps were stopped and the rig emptied. This operation was repeated twice.
4. **Preparation of the Perspex™ cells:** Following the DI wash, the cells were finally fitted with the copper elements that would be used throughout the run. Contamination between the heating-loop water and the test water was avoided by means of rubber seals.
5. **Starting-up of the rig:** Each tank was filled with 75 litres of DI water which was then pumped through the rig. Appropriate quantities of calcium chloride and sodium bicarbonate were added and the run started.

In addition, the levels of hardness and alkalinity were adjusted daily to meet the hardness and alkalinity levels required for the runs.

A series of experimental runs were undertaken to investigate the influence of magnetic treatment on the growth of CaCO_3 crystals. For these experiments, the copper elements were precoated by a thin layer of calcium carbonate. The precoating was achieved by running the re-circulating rig with scale-free copper elements using experimental conditions similar to those used throughout the scaling tests (120 hours runs, heating loop at 65°C, hardness of 250 ppm and alkalinity of 500 ppm). This approach is validated by the fact that nucleation of CaCO_3 on a metallic surface occurs at a rate which is not significantly different from that of the subsequent growth on CaCO_3 crystals [72]. During these experiments the following steps performed daily were added to the experimental procedure previously described:

1. **Removal and drying of the copper elements:** The copper elements were removed from the scaling cell and placed for 20 minutes in a drying cabinet at about 80 °C. At the same time, the Perspex™ cells were bypassed to insure the continuity of magnetic treatment throughout the weighing procedure.
2. **Weighing of the copper elements:** After 20 minutes of drying, the copper elements were weighed on a scale to measure the amount of scale that had formed during the previous 24 hours.
3. **Refitting of the copper elements:** The copper elements were refitted in the scaling cell in the inverted position and the bypass removed.

The above-described protocol was used to determine the mass of scale formed during the pre-coating preliminary step on the copper elements used in scale growth trials.

As Figure 12 shows, the two ends of the copper elements were not exposed to the same temperature. One end was in contact with the heated water at a temperature which was close to the boiler's setting (T_s) whereas the other end was in contact with heating water that has lost part of its heat during its passage on the copper element ($T_s - \Delta T$). The change in the orientation of the copper elements was a measure taken to even as much as possible the heat-exchanging conditions on the surface of the elements.

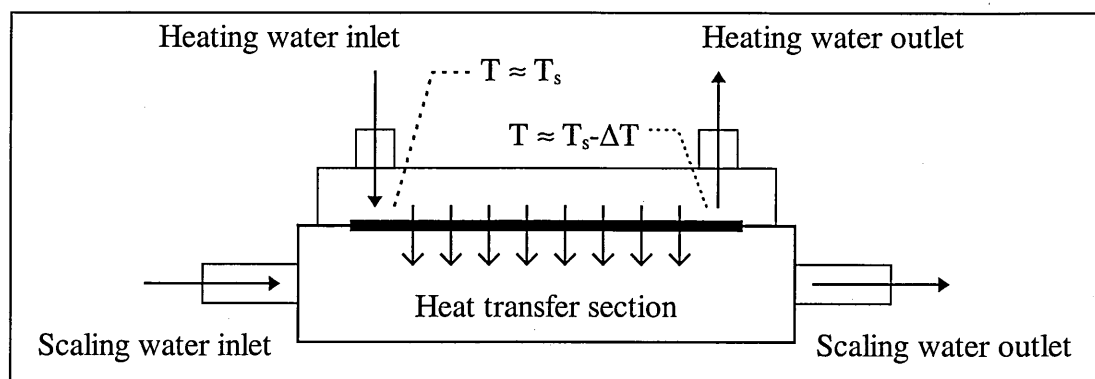


Figure 12: Diagram of the heat transfer conditions in the scaling cell

3.4 *CHEMICALS, EQUIPMENT AND ANALYTICAL TECHNIQUES USED*

3.4.1 *Chemicals used*

All chemicals used in this study were supplied by BDH and are AnalaR grade. DI water is supplied by a ELGA Optima 60 Water Purifier. The commercial scale inhibitor is an “I_E inhibitor” supplied by American Technologies Group (ATG) USA.

3.4.2 Hardness and alkalinity

Hardness level is determined by EDTA titrimetric method [73] method 2340 C.

Alkalinity level is determined by HCl titrimetric method [73] method 2320 B.

All the corresponding reagents are supplied by BDH and are of AnalaR grade.

3.4.3 pH and temperature

The pH in each tank was monitored using two Blackstone pH controllers (Hanna Instruments) equipped with Gelplas General Purpose pH probes (BDH). Calibration of the probes was achieved using pH 9.22 and pH 7.00 buffer tablets (BDH).

Conductivity was measured with a 3410 Electrochemistry analyser (JENWAY). Calibration was carried out monthly according to the supplier's specifications using KCl AnalaR standard solutions.

3.4.4 Analytical equipment

Particle size analyses were performed using a HIAC/ROYCO 'HIAC LV VersaCount' instrument (Pacific Scientific). Turbidity measurements were made on a 'HACH Ratio Turbidimeter' model 18900 (CAMLAB).

3.4.5 Magnetic devices

3.4.5.1 GMX 800 devices

The 800 device consists of two ceramic magnets held in a clamp which fits around the pipe. It produces an average magnetic field of 125 mT. Figure 13 shows the orientation of the magnetic field to the water flow:

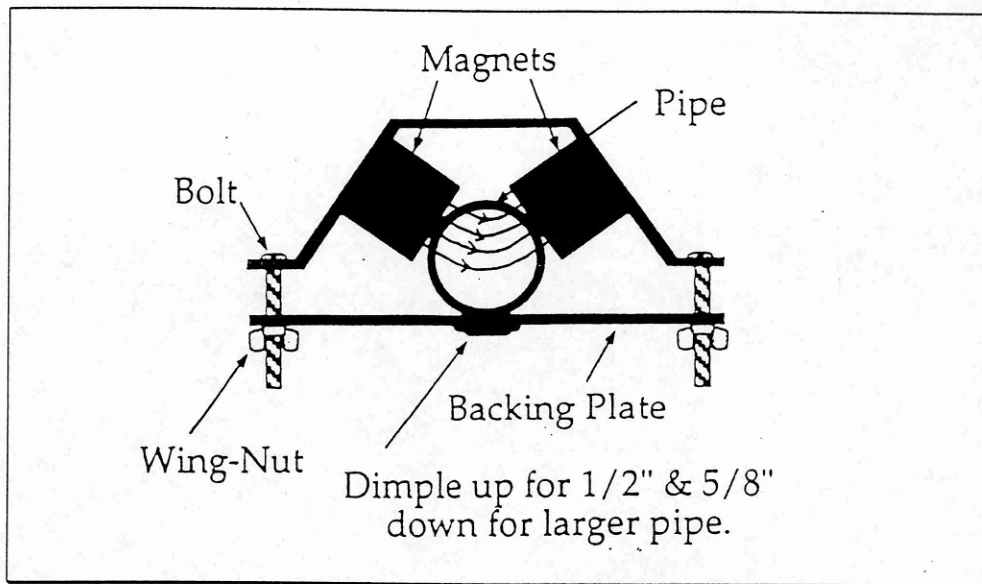


Figure 13: Representation of the magnetic field produces by an 800 element [74]

3.4.5.2 Calcat devices

The Calcat magnetic treatment device used during the last of the trials was a non-intrusive, clamp-on type (model RE6) comprising two permanent ceramic magnets in a PVC casing. The device was fitted onto the pipe with the two south poles facing, i.e. in dipolar mode, such that the poles repel. The field produced by this device ranges from 34 mT at the periphery to 16 mT at the centre. Each magnet has a maximum field strength of 65 mT.

Chapter 4: RESULTS AND DISCUSSION

4.1 BOILER RIG

4.1.1 Results discussion

A total of eight runs were carried out on the boiler rig, using different configuration of magnets and different levels of alkalinity and hardness. The duration of runs varied from 2 to 8 weeks. Results are presented in Appendix A and are summarised in Table 7 and Figure 14

Table 7: Summarised results of boiler rig trials

Run number	Duration of the runs (weeks)	Hardness and alkalinity levels (ppm)	Scale reduction (%)
1	8	200	53
2	2	300	40
3	2	300	9
4	2	300	- 14
5	4	300	0
6	4	300	8
7	8	300	- 38
8	4	400	- 1

Overall, a large variability in the results is evident. The average value for scale reduction over the whole trial reaches 7 % for a standard deviation of 29 %, with values ranging from a 53 % decrease to a 38 % increase in scale formation.

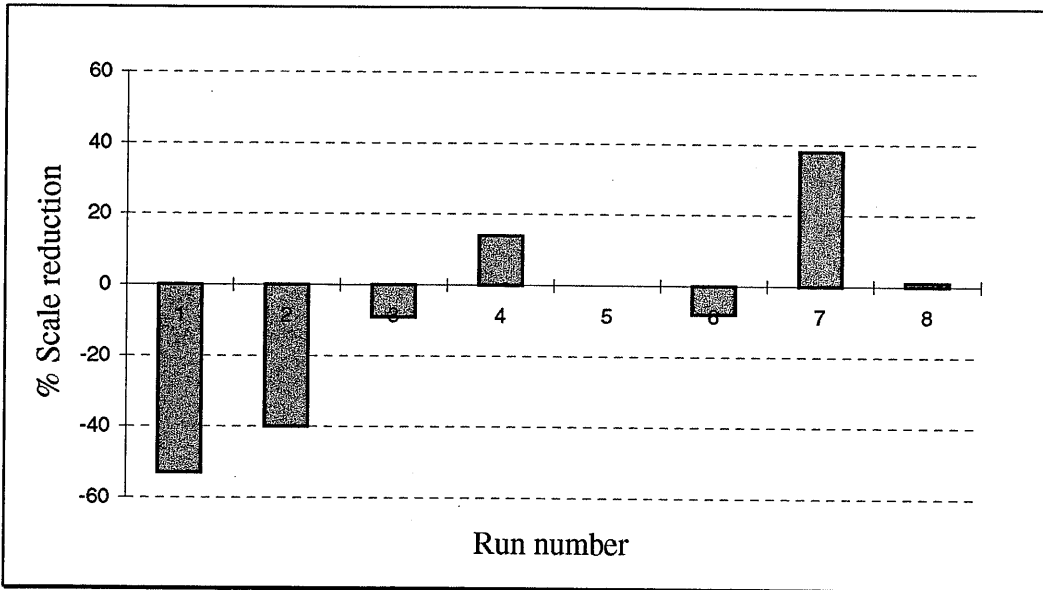


Figure 14: Chronological performances of magnetic treatment on the boiler rig

Among a general background of fluctuating results, the first two runs clearly stand out. They both present positive scale reduction figures, specifically 53 and 40 % for runs 1 and 2 respectively. With such significant improvement in scale formation, it seems unlikely that such results can be considered as being experimental artefacts. However, the placement of these two experiments in the chronology of the overall trial may be significant, in that no pattern in scale reduction was observed in subsequent runs. Several hypotheses can be formulated to account for this observation:

First of all, it appears that in addition to crystallising on the surface of the heating elements (Figure 15), scale also precipitated in large quantities in the bottom of the tank. Since this scale has been quantified only in the last run of the trial where it is apparent that the detached scale may make up as much as 64 % of the total scale formed, it seems reasonable to assume that the figures reported in runs 1 through 7 do not represent the true extent of the boiler scaling. This would explain the inconsistency of the results in runs 3 through 7 but still could not explain the positive results of the first two runs.

The different experimental conditions used throughout the trial may also account for the drop in scale reduction and the subsequent fluctuations. This seems unlikely however, considering the results showed by runs 2, 3 and 4, all of which were performed under similar “controlled” conditions and presenting a wide-spread character (scale reduction of 40, 9 and - 14 %).

Finally, a drift of uncontrolled scaling parameters could well explain the drop in scale formation that followed run 2. The most plausible scenario is a progressive modification over the course of the runs of the chemical composition of the tap-water used on the boiler rig. Knowing the influence certain metallic ions can have on the crystallisation of scale, even a drift of a few ppm in Zn^{2+} for instance could bring major modification in the amount of scale formed.



Figure 15: Picture of the heating elements taken at the end of a run

Considering the limited number of parameters actually monitored over the duration of this trial, hypotheses relating to changes in experimental conditions (controlled or otherwise) cannot be verified. Run 8, however, gives firm support to the idea that the values reported in runs 1 through 7 do not give a true measure of the extent of scaling. This run is the only one for which all of the scale formed in the boiler has been quantified, including the settled particles present in the bottom. In that respect, all the significant differences in scale formation reported so far could be simply due to the

mechanical vibrations involved in the removal of the heating elements, causing detachment of scale deposits from the elements.

Because of the limited number of runs performed on the boiler rig and the fact that among these runs, very few were conducted under identical experimental conditions, statistical analysis of the data is limited to calculating averages and standard deviations : Just two couples can be compared (2-3 & 5-6). Performing a t-test on these two samples would not be statistically significant.

Plotting the values of scale reduction against experimental parameters is probably the best way to identify any effects magnetic treatment may have on scale formation under the conditions used on the boiler rig. In particular (figure 16), increasing the number of magnets in use seems to have the effect of spreading the values of scale formation. Again, the fact that all other parameters were not kept identical during the experiments limits the validity of this observation. Additional experiments would be needed to confirm this observation.

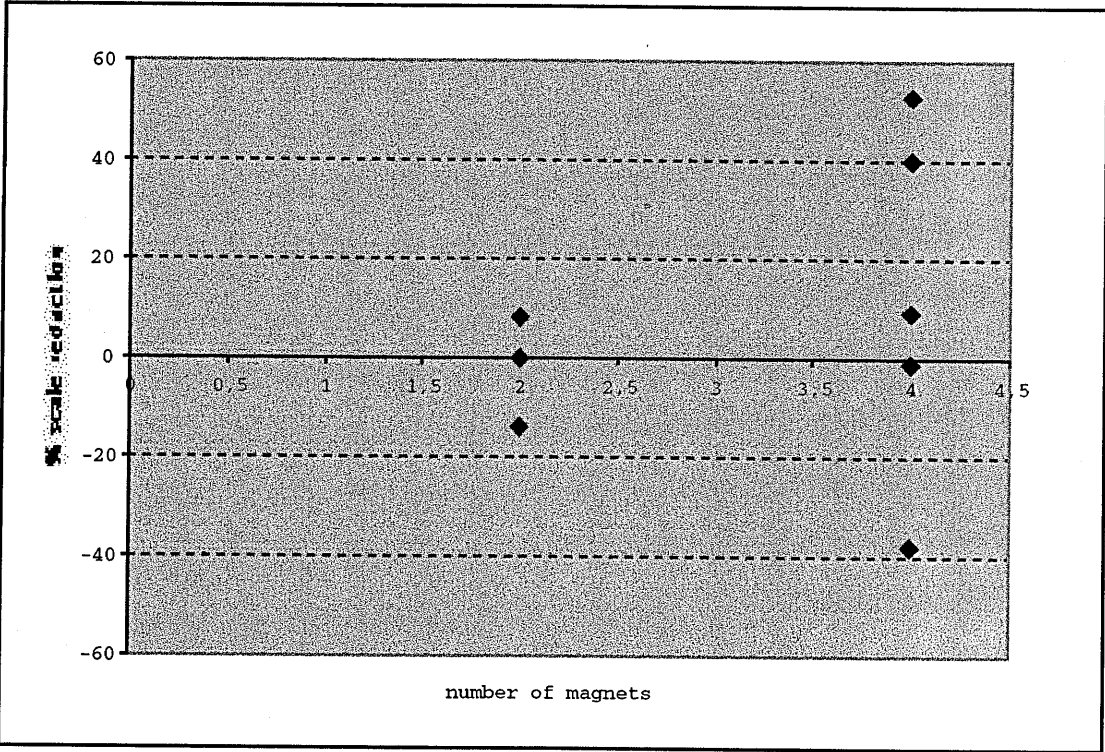


Figure 16: Percentage of scale reduction vs. number of magnets in use

4.1.2 Conclusion

Results from the trial conducted cannot prove nor infer any effects of magnetic treatment on scaling. However, the only run for which the scale content of the boilers had been properly quantified exhibited no difference between treated and untreated boilers. Any unequivocally positive effect on the overall scaling of the boilers remains to be verified.

4.2 RECIRCULATING RIG

Results and their discussion are presented according to the chronology of the trials:

1. first GMX trial
2. second GMX trial
3. ATG trial
4. third GMX trial
5. Calcat trial

An additional sixth part includes the discussion of the effect of the magnetic treatment on the allotropic composition of the scale layer. Raw data is appended (Appendix B).

All GMX trials comprised a series of runs performed to investigate the effects of magnetic devices on the scaling of heated surfaces. Two elements were used in accordance to the supplier's recommendations.

The third part of the study was carried out to check how the recirculating rig would respond to a recognised scale inhibiting chemical. The chemical used was an additive called "I_E solution" and was supplied by American Technologies Group USA (ATG).

Finally, a fifth and final trial investigated the efficiency of a second type of permanent clamp-on magnet. The devices used were supplied by Calcat, again used in accordance to the supplier's recommendations.

4.2.1 First GMX trial

This trial consisted of a total of 11 runs, 7 using magnetic treatment and 4 blank runs assessing the reproducibility of the scaling test. Results are presented in Appendix B and chronologically plotted in Figure 17.

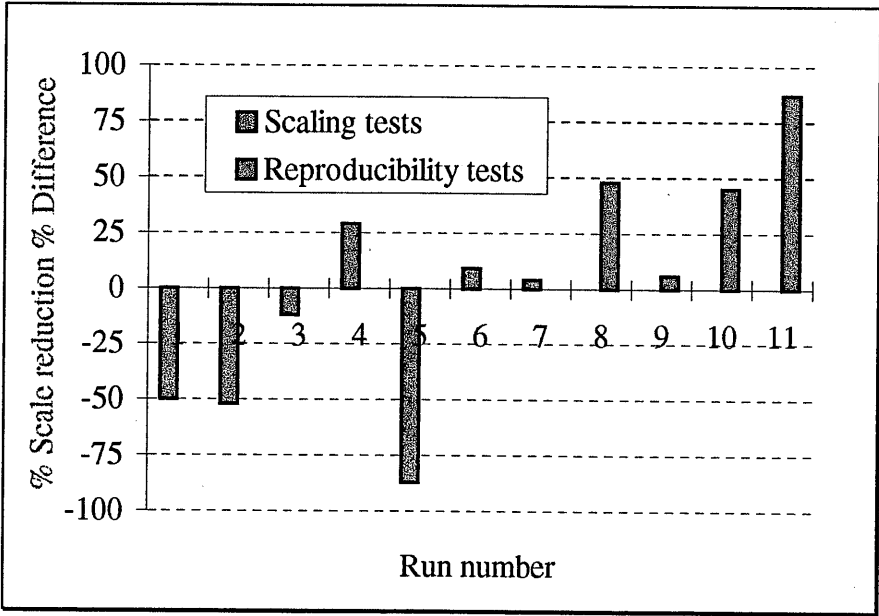


Figure 17: Results of the scaling tests performed during the first GMX trial

Overall, the results exhibit great fluctuations, both in the reproducibility and in the scaling tests. The average scale reduction over the 7 scaling tests is 23 % with a standard deviation of 41, with values ranging from an 87 % scale reduction to a 29 % scale increase.

At first glance, the first seven runs show striking similarities with the results obtained on the boiler rig. The two trials both exhibited significant scale reduction in the first two runs, followed by a pattern of fluctuating results. This observation may imply that the GMX devices, whenever installed for the first time on a system, would induce a reduction in scale formation on heated surfaces, only to see their performance gradually fall over time. However, it seems unlikely that this behaviour would appear in totally different experimental conditions. More reasonably, the lack of reproducibility observed in runs 8 through 11 (average of 46 % for a standard deviation of 33) could be

accounted for the fluctuations observed, with the first two results merely reflecting a chance deviation. Simple observation of the experimental data tends to point towards this possibility:

First of all, a closer look at the results shows that during the last four runs scale formed in excess on both loops (Appendix B). We can thus rule out a possible asymmetry between the two loops leading to preferential scaling, all the more since runs 9 and 10 have been carried out with inverted cell-tank connections; in other words, scaling cell A has been connected to tank B instead of tank A during runs 9 and 10 (and vice-versa for cell B).

Another simple observation is that if the amount of scale formed is summed for each run on each loop, the figures vary greatly: from 167 mg for the first and last run to 849 mg for the second run. Differences of such amplitude can not be related to changes in experimental parameters. Moreover, even for two consecutive runs like run 1 and run 2, the total amount of scale formed can drastically change (158 mg and 849 mg).

It seems that no definite conclusion can be drawn from this trial. Although it has been demonstrated that the scaling test was in great part irreproducible, it remains impossible to completely rule out the possibility of an effect of magnetic treatment on scaling of heated surfaces. The average overall scale reduction value of 23 % remains in that respect unexplained.

By performing a t-test on the first seven runs (scaling tests) under the following conditions :

- Null hypothesis : identical means (control and treated)
- Two-tailed test
- 7 Paired observations, thus $7-1 = 6$ degrees of freedom

The following conclusion can be drawn :

$t_6 = 1,649$; t-test statistically insignificant, null hypothesis accepted.

To have the null hypothesis rejected with a significance level of 95 % (usual value for statistical analysis of data), t_6 should be greater than 2,447.

Statistically speaking, the first seven tests taken as a whole provide two samples (treated and control) that are part of the same population. In other words, under the conditions of the first GMX trial, magnetic treatment has not inhibited scale growth.

Confronted with the seemingly unpredictable behaviour of calcium carbonate precipitation previously reported [69], subsequent runs (following GMX trials, ATG and Calcat trial) were subjected to more rigorous control and monitoring of all the scaling parameters involved.

4.2.2 Second GMX runs

The following modifications were made to the experimental procedure:

- the copper elements were abraded using 1200 grade sand paper
- water hardness and alkalinity were brought respectively to 200 and 400 ppm

The aim in abrading the copper elements was to suppress as much as possible any preferential nucleation sites. Levels of hardness and alkalinity were chosen so as to create enhanced scaling conditions. Moreover, by keeping these levels identical during the whole duration of the trial, the comparison of the results would prove more significant. Results are presented in Appendix B and chronologically plotted in Figure 18.

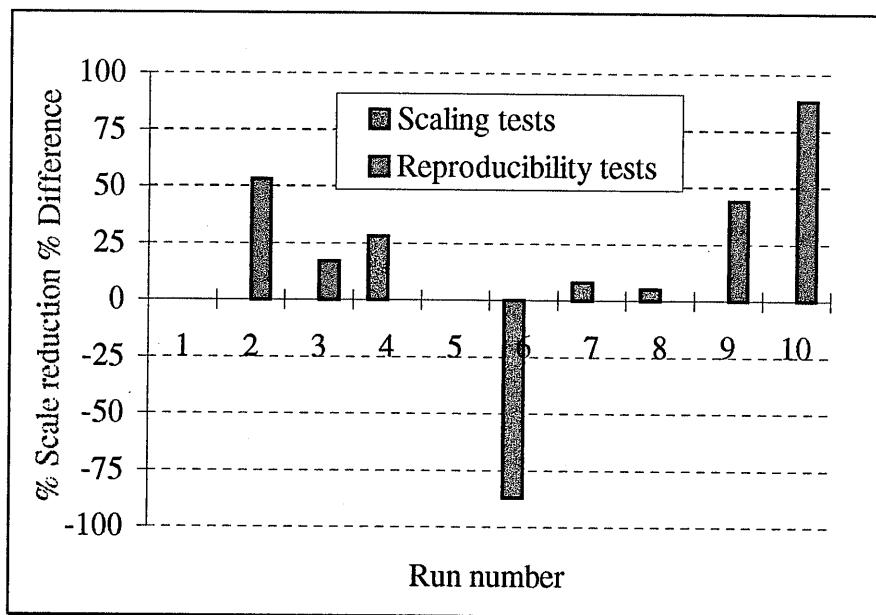


Figure 18: Results of the scaling tests performed during the second GMX trial

The average scale reduction over the 4 scaling tests is 11 % with a standard deviation of 51 %. Values range from a 87 % scale reduction to a 28 % increase.

Out of the four scaling tests, only run 6 exhibited scale reduction in the treated loop. A closer look at the results shows us that during this run, only 25 mg of scale actually formed on the copper element placed in the treated loop. As a consequence, the overall scale reduction reached the value of 87 %. If we consider all the other runs of this trial (comparable because of same operating conditions), just one single other run lead to less than 50 mg of scale forming on one loop (run 10). This tends to suggest that the 87 % reduction in scale formation observed during run 6 is probably due to some experimental artefact, such as a rogue contaminant inhibiting nucleation.

In addition to the lack of runs exhibiting scale reduction on the treated loop, this trial produced great fluctuations in the experimental data. However, if we compare the total amounts of scale formed during each run (sum of the scale formed on each loop), this time the statistical population is much closer to the mean (average value of 243 with a standard deviation of 46). This observation proves that the control over the scaling conditions of the rig has greatly improved since the last trial. In that respect, the fluctuating results observed tend to point out increasingly in the direction of the ineffectiveness of the magnetic treatment.

4.2.3 Chemical inhibitor trial (ATG)

Confronted with inconclusive results with respect to the efficiency of the magnetic treatment, a new trial was carried out to investigate the rig’s performance when treated with a scale-controlling chemical. The aim was to validate the use of the recirculating rig as a test of scale inhibiting processes.

A scale inhibiting additive produced by ATG Technologies USA was chosen to perform the scaling tests. In addition to the concentration of 1000 ppm recommended by ATG, other tests were carried out with concentrations of 500 and 2000 ppm to investigate the relation between dose and efficiency.

Finally, to induce significant scale formation on the heating elements, enhanced scaling conditions were created, by raising the heat exchanger temperature to 65 °C and the levels of hardness and alkalinity respectively to 250 and 500 ppm. Results are presented in Appendix B and chronologically plotted in Figure 19.

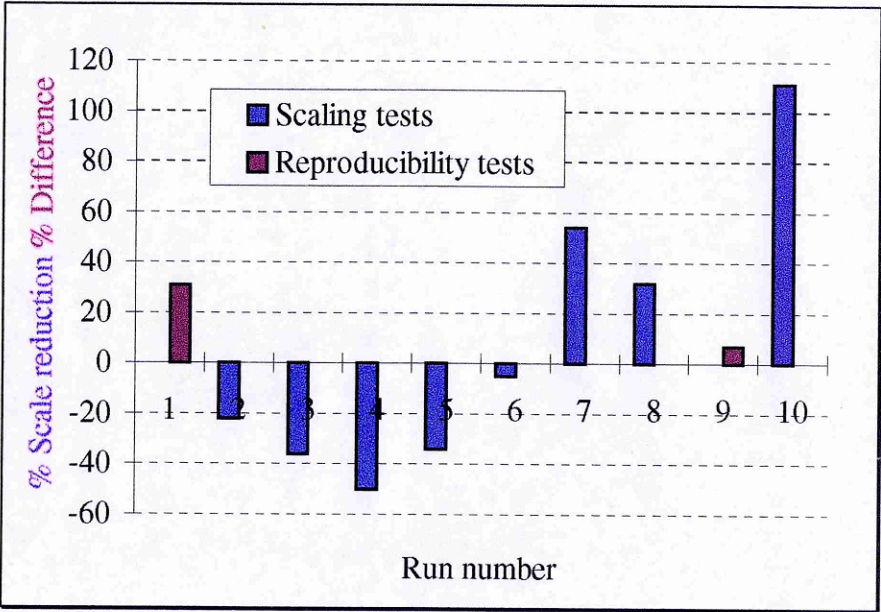


Figure 19: Results of the scaling tests performed during the ATG trial

A first reproducibility run was made prior to the scaling tests, and the result judged to be satisfactory. The first three scaling runs (runs 2 to 4) performed at 1000 ppm all exhibit significant levels of scale reduction (22, 36 and 50 %). Moreover, a sequential increase in the level of scale reduction is clearly visible on Figure 19. Considering, however, that the first two runs are commutated, this sequential enhancement seems to be of no particular significance.

The time and resources available only permitted the completion of 3 runs at different concentrations of scale inhibitor. With 34 % scale reduction at 500 ppm, the additive still remains effective at half the concentration recommended by ATG. The initial test performed at 2000 ppm, however, shows insignificant levels of scale reduction (5 %). The next run, performed under the same conditions, displays a increase in scaling of 54%.

At that point of the trial it was decided to repeat runs at 1000 ppm to try to determine why the scaling process wasn't inhibited during run 6. Three more runs were thus conducted, two at concentrations of 1000 ppm and one to test the reproducibility of the scaling test.

With a 7 % reproducibility observed on run 8, the 32 and 111 % scale increase exhibited by runs 7 and 9 cannot be considered as a consequence of asymmetric scaling conditions between the two loops. Discussions with the supplier suggested a loss of performance of the product related to premature ageing of the samples provided. By plotting the total amount of scale formed during each run (i.e. from both the treated and the control loop) vs. time (Figure 20), an overall decrease in the amount of scale deposition, punctuated by a few odd points is clearly evident.

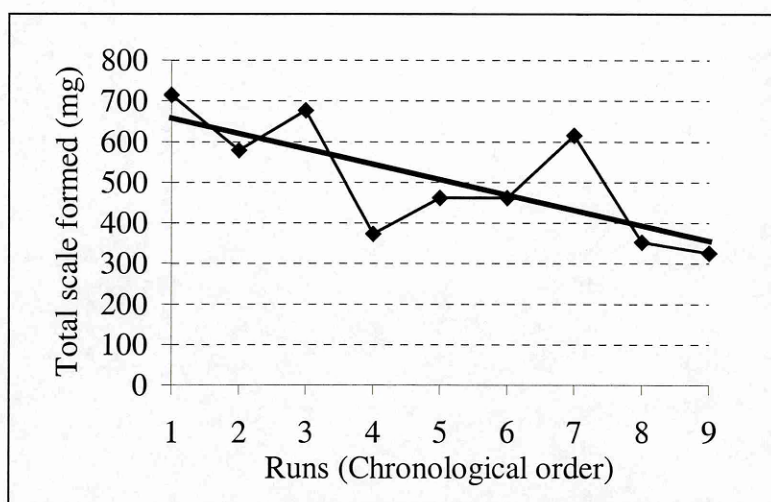


Figure 20: Total amount of scale formed vs time

This trend can be an indication of a regular drift in scaling conditions over time, or an additional argument in favour of the premature ageing of the chemical additive. Since the recirculating rig allows a significant level of control over the scaling parameters, any drift in scaling conditions seems unlikely. Improper conditions of storage of the chemical additive could on the other hand explain a deterioration of the scale-inhibiting properties of the chemical additive.

Over the duration of the trial, visual observation of the scaling process revealed the induction period to vary significantly from one run to the other (i.e. the time for nucleation process to take place). Approximate measurements gave values ranging from less than an hour to 24 hours. Consequently, scale growth occurred during periods ranging from 72 hours (96-24) to 95 hours (96-1) depending on the run. A 28 % difference in the period of time allowed for scale to grow could well be responsible for the fluctuations observed in Figure 20. This then raises doubts, about the relevance of total scale formed after a fixed time period as an indication of a scale-inhibiting treatment's efficiency. Rocques (1994) reported on the unpredictable nature of the nucleation of calcium carbonate, mainly because of its heterogeneous mechanism. This unpredictability provides a reasonable explanation for the induction time variations.

Overall, this trial proved that the recirculating rig is a valid tool to evaluate the effectiveness of a scale-control process. A better control of the induction time, however, could significantly improve the relevance of the scale measurements.

4.2.4 Third GMX trial

Data presented this far permits no definite conclusions to be drawn on the effect of magnetic treatment on scale formation, mainly because of a lack of reproducibility. In subsequent experiments the protocol was modified to try to reduce as much as possible the influence of the experimental factors leading to the irreproducibility of the runs. The rig was re-built to reduce the risk of contamination (section 3.3.2). Moreover, the copper elements were precoated by a layer of calcium carbonate in order to overcome the discrepancies introduced by a varying induction time. The experimental conditions for this trial were:

- hardness of 250,300 ppm
- alkalinity of 500,600 ppm
- flow rate of 16,22.7 l.min⁻¹
- heat exchanger temperature of 65 °C
- run duration of 72 hours

Results are presented in Appendix B and chronologically plotted in Figure 21.

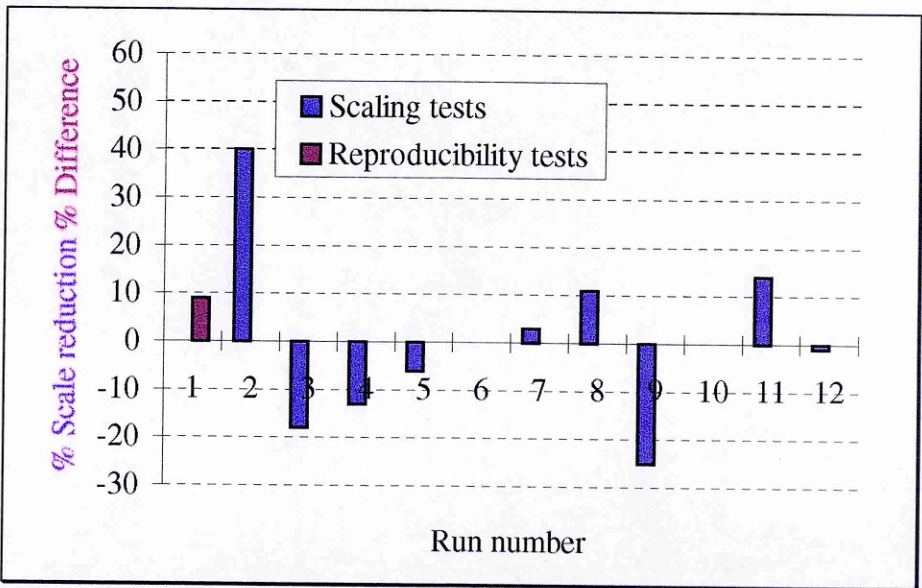


Figure 21: Results of the scalin tests performed during the third GMX trial

This trial consisted of a total of 12 runs, 11 GMX scaling tests (runs 2 through 12) preceded by a reproducibility test (run 1). Among the 12 runs, 4 have been conducted using no pre-coating of the elements (Runs 1,2,3 and 6). There is no difference overall in scale formation between treated and untreated loop (difference < 1% with a standard deviation of 20). If the statistical population is restricted to the runs conducted with precoated elements, the average scale reduction is 2.5 % with a standard deviation of 15.

Reproducibility test discussion

With only a 9 % difference in scale formation for a total amount of scale formed of 1042 mg, the first run validates the reproducibility of the scaling test. However, this run exhibited particularly unusual scaling behaviour. Both the copper elements and the Perspex™ cells were heavily scaled and the induction period was under 15 minutes. Finally, with 1042 mg of scale this run produced the most scale of all the trial by some significant margin.

The underlying reasons for these unusual observations are likely to lie in the fact that the reproducibility run followed the rebuilding of the rig. The fact that the induction period was reduced suggests that somehow, the nucleation process was altered by the rebuilding of the rig. It is probable that although washed several times with 5 % hydrochloric acid, the rig still contained traces of contaminant, which

- a. enhanced heterogeneous nucleation by seeding effect, and
- b. modified the scaling characteristics of water.

Both effects could have been induced by the presence of “by-products” of the rig’s building in the piping, either organic for example:

- the solvent used to connect PVC elements together (MEK),
- the silicone sealant used to prevent leaks,
- grease coming from the newly installed coolers etc.

or inorganic such as iron oxides and associated insoluble salts from the pipework or framework.

Enhanced nucleation is a particularly plausible explanation in view of published work on CaCO_3 nucleation. The scaling characteristics of the water have been assumed to be determined by the bulk chemical properties such as hardness, alkalinity and pH. There is no reason to suppose that there is an accumulation of microscopic scale inhibiting species within the rig over the course of time since these species (such as Zn^{2+} and Fe^{2+}) are largely water soluble and would be expected to be flushed out of the rig between runs.

In any cases, the drop in the amount of scale formed during the subsequent runs clearly suggests that the unusual conditions that induced heavy scaling during the first run did not arise in the following runs.

Scale growth discussion

The first two scaling runs were conducted with the same procedure as reported for the previous trial, i.e. no precoating of the elements. Experimental difficulties forced an abandonment of the third run. The results (40 % increase of scaling in run 2 and 20 % decrease in 4) indicate runs characterised by two induction periods of different length.

8 runs were then conducted using precoated elements and used to investigate the effects if any of magnetic treatment on the scale growth process. Results of the first two sequential runs performed using the new experimental procedure are presented in Figure 22.

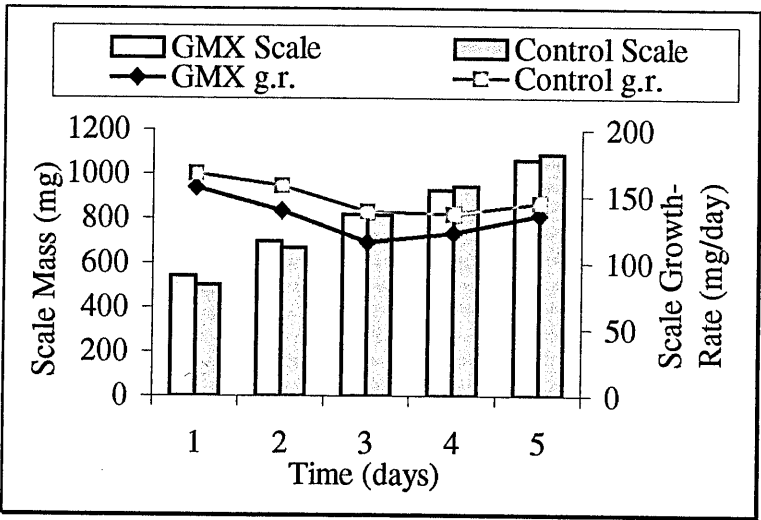


Figure 22: Scale growth monitoring over runs 4 (4 days) and 5 (1 day)

As the relative position of the two growth-rate trends (GR trends) suggests, the magnetically treated loop produced originally less scale than the control loop. The difference between the two growth rates is such that it brought about an inversion in the relative quantities of scale between the two copper elements.

The trends for both treated and control are similar. It appears that all the uncontrolled parameters influencing scaling had comparable effects on both loops such that their influence may be ignored.

The initial downward trend can be explained by the drop in heat transfer over time resulting from the progressive thickening of the CaCO_3 layer. The break in the trend observed from run 3 is probably due to the fact that the fifth day corresponds to the start of a new run. The scale copper elements are thus submitted to a concentration 'shock load' which could explain the rise monitored.

The sixth run was a diagnostic run conducted to identify and, plug leaks appearing during run 5. No results concerning the effects of magnetic treatment on scale were produced from this run.

Following evidence suggesting an influence of magnetic treatment on crystal growth, the following tests were performed under enhanced magnetic exposure. The flowrate was thus increased from 16 l.min^{-1} to 22.7 l.min^{-1} to bring the exposure rate from 12.8 to 18.2 exposures to the magnetic field by hour (calculations based on [41]). The results are presented in Figure 23.

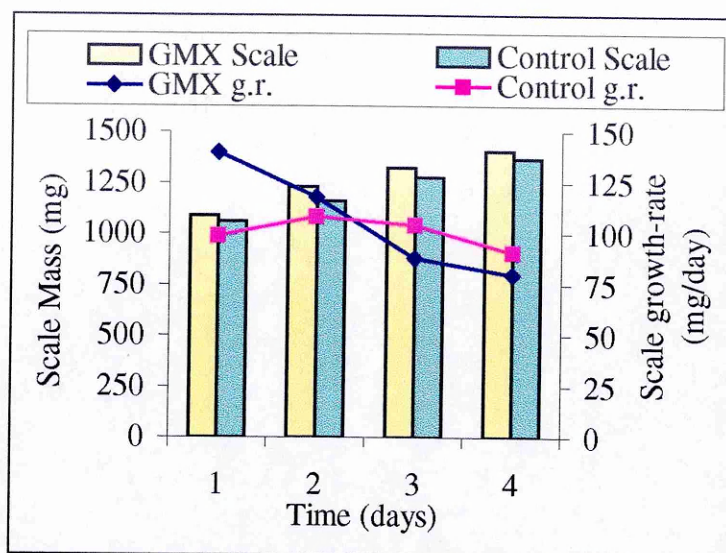


Figure 23: Scale growth monitoring over run 7 (4 days)

Overall, the magnetically treated loop produced more scale than the untreated one. However, a closer look at Figure 23 shows that this negative result is due to an abnormally high scale growth on the magnetically treated loop during the first day. Clearly the trend inverts itself and from day 3, the GMX growth rate becomes lesser than the control one. Moreover, during the last two days, the two trends regain a certain parallelism which we have observed all along during the last experiments. The 'shock load' effect encountered at the beginning of a run or a wrong measure taken on the second day can explain the results produced by run 7. The nature of the scale formed in particular (soft scale) makes the daily weighing of the heating element a very difficult manipulation. Scale tends to come off the copper at the slightest vibration and it is probable that this induced false measurements. More precisely, over 1000 mg of deposit per copper element, the soft scale layer becomes too thick and too brittle. The decision was thus taken to start the following run with freshly coated copper elements.

At the start of the following run both elements were scaled with 260 mg of calcium carbonate forming a regular layer. The experiment was conducted over two commuted runs; the results are presented thereafter:

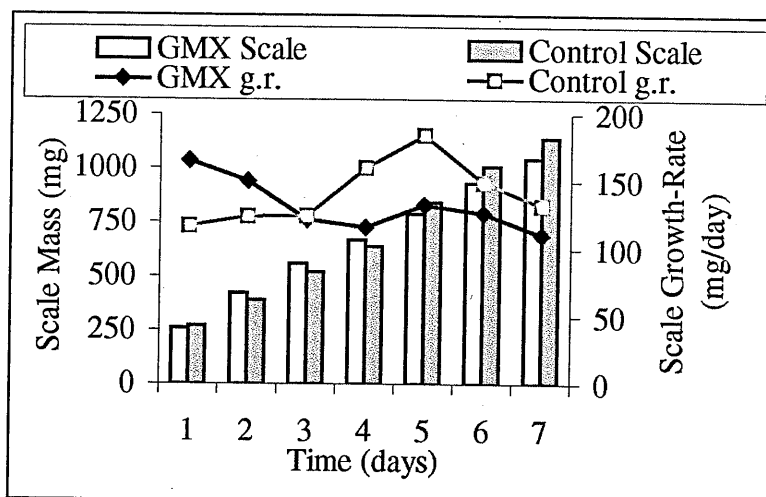


Figure 24: Scale growth monitoring over runs 8 (4 days) and 9 (4 days)

The general scale growth trends observed on this figure actually combines elements which have been observed and explained in previous discussions

:

1. apparent paradoxical behaviours of the control's scale growth during the first two days
2. control GR becoming inferior to the GMX GR after three days
3. rise in both GR trends after day 4 (corresponding to the start of a new run: 'shock load' effect)
4. GR trends regaining a parallel regular downward trend after 4 complete days of operation

After the end of run 9, the decision was taken to try to extend the experiment (run 10). Unfortunately, the same problem as for run 7 appeared, that is to say a mechanically unstable scale layer leading to the impossibility to manipulate the copper element.

A last attempt using new freshly coated elements was decided at this point. The results are presented in Figure 25:

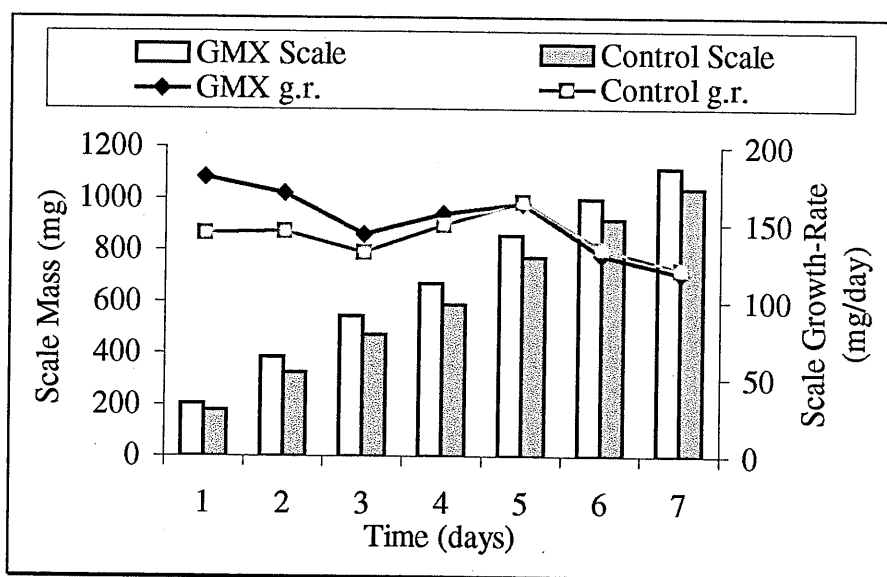


Figure 25: Scale growth monitoring over runs 11 (4 days) and 12 (4 days)

The results present the same characteristic features described previously at an attenuated extent. The analysis previously made, however, can still apply on the GR trends observed in Figure 25. The late crossing of the trends could find its cause in a two-hour power failure that occurred precisely during the third day, day of the inversion in GR trends on previous runs.

The following table summarise the results obtained on the recirculating rig concerning scale growth:

Table 8: Scale growth results on the third GMX trial

Run number	Control loop	Treated loop	Average amount of pre-coating (mg)
4 - 5	149	134	520
7	101	107	1075
8 - 9	142	132	264
11 - 12	143	147	192
Average	134	130	
Standard deviation	22	17	

By performing a t-test on this set of data under the following conditions :

- Null hypothesis : identical means (control and treated)
- Two-tailed test
- 4 Paired observations, thus $4-1=3$ degrees of freedom

The following conclusion can be drawn :

$t_3 = 0,725$; t-test statistically insignificant, null hypothesis accepted.

To have the null hypothesis rejected with a significance level of 95 %, t_3 should be greater than 3,182.

This means that the two set of results, treated and control are in fact two samples from the same population. In other words, in the conditions under which the third GMX trial was conducted, there is no statistical difference in scale growth between treated and untreated samples.

In view of this result, it seems that under the experimental conditions of the third GMX trial, magnetic treatment doesn't significantly affect scale growth. However, in 3 cases out of 4 (runs 4-5, 7, 8-9), the grow rate on the treated loop overcame its counterpart on the control loop after a few days. This suggests that over an extended period of time, magnetic treatment may significantly inhibit scale growth. Low standard deviations on both sets of results (control and treated) show that the control on the recalculating rig over the third GMX trial was satisfactory.

4.2.5 Calcat runs

To rule out any possible effect resulting from the nature of the magnet used, two commutated runs were carried out with different commercial magnet. The two GMX 800 elements were replaced by two Calcat permanent clamp-on magnets. The main difference between the two types of magnet lies in the orientation of the magnetic field, orthogonal to the water flow for GMX and parallel for Calcat. Results are presented in Appendix B.

The first run exhibited a 9 % scale reduction whereas the second produced a 8 % augmentation. These two results show that under similar experimental conditions, permanent non-intrusive magnets have similar inconclusive effects on the whole of the scaling process. Considering the fact that the elements hadn't been precoated during these two runs, the influence of the Calcat treatment on scale growth can't be assessed.

4.2.6 Analysis of the structure of the CaCO_3 layer

In order to determine any possible influence of the magnetic treatment on the structure of the CaCO_3 layers, two studies were undertaken:

First of all SEM pictures of the scale samples were taken. Secondly, the relative proportion of the two main allotropic forms of calcium carbonate was evaluated.

These two studies were made possible because of the difference in physical properties of the two allotropic forms of CaCO_3 (calcite and aragonite). Calcite tends to form what has been referred in literature as 'hard scale' whereas aragonite is referred as 'soft scale' [5]. The main difference on the macroscopic level between these two types of scale is that calcite tends to adhere quite strongly to the surface it crystallises on whereas aragonite adheres rather weakly. By gently tapping the scaled copper element on a hard surface, it was possible to separate the two types of scale. This suggests that CaCO_3 crystallised on the copper element according to the following structure (Figure 26):

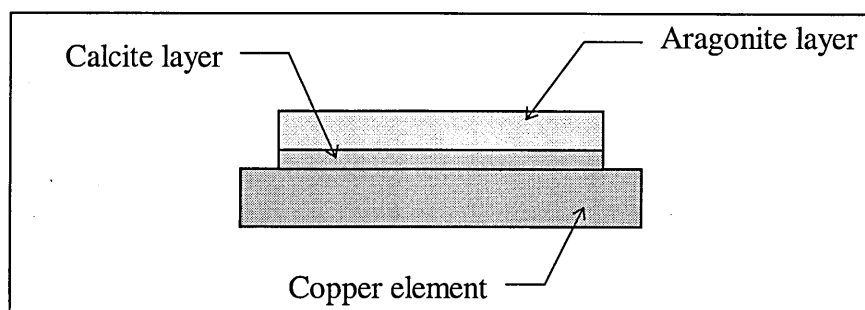


Figure 26: Cross-section of the organisation of the scale deposits

This observation was later verified by SEM pictures (Figure 27):



Figure 27: SEM picture of the interface between hard scale and soft scale layer

On Figure 27, it is clearly visible that the top layer consists mainly of needle-shaped aragonite whereas the bottom layer consists of cubic-shaped calcite. This organisation is paradoxical in the sense that aragonite is the preferred allotropic form of crystallisation for calcium carbonate at temperature over 60°C [5]. Calcite should thus form the first layer of scale, layer which is in direct contact with the copper surface maintained at 65°C. Scale build-up gradually reducing the heat transfer, the temperature should progressively decrease and aragonite crystals form. This paradoxical behaviour described in Figure 28 has been stated in previous published works [75].

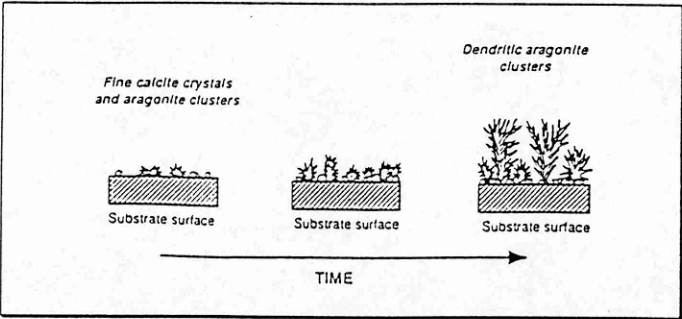


Figure 28: Structural organisation of the scale layer on a heated surface [75]

This structural organisation of scale allowed the two different layers to be separated for further analysis.

By cutting a square piece of the aragonite layer and weighing it, knowing the total surface of scale and its total mass, it is possible to determine the mass of both layers. This calculation is based of course on the hypothesis that CaCO_3 crystallises isotropically, that is to say that each layer has a homogenous structure.

The following calculation based on the measures displayed in Figure 29 provides an estimation of the mass of each layer, for both loops:

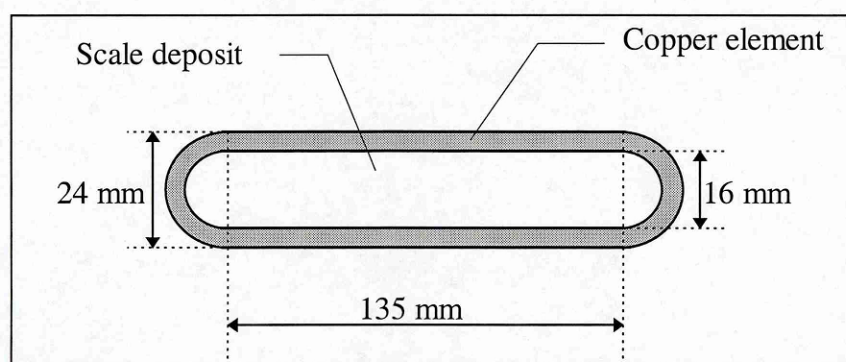


Figure 29: Dimensions of the copper element

Calculation of the scaled surface's area:

$$\begin{aligned}
 \text{Scaled surface} : S_s &= (135 \times 16) + (64 \cdot \pi) \\
 &\approx 2160 + 200 \\
 &\approx 2360 \text{ mm}^2 \\
 &\approx 23.6 \text{ cm}^2
 \end{aligned}$$

Let M_{sa} be the mass of the scale layer of aragonite, M_{sc} the mass of the scale layer of calcite, M_t be the total mass of scale:

On the treated sample:

A 16 by 16 mm sample of soft scale (surface s) was sampled and found to weigh 135 mg (mass m), this leads to the following calculation:

$$M_{sa} = \frac{S_s}{s} \times m = \frac{2360}{256} \times 135 = 1244 \text{ mg}$$

hence : $M_{sc} = M_t - M_{sa} = 1368 - 1244 = 124 \text{ mg}$

On the untreated sample :

A 13.5 by 15 mm sample of soft scale (surface s) was sampled and found to weigh 101 mg (mass m), this leads us the following calculation:

$$M_{sa} = \frac{S_s}{s} \times m = \frac{2360}{202.5} \times 101 = 1177 \text{ mg}$$

hence : $M_{sc} = M_t - M_{sa} = 1405 - 1177 = 228 \text{ mg}$

The results are summed up in Table 9 and include the analyses of two sets of copper elements:

Table 9: Compared size of the scale layers after MAGNETIC treatment

	First set of elements		Second set of elements	
	GMX loop	Control loop	GMX loop	Control loop
Hard-scale mass (mg)	124	228	101	198
Soft-scale mass (mg)	1244	1177	1046	1134
% difference in hard scale mass between GMX and control	59 %		51 %	

The main consequence of this observation is that the magnetic devices as they have been used during these trials induce a 55 % decrease in the size of the hard-scale layer. This implies that if we consider the formation of less hard scale as being a scale-control method, the magnetic treatment proves to be effective.

Chapter 5: CONCLUSION AND RECOMMENDATIONS

From the runs performed on the boiler rig, the following conclusions arise:

1. Magnetic treatment induced by commercial clamp-on magnets had no statistically significant influence on the overall scaling of domestic boilers.
2. The chronological plotting of scale reduction values tend to show a deterioration of the positive results observed during the first three runs over the duration of the trial. This observation could possibly due to the diminution of the magnetic effect over time, due to some unknown phenomena, but could also be the result of the vagarious nature of calcium carbonate chemistry, and more specifically its behaviour when supersaturated.
3. It appeared, from correlation of scale reduction values against the number of magnets employed, that an increased standard deviation in scale-reduction values arose when a greater number of clamp-on magnets were used.
4. It is evident that whenever performing a scaling test on a domestic boiler, great care must be taken when removing the heating elements. The scale which forms from tap-water is brittle and detaches itself easily from the heating-element, distorting the experimental results.

From the runs performed on the recirculating rig, the following conclusions arise:

5. The recirculating rig can reliably be used to measure the effects of a scale-inhibiting treatment, provided the copper surfaces are precoated with scale (see also (7) below). The aim of precoating the copper elements is to measure the effect of magnetic treatment on scale growth, obviating the less controllable nucleation process. The heterogeneous mechanism governing CaCO_3 nucleation produces a widely variable induction time (i.e. the time before scale growth starts), which distorts the measurements.
6. Magnetic treatment had no statistically significant effect on the growth rate of scale over the duration of the runs (4 days maximum). This was established by performing a *Student t-Test* on scale reduction results, with the treated and control values considered to be paired observations. However, in three cases out of four in a similar series of trials (the “third GMX trial”), the treated scale grow rate after

4 days was smaller than the control growth rate. This phenomenon was observed even in the cases where treated growth rate was significantly greater than the control growth rate at the start of the run.

7. Scaling appears to be composed of two layers under the conditions of operation: a first hard layer of mainly calcite and a second soft layer of principally aragonite. The temperature of the scaling surface seems to be the main factor governing the allotropic form under which scale precipitates. Magnetic treatment appears to consistently reduce, by 55 % on average, the thickness of the hard scale layer. This implies that if it is the formation of softer scale which constitutes the main factor by which the undesirable effects of scale are ameliorated, the magnetic treatment can be considered to be effective.

In view of these results, it is suggested that further work on magnetic treatment on the boiler rig should be carried out according to the following guidelines :

1. Additional tests should be conducted to confirm the influence of the number of clamp-on magnets used on the standard deviation of the scale reduction values. During these tests, great care should be given to the removal of the heating elements. In view of this, the use of rubber seals should reduce the vibrations involved in the removal of the heating elements.

The following guidelines apply to further work on the recirculating rig :

2. The precoating of the elements should be carried out according to the protocol described in this thesis. In particular, it is important that this precoating of the elements be achieved under the same experimental conditions as those for the subsequent scaling trials.
3. The duration of each experimental run should be set between 7 and 10 consecutive days, depending on the experimental conditions used and in particular the levels of hardness and alkalinity. It is especially important that these runs should be conducted with no interruptions, to avoid chemical shock-loads that distort experimental results. Additional work should be conducted on the recirculating rig to confirm the validity of observations reported on the influence of magnetic treatment on the allotropic form.

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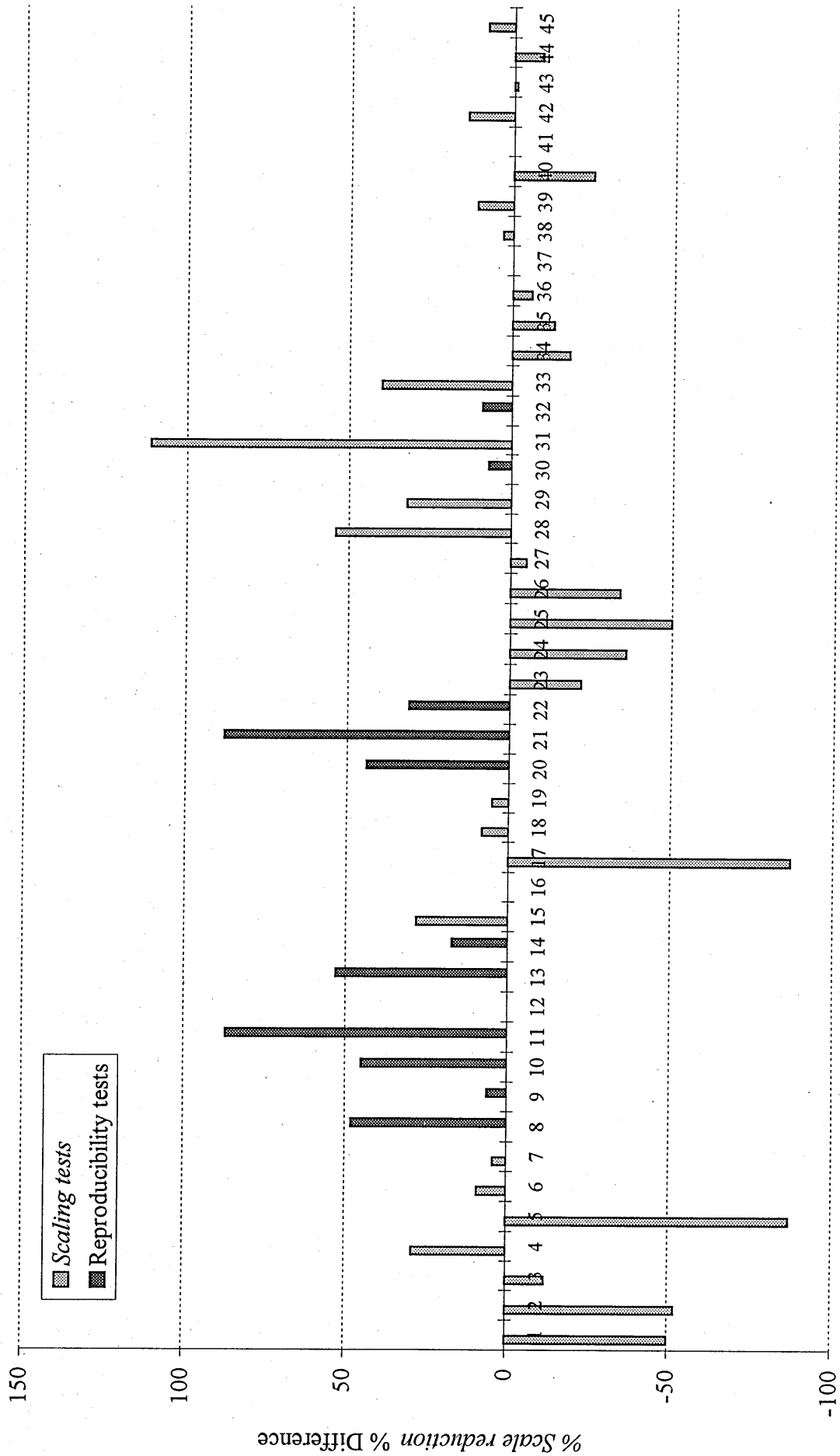
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APPENDIX A: BOILER RIG EXPERIMENTAL RESULT

Run number	Duration	Number of magnets treated boilers	Treated 1	Treated 2	Control 1	Control 2	% reduction
run 1 (225 ppm) top elements bottom elements total average <i>% reproducibility</i>	8 weeks	4 - 1&4	99 308 407 422 7	201 236 437 900 7	63 870 933 900 7	67 801 868 900 7	53
run 2 (300 ppm) bottom elements average <i>% reproducibility</i>	2 weeks	4 - 3&4	870 1015 29	1160 1700 44	1325 1700 44	2075 1700 44	40
run 3 (300 ppm) bottom elements average <i>% reproducibility</i>	2 weeks	4 - 3&4	748 741 2	734 816 9	778 816 9	854 816 9	9
run 4 (300 ppm) bottom elements average <i>% reproducibility</i>	2 weeks	2 - 1&2	499 592 31	685 519 3	510 519 3	527 519 3	-14
run 5 (300 ppm) bottom elements average <i>% reproducibility</i>	4 weeks	2 - 1&2	1093 1057 7	1020 1052 3	1070 1052 3	1034 1052 3	0
run 6 (300 ppm) bottom elements average <i>% reproducibility</i>	4 weeks	2 - 3&4	2742 2516 18	2290 2724 9	2601 2724 9	2846 2724 9	8
run 7 (300 ppm) top elements bottom elements total average <i>% reproducibility</i>	8 weeks	4 - 2&3	37 879 916 756 42	91 504 595 549 20	57 548 605 549 20	84 409 493 549 20	-38
run 8 (400 ppm) top elements bottom elements bottom boiler ** total average <i>% reproducibility</i>	4 weeks	4 - 2&3	68 88 221 377 392 8	66 79 262 407 387 2	74 74 235 383 387 2	65 76 249 390 387 2	-1



Run number