Petroleum Res. J. Vol. 21 (2008/2009); P. 39–48, 12 Figs.

Role of Magnetic Field at High PH on Scaling Tendency

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Abstract: Scale formation has always been a tedious problem to scientists and heating equipment manufacturers as well as production engineers. Scale is encountered most of the time in heat exchangers using hot water or steam as the heating fluid, and in steam production with boilers and various calcium concentrations.

Series of experiments have been undertaken to investigate the formation of calcium carbonate scale on boiler elements. A test rig designed to meet the DGVW testing protocol was used. The effect of physical condition was also investigated. Scaling behavior was assessed and calculated when the flow rate and temperature were kept constant at 25 1/h and 80ºC. The pH was kept at 7-8.5 and the hardness typically greater than 300 mg/1. The tests have shown that reduction in scaling tendency was maximal at 40% and the effect of flow rate was also observed.

Keywords: scaling, hardness, DGVW, calcium carbonate.

INTRODUCTION

The calcium carbonate, which is the preponderant agent for scale, forms a thin layer over the plate or tubing material such that the overall heat transfer is affected negatively. To overcome these shortcomings, manufacturing engineers have to over-design the installation, and production engineers usually have to shut down the production to clean the heat transfer equipments.

It goes without saying that this procedure is of a substantial impact on the budget and maintenance costs. Scientists and engineers have addressed this serious problem since the nineteenth century, suggesting different technical processes to reduce or inhibit the scale formation. The techniques suggested, which differ form one another and apply to specific processes, are chemical (acid washing, inhibitor injection, precipitation, *etc.)* mechanical (over sizing, hydro-blasting, fluidized media, *etc.)* or physical (electric treatment, magnetic treatment, *etc*.)

This paper investigates the scale reduction with a magnetic treatment device plugged on line with two water boilers operated in parallel. The laboratory setup, supplied by Kennikot Ltd., along with a magnetic treatment Aqua Total supplied by BWT , both UK Companies, have been run for a constant surface temperature , a constant liquid flow rate, and various calcium concentrations.

The concept of hardness and alkalinity are closely related to the description of scaling system. Hardness, which is defined as the ability to form a scum with soap[1], is in fact the measure of the water content of and Mg^{2+} both of which tend to form insoluble Ca^{2+} salts with organic anions from detergent. The natural hardness of water is a consequence of the presence in the ground of Ca^{2+} and HCO^{-3}. When natural water boils, calcium and magnesium bicarbonate decompose to carbonates which have a low solubility in water. The amount of hardness, which precipitates in this way, is called the temporary hardness[2]. After all the ions responsible for the temporary hardness have precipitated, the hardness, which is left, is called the permanent hardness.

Alkalinity is the measure of the water's ability to neutralize acid[1]. In natural water, it can be considered as a measure of the waters content in HCO^{-3}. As in the case for hardness, alkalinity is the consequence of the presence in earth's ground of $CaCO_3$. In addition to that, under Henry's law, CO_2 tends to dissolve in water, dissociating into the species responsible for alkalinity.

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Boiler waters contain both carbonate and hydroxide alkalinity. Both are derived from bicarbonates in the feed water. Carbon dioxide is insoluble in boiling water; hence, it is removed with the stream. This causes an increase in the pH and shift in alkalinity from bicarbonate to carbonate and from carbonate to hydroxide. Moreover, under these extreme conditions, pH levels in excess of 11.0 are often obtained[1].

When the solution is heated, CO_2 is removed, favouring the bicarbonate decomposition reaction followed by $CaCO_3$ precipitation. For calcium carbonate to appear in an irreversible manner in a liquid, the sequence of a germination step by growth could take place in the liquid phase. In fact, the germination phenomenon starts with the agglomeration of the hydration ions *i.e.* CO^{-}_{3} and Ca^{2+}

These two ions will then join together to form a colloidal germ having an electrical charge that characterizes the so-called *zeta* potential. Afterwards, this colloidal germ can grow and dehydrate at the same time till a crystal is produced with inherent capability.

If a germ is transferred to a close layer of a metallic wall, it may be adsorbed by the nearby surface, which has a negative electrochemical potential. Hence, one of the two scenarios may take place, either the germ adheres strongly to the wall, and initiates scaling of the metal wall, or it is attracted without being really adsorbed.

A solution is said to be super-saturated when it contains species in concentration such that the corresponding salt's solubility defined by thermodynamic equilibrium is exceeded[3]. This situation arises, if for instance, a solution temperature is modified. Super-saturation is then a consequence of sluggish crystallization kinetics caused by a high activation energy barrier. The formation of crystals (also called nucleation) usually follows and either occurs spontaneously (homogeneous nucleation) or can be aided by the presence of a suitable nuclei, which may be either solid impurities in suspension in the solution or sites on the tubing boiler 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[4].

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 scaling of their surface[4, 5].

When calcium carbonate precipitates, it forms 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 on the conditions under which the precipitation occurs, mainly the solution's temperature, and subsequent transformation, particularly in the case of vaterite[5].

Each allotropic form is easily recognized by the shape of the crystal it forms, a needle shape for aragonite, a cubic shape for calcite, and a spherically shape for vaterite.

Water boilers may be considered as heat exchangers in the sense that the heat transmission is similar to that in classical tube and shell heat exchangers. Nevertheless, the heating stream, instead of being a fluid (either liquid or gas), could be a gas combustion or an electrical energy source.

The scaling in water boilers represents a tedious problem. The fouling, due to scaling, can cost a medium size oil refinery as much as one million USD a year in terms of increase in the capital and operating costs. This implies the importance of the market for scaling control. The problems caused by fouling of a water boiler fall into two categories, namely, the operation difficulties and the additional costs. The complexity of these phenomena with their corresponding interaction makes fouling reduction a difficult problem to tackle. In the particular case of scale reduction, it should be noted that crystallization in general, and crystallization of calcium carbonate in particular is a process that is not yet fully understood, and even today is subject to speculation and thorough discussions among chemical scientists[6]. The scale control market incorporates therefore a very wide range of methods based on a variety of fundamental mechanisms, some of which have little scientific credibility. However, scale control methods are generally based on either prevention or inhibition of scale by the injection of chemicals.

The prevention of scale is achieved by eliminating the scale-forming cations (*i.e.* the ions contributing to the hardness) from water. In the case of inhibition, the aim of the technique is to retard as much as possible the appearance of scale formation.

The existing scale controlling techniques 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, or processes using physical treatment.

The various methods to remove existing scale belong in general to the first category These include acid- washing of the surfaces as well as the various mechanical methods in use, such as brushing and scraping.

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 requires sophisticated process control since the process is highly sensitive to fluctuation of the operating parameters[7, 8].

The pellet softening can also be used as a method of scale reduction. A pellet softener consists of a cylindrical vessel containing a fluidized bed of grains of feed material that provides a large surface on which the crystallization 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 crystallization. The pellet softening technology presents the advantage of generating recyclable products, solid grains of calcium and bicarbonate cannot be removed to the low concentration produced by conventional softening and the crystallization process only proceeds for as long as the solubility product of calcium carbonate is exceeded. Also, hardly any magnesium is removed.

The physical conditioning can be based on electric, magnetic or ultrasonic treatment. Such treatment does not modify the mineral content of water but the morphology of the precipitated which is then mainly made up of fine particles[9] Moreover by their very nature, these methods do not generally add the chemical content of the water.

The 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. 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[6].

The ultrasonic treatment is based on a generator which produces electrical impulses at high frequency, which are transmitted via a coaxial to transducers mounted externally. Each transducer contains piezoelectric ceramic crystals which, when excited by the electrical impulses, generate an ultrasonic beam[4, 10].

The magnetic water treatment (MWT) has an extensive history. Based on the application of magnetic field to prevent scale, an early patent by Faunce and Cable was registered in 1890. The MWT works on the principle of forcing oppositely-charged ions to move in opposite directions, hereby producing collisions which result in the formation of microscopic nuclei that cause the calcium carbonate to precipitate within the water instead of on the surfaces of the pipes or heat exchangers.

The process changes the crystalline structure by the use of a magnetic induction field, which when exposed to moving water, interacts with the water's electric dipole moment and applies a torque to the water molecule. The resulting electric double layer of the colloidal particles, when distorted by the external magnetic field, tends to absorb calcium and magnesium ions, thus inhibiting their precipitation on the pipes or heat exchanger surfaces.

MATERIALS AND METHODS

The comprehensive laboratory setup, that is described below has been supplied by Kennicot Ltd, a UK company. Tap water is pumped from a one half-cubic meter tank to two water boilers, with 5.0 liters capacity each, operated in parallel. The flow to each boiler is controlled individually by means of two rotameters. The water, pumped at an approximate pressure of 15 *psig* to the boilers, is heated by an electric source, where the energy is controlled through an electric power recorder. The temperature in both boilers is controlled separately by two digital temperature controllers, as shown in Figure 1. The overflow of the two water boilers is returned to the main water tank after being cooled in a water heat

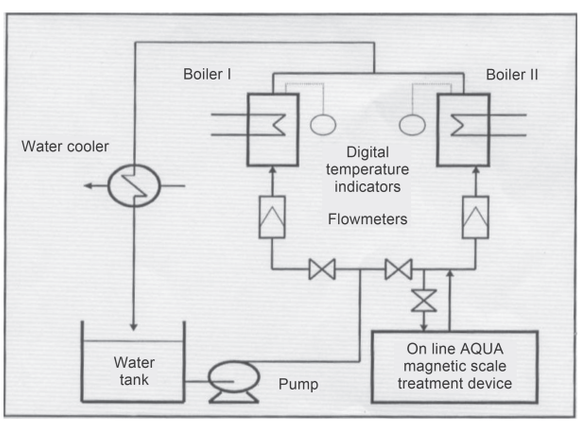


Fig.1. Schematic flowchart of the laboratory setup.

exchanger. The water flow is electrically controlled by a solenoid valve.

The temperature of the water is controlled by the liquid flow rate to each water boiler. The higher is the flowrate; the lower is the temperature in the boiler. The laboratory setup was run at a water temperature nearby 80±1^{0}C which is equivalent to a water flow rate of 25 l/h for most of the experiments carried out in this study.

The magnetic water treatment device plugged on line with a laboratory setup has been supplied by AQUA Total, a UK company, and works according to the DVGW Standard W 512[11] Deutsche Vereinigung des Gas und Was serf aches e.V., English: German Association on Gas and Water[12]. The technical specifications of this device are detailed in Table 1.

Table 1. Technical specifications of the AQUA total 2500.

Characteristic specification	Units	Value
Nominal connector bore	*mm*	25.0
Rated flow	m^3/h	2.50
Pressure drop at rated throughout	*bar*	0.35
Nominal pressure PN	*bar*	10.0
Water temperature max.	^oC	30.0
Ambient temperature max.	^oC	40.0
Dimensions Height Width Length	 *mm* *mm* *mm*	 1060.0 65.0 330.0
Power input	*V/Hz*	230×50
Power consumption max.	*Watts*	60.0
Power consumption approx.	Wh/m^3	55.0
Protection	-	IP54

The water solutions were prepared by adding sodium hydrogen hydroxide to calcium chlorate to form calcium carbonate in a 300 liters capacity tank by adding water and stripping until all the salts were dissolved. The equation below describes the reaction that takes place in the tank:

$$CaCl_2 + NaHCO_3 \rightarrow CaCO_3 + NaCl + HCl$$

Before and after each run, all the equipment was drained and refilled with de-ionized water in order to remove all suspended and scaling matters.

The hardness was measured by the EDTA (ethylene diamine tetra acetic) solution and the alkalinity by the volumetric titration using an N/50 sulphuric acid by means of phenolphthalein and bromocresol colour indicators.

RESULTS AND DISCUSSION

The boiler apparatus has been studied at five different running times in blank and treated modes at different operating conditions (water flowrate and calcium carbonate concentration) as shown in Table 2. The pH was maintained constant around 7.0 to 8.4 during all the different runs.

After each run, the measure of the scaling mass in both boilers was dissolving 5 litres of hydrochloric acid in the boilers. The scaling rate was calculated as the ratio of the scaling amount by the running time. In the first run, when water is circulated at 981/h, the scaling rate is 1.97 mg/h whereas it decreases to 0.98 mg/h, nearly by half, when the flow rate is lowered to 25 l/h. The flow rate has a substantial effect on the scaling rate, in the sense that the scaling rate increases as the fluid velocity is augmented.

The laboratory setup has been run for quite long times to enhance scale deposit as much as possible. The hardness decay of the prepared solution in the water tank during both treated and untreated runs were linear as shown in Figure 2. The behavior of the alkalinity decay in the water tank observed during different runs was also linear as shown in Figure 3.

Figure 4 shows that the pH fluctuated from 7.9 to 8.1 which represent a 2.5 % change. There was slightly no effect on the pH while running the experimental setup in a blank regime. However, a substantial change on the pH was observed when the magnetic treatment was incorporated in the loop. The pH fluctuated from 7.6 to 8.3 in a parabolic

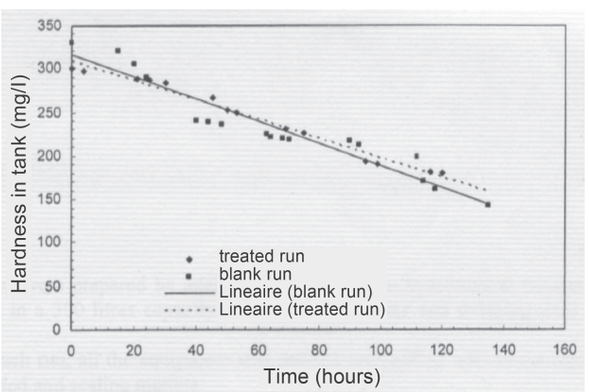


Fig. 2. Depletion of hardness in treated and untreated regimes.

behavior. Some authors[13, 14] have mentioned that the influence of the magnetic treatment on low pH, whereas for high pH's the impact is considerable.

The incorporation of the magnetic treatment device in the experimental station loop reduces drastically the scaling rate as shown in Figure 5. A considerable decay of around 40% has been observed between the treated and untreated regimes as exhibited by Figure 6. The scale amount deposited in boiler I (left) is slightly higher compared to that in boiler II (right) due to the fact that the latter is located nearer to the magnetic device and, henceforth the circulating water benefits from a better treatment (Fig. 7).

The morphology analyzed by SEM (Scanning Electronic Microscope) of the scale crystals deposited at the walls and elements of both left and right boilers at the end of run 1 (blank) and run 3 (treated) are summarized in Table 3. The scales deposited at the walls of the right boiler are needle shape and smooth, whereas those deposited on the left one are soft.

Figures 8 and 9 show SEM pictures of the scale deposited on hot surface areas qualified usually as if calcite, a hard scale, and aragonite are soft scale. This depends on the solution chemistry and surface temperature. It has been reported[13] that aragonite shape formed at around 60°C. The soft scale has formed on walls and hard scale on elements during the blank run while in the treated one, the formation of scale on elements is soft and deposit as aragonite and calcite with a larger size.

The trace amounts of iron in water form paramagnetic FeOOH clusters that are retained and

Table 2. Operating conditions of scale laboratory setup.

	Run#1	Run#2	Run#3	Run#4	Run#5
Mode of running	Blank	Blank	Treated	Treated	Blank
Flow rate (l/h)	98 25	25	25	25	25
Running time (h)	75 151	109	105	116	123
Tank temperature (°C)	33 20	35	35	30	30
Left boiler temperature (°C)	80	80	80	80	80
Right boiler temperature (°C)	80	80	80	80	80
Initial hardness (mg/l)	300	450	340	300	300
Initial alkalinity (mg/l)	450	450	340	340	340

Table 3. SEM of scale crystals formation during run 1 (blank) and 3 (treated).

Run. No.	Right boiler				Left boiler			
	Element		Wall		Element		Wall	
	Shape	Size	Shape	Size	Shape	Size	Shape	Size
Run1 (blank)	Aragonite	25-30 microns	Needle shape	Tiny	Aragonite	20 microns	Soft scale	Small
Run 3 (treated)	Aragonite	200-300 microns long	-	-	Calcite	150-200	-	-

Table 4. Summary of changes on water quality in the tank.

Run number	Amount of dosing	Change in Ca	Change in HCO_3	Change in pH	Time	Flow rate	Reduction rate
	mg/1	mg/1	mg/1		h	L/h	$g/h10^{-3}$
Run 1(B)							
Dosing 1	280	132	216	0.36	75	98	1.75
Dosing 2	290	186	0.14	0.14	30	25	6.20
Dosing 3	300	162	0.38	0.38	25	25	5.40
Dosing 4	298	176	0.19	0.19	23	25	7.60
Run 2 (B)							
Dosing 1	422	292	176	-0.88	85	25	3.43
Dosing 2	290	120	192	0.13	24	25	5.00
Run 3 (M)	340	142	101	0.57	105	25	1.35
Run 4 (M)	300	121	150	-0.71	116	25	1.04
Run 5 (B)	330	170	165	-0.31	123	25	1.98

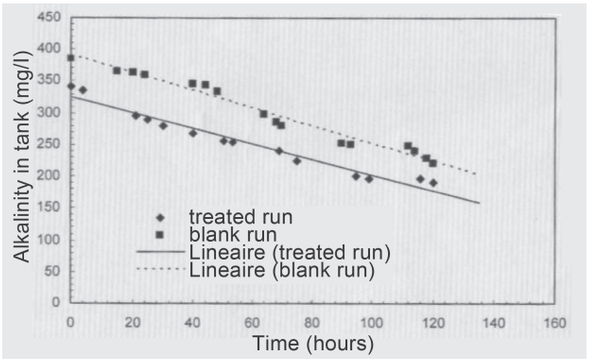


Fig. 3. Depletion of alkalinity in treated and untreated regimes.

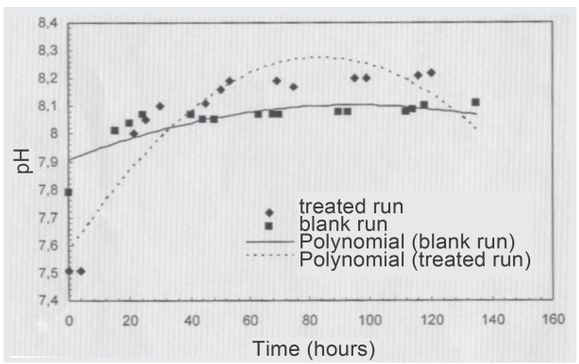


Fig. 4. Effect of the scaling on the pH.

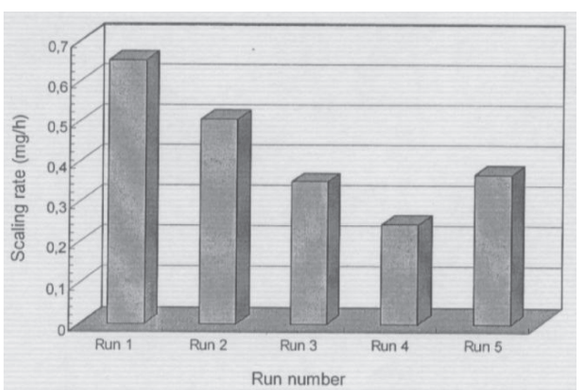


Fig. 5. The evolution of the scaling rate.

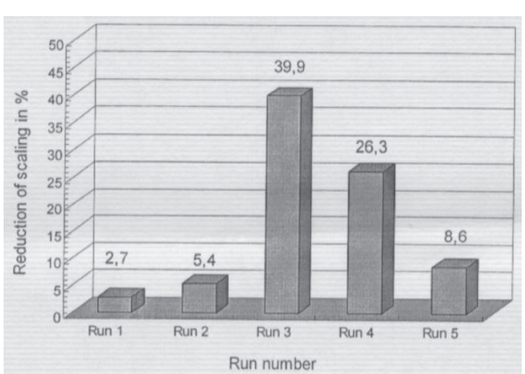


Fig. 6. The reduction of scale deposited in both boilers in %.

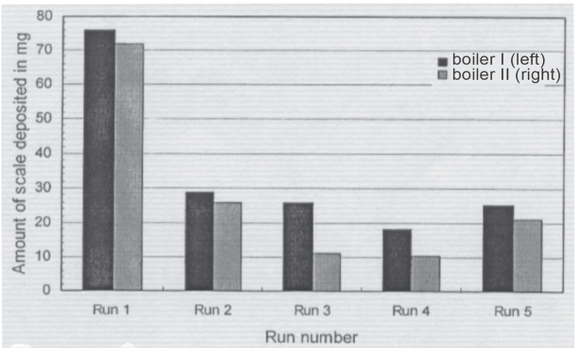


Fig. 7. The amount of scale deposited in both boilers.

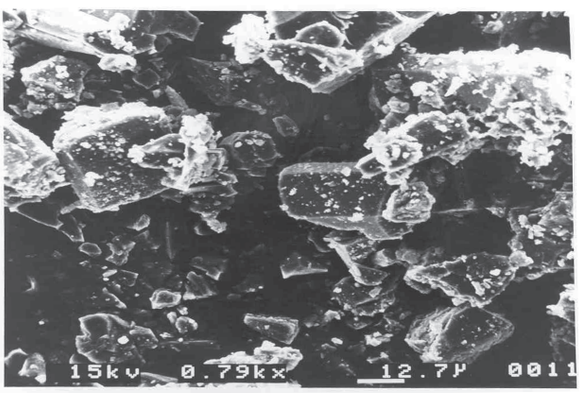


Fig. 8. SEM photograph of calcite crystals deposited in a treated run.

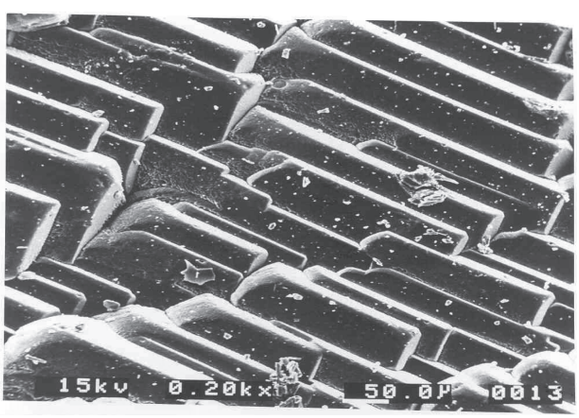


Fig. 9. SEM photograph of aragonite crystals deposited in a treated run.

which serve as nucleation centers which enhance the development of aragonite formation. The aragonite, being slightly less stable than calcite, tends to form elongated needle-like crystals as pictured in Figure 9.

Calcium carbonate samples of scale formed on water boiler deposited on the wall and the elements were taken at the end of run 1 from left and right boilers and analysed by Scanning Electronic Microscope (Table 4).

The scale shown in Figures 10(a) and (b) is that of the right boiler whereas Figures 11 (a) and (b) show the crystals formed in the wall region from the left boiler. Different types of scales can be clearly recognized:

- needled smooth shape in the wall, nearly 10 mm in size, classified as soft scale.
- aragonite shape in the elements (both from left and right boiler) near 20mm in size, and classified as hard scale.

From the three calcium carbonate po1ymorphs (calcite, aragonite and vaterite), calcite is the most thermodynamically stable form at standard temperatures and pressures[15]. However, at the surface temperature commonly encountered in systems such as heat exchangers and boilers, aragonite is normally the first phase to precipitate out of solution. In this case, recrystallisation of the aragonite into calcite overtime may enhance the formation of a more tenacious encrustation [16].

Magnetic treatment has been found to cause occasional difference in the precipitated crystal habit in order to determine any possible influence of the magnetic treatment on the structure of the $CaCO_3$ layers. Two studies were undertaken: first, SEM pictures of the scale samples were taken, and secondly, the relative proportion of the two main allotropic forms of calcium carbonate was evaluated. The two studies were made possible because of the difference in physical properties of the two allotropic forms of $CaCO_3$ (calcite and aragonite). The calcite tends to form what was referred in literature as hard scale, whereas the aragonite referred to as soft scale.

The main difference in 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. In our experimental work, the boilers were consisted with copper element. It basically describes the ($CaCO_3$ crystallised on the copper element according to the simple graph of Figure 12. In addition, by gently removing the scaled copper element on the hard surface, it was possible to separate the two types of scale as illustrated in that figure.

The treatment of calcium carbonate solutions with

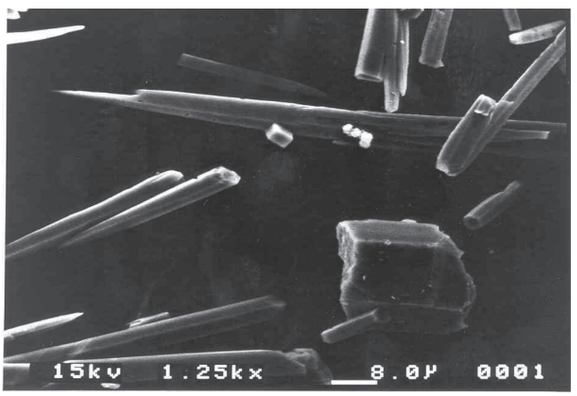


Fig. 10a. SEM photograph of scale formed on boiler wall during run 1.

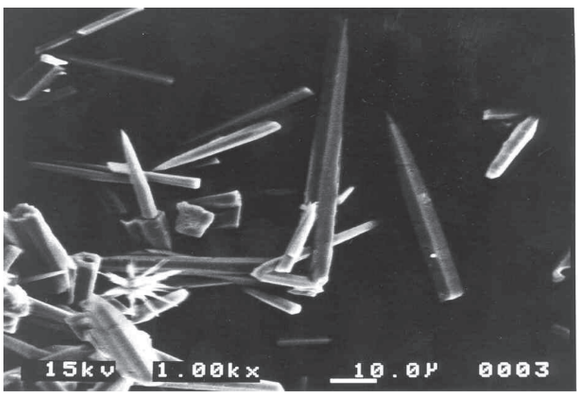


Fig. 11a. SEM photograph of scale formed in boiler wall in run1.

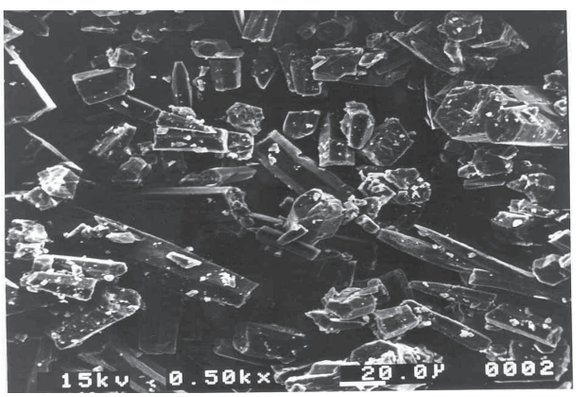


Fig. 10b. SEM photograph of scale formed on the element during run 1.

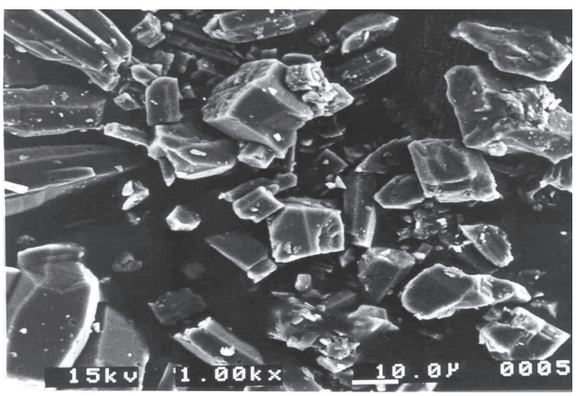


Fig. 11b. SEM photograph of scale formed in element boiler in run 1.

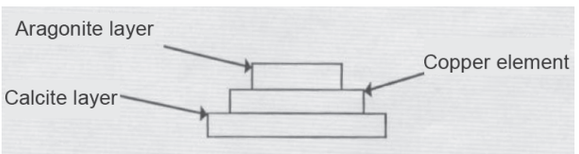


Fig. 12. Cross section of the scale deposits.

substantial orthogonal fields [7000 Gauss] can, depending on the chemistry, reduce precipitation of calcium carbonate and calcium sulphate. Scaling of surfaces on heat exchangers can be reduced by 80% as mentioned by Coetzee[17], and by 90% as mentioned by Aqua Total on DGVW. An effect has been shown quantitatively in both static and flowing systems, results have shown that colloidal stability is influenced by the application of a magnetic field that will lead to accelerated coagulation confirmed by the increasing agglomerates found in the scale, nucleation and crystal growth rates are also reduced leading to the formation of irregularly shaped crystal forms.

HOW DOES IT WORK?

There was a wide range of mechanisms proposed for how magnetic treatment works, but most of them are unproven yet. The most likely mechanism is the effect of micro contaminants[17], interfacial phenomena-macroscopic or surface/interfacial phenomenon. The intra-atomic effect will be on stages which can be summarised as the following process: electron excitation - electron spin interaction -electron transfer - molecular bond breaking. In recent works, it was identified that the key roles of micro-contaminants which affect the crystal nucleation grout rate[17]. Gotezee[18] reported a reduction in carbonate precipitation following adsorption of free Zn (II) cations present at the ppb level.

CONCLUSION

The conditions of running the experimental setup were similar to the DGVW test.

The application of temperature, pH and concentration, was reached through the blank run.

The use of photographic images from SEM analysis proved too subjective from use as a qualitative indication in the change of crystal morphology. It was apparent that the microscope operator could manipulate selection of the crystal images to illustrate the difference in morphology.

In addition, it can be said that magnetic treatment can reduce the scaling under the correct conditions of temperature, pH, hardness and flow. Also the once through magnetic treatment can reduce the scaling.

- Morphology of scale different between treated run and untreated run.
- No scale despite on wall boiler in treated run.
- Maximum reduction on hardness in tank 30-35% were $5x10^{-3}$ g/h.
- Reduction rate in tank were high at small flow rate.
- No effect of flowrate on scale formation, were observed at a rate of 98 l/h.
- Effect of flow rate on surface temperature.
- Maximum reduction of 40% in scaling formation in boilers.
- The scale in left boiler was less than in right one.
- Formation of scale on surface at high hardness.

The magnetic anti scale treatment knows, since the last few years, an overwhelming interest among the" specialized scientific community as a scaling inhibitor. The experimental study of this process has clearly shown that this one is capable of reducing the scale formation by up to 40 % with a negligible effect on the pH of the circulating water. In a future work, higher initial concentrations with longer running times will be investigated for collecting a wide range of data with the laboratory setup run at different operating conditions. A budgetary and investment study is aimed to be performed for comparison with the classical treatments processes.

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