

Design and application of a bench scale evaporator for the treatment of coal power plant waste water

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Declaration of Authorship

I declare that this report is a presentation of my own original work.

Whenever contributions of others are involved, every effort was made to indicate this clearly, with due reference to the literature.

No part of this work has been submitted in the past, or is being submitted, for a degree or examination at any other university or course.

Signed on this, 7th day of November in Potchefstroom.

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INITIALS AND SURNAME

Academic and Technical Outputs

Conference Proceedings

Redelinghuys J, Fosso-Kankeu E, Waanders F, Rogers D, Gericke G. 2017. Scaling conditions inside improved bench-scale single effect vacuum evaporator. In *Advances in Science, Engineering, Technology & Waste Management (ASETWM-17)* conference proceedings organized by EAP (Eminent Association of Pioneers) and hosted in Parys, North-West Province, SA.

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Fosso-Kankeu, E., Redelinghuys, J., Waanders, F., Rogers, D., Bruinsma, D. and Gericke, G., 2016. Determination of water evaporation rate in an assembled bench scale MED and impact of anti-scaling agents on the morphology of scale. In *International Conference on Advances in Science, Engineering, Technology and Natural Resources (ICASETNR-16)* hosted in Parys, North-West Province, SA.

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Abstract

The potential of scale formation during the application of Multi-Effect Distillation (MED) technology for the treatment of Reverse Osmosis (RO) retentate was investigated in this study. An improved bench scale single effect evaporation unit was designed using the Solidworks Simulation Package and appropriate materials. Operating conditions were determined to be 80°C and 0.48 bar with the design constructed to maximise evaporation. Once assembled, RO-retentate was introduced to the evaporator at an evaporation rate of 4 L/h (22.3 L/m²/h), and the variation of the concentrations of scale forming elements determined. The evaporation observed translates to 34.5% water recovery. Speciation using PHREEQ-C modelling software showed that the concentrations of scale forming ions increased during evaporation. Scale prediction and prevention were explored using French Creek software, with anti-scaling agents being used to minimise scaling.

The dosage of the anti-scaling agents inside the MED was determined using French Creek software. The anti-scaling agents yielded confirmation of their capability of keeping ions in suspension and preventing them from forming scale. When measuring the performance of the anti-scaling agents on this basis, AMPS (Acrylic Acid-2-Acrylamide-2-Methylpropane Sulfonic Acid Copolymer) fared better than PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid). However, HEDP (1-Hydroxy ethylidene-1,1-Diphosphonic Acid) yielded concentrations of scale forming ions lower than when no anti-scaling agent was dosed. This may be ascribed to the nature of complexes that HEDP forms with the scale forming ions.

The application of MED technology combined with the use of anti-scaling agents to treat inland waste waters can see the MED evaporator serving a dual purpose. The primary purpose is to serve as water producing/recycling technology that can treat saline solutions to recycle as much fresh water as possible. The MED reject will be suitable for further treatment using other separation technology to ultimately produce fresh water and salts. The secondary purpose of the MED technology when applied to a power plant could be to dissipate some of the abundant heat present. The MED technology possesses the potential of alleviating the amount of heat energy the cooling towers must dissipate to some extent, thus lowering the amount of cooling water needed, and this should be investigated. Thus, a combination of membrane technology and thermal technology could theoretically be utilised in order to adhere to the zero liquid effluent discharge policy Eskom has, whilst lowering the amount of fresh water needed for cooling purposes.

Additionally, the laboratory evaluation of anti-scaling agents prescribed by scale modelling software was investigated. The considered water contained high levels of scale forming agents. The selected test method to determine anti-scaling agent induction times was found to be inefficient and an improvement on the current method was proposed. The possible causes for the inefficiency of the selected induction time test method was mainly ascribed to an insufficient heating apparatus setup

Key Words: MED, anti-scaling agents, Reverse Osmosis retentate, French Creek

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List of Abbreviations

ATMP	Amino Trimethylene Phosphonic Acid
EDTA	Ethylene-diamine-tetra-acetic acid
CW	Cooling water
PAA	Polyacrylic acids
PASP	Polyaspartic acid
AMPS	Acrylic Acid-2-Acrylamide-2-Methylpropane Sulfonic Acid Copolymer
HEDP	1-Hydroxy ethylidene-1,1-Diphosphonic Acid
PBTC	2-Phosphonobutane-1,2,4-Tricarboxylic Acid
PESA	Polyepoxysuccinic acid
PMA	Polymaleic acids
RO	Reverse osmosis
MED	Multi-Effect Distillation

CHAPTER 1: Background and Motivation

1.1 Introduction

More than half of countries worldwide potentially face water shortages in the future. Projections indicate that, by 2050, up to 75% of the world's population may be confronted with water scarcity (Afrasiabi & Shahbazali, 2011). South Africa has already been deemed a water-scarce country. All water consumers are forced to explore the utilisation of all available water sources, and this water scarcity is further being affected by climate change. Despite the water shortage the country is currently facing, the demand for water usage in industry and human consumption remains high, creating an ever-increasing dependence on seasonal rainfall (Fosso-Kankeu et al., 2009). Waste water effluent is becoming more valuable as advances in technology makes the recovery, treatment and re-use of waste water more attractive and viable (Fosso-Kankeu et al., 2016).

1.2 Problem Statement

Eskom, South Africa's national power utility, is allocated 2-3% of the nationally available fresh water to generate electricity. Eskom is under pressure to minimise its water usage and has set a target of lowering its usage to 1.34 L of water per kilowatt hour (kWh) electricity produced by 2020, from the 1.39 L/kWh in 2017 (Roos, Rogers, & Gericke, 2017). Of the total water intake, 98% is lost via evaporation through the cooling towers at the power plants. The re-usage and recovery of certain streams may potentially lower the amount of fresh water intake needed to replenish the amount of water lost due to evaporation. Furthermore, Eskom has a zero liquid effluent discharge (ZLED) clause in its water use licences – leading to the exploration of lowering the amount of effluent waste water produced and improved disposal methods. Eskom has thus initiated various investigations towards water management and proper usage of all available water sources. This investigation will primarily focus on retentate/saline water stream from the primary reverse osmosis (RO) module. This stream has a salinity above 8000 parts per million (ppm) and recirculation through the RO system is not economically viable as the balance between optimal membrane performance, maintenance and cost dictates. Yet, there remains the potential to recover water from this retentate.

1.3 Aim and Objectives

1.3.1 Aim

The aim of this study was to determine the effectiveness of an evaporator system as a possible water treatment technology for saline waste water streams in Eskom power plants.

1.3.2 Objectives

This aim was achieved by the following objectives:

- i. Design, construct and operate a functioning bench scale single effect evaporator.
- ii. Determine the most suitable anti-scaling agent required to use inside the evaporator when treating a saline waste water stream obtained from an Eskom power plant.

1.4 Research Questions

The research was aimed at addressing the following questions:

- i. What are the optimal operating conditions when applying evaporation technology to saline waste water streams produced inside Eskom's power plants?
- ii. What anti-scaling agents should be used to optimise the heat exchange efficiency inside the constructed bench scale single effect evaporator?
- iii. How much water can be reclaimed when using evaporation technology to treat saline waste water produced inside Eskom's power plants?
- iv. What is the composition of the bench scale single effect evaporator's reject?
- v. How well does anti-scaling agents work on different saline waste water streams obtained from an Eskom power plant?

1.5 Dissertation Structure

The research presented in this dissertation has been conducted at the North-West University, in the laboratory and in the workshop. Three articles were written for this dissertation, and they are presented to conform to the requirements of the North-West University (Potchefstroom Campus) for the degree Master of Engineering. This dissertation comprises 5 chapters; with a summary of each chapter to follow:

CHAPTER 1: Background and Motivation

This chapter provides a background into the reasoning and motivation for the study. The problem statement, objectives and research questions were briefly discussed.

CHAPTER 2: Literature Review

This chapter discusses the literature relevant to the study and examines information from other studies under the same research topic. It includes the in-depth examination of scale forming and inhibition mechanisms, the discussion and comparison of relevant saline waste water treatment technology and the proposed

theoretical optimal combination of water treatment technological solution for inland coal powered, wet-cooled cooling tower power plants.

CHAPTER 3: Design, configuration and construction of the bench scale MED

This chapter contains the design, configuration and construction of the bench scale single effect evaporator, the determination of relevant anti-scaling agents, as well as the evaluation of the performance of the evaporator.

CHAPTER 4: Determination of suitable anti-scaling agent to inhibit scale formation inside the constructed bench scale MED.

This chapter contains the evaluation of the performance of anti-scaling agents applied to waste water streams from Eskom's power plants at different temperatures.

CHAPTER 5: Conclusions and Recommendations

This chapter contains the conclusions and recommendations to benefit the relevant stakeholders.

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CHAPTER 2: Literature Review

2.1 Introduction

Coal-fired power stations that use wet-cooled cooling towers produce large amounts of mineral rich waste water streams due to the vast amounts of evaporation during the cooling process. The evaporation of the cooling water concentrates the salts and minerals found in the fresh water entering the power plant. This water is treated on site to recover as much water as possible, and various water streams are treated using membrane technologies (nano-filtration and reverse osmosis). When water is being treated for re-use, scaling is common when any form of heat exchange or membrane technology is used if precautions are not taken (MacAdam & Parsons, 2004). This is due to the increase in mineral concentration. The negative effects of scaling can take various forms, including fouling of membrane systems, reduced heat transfer efficiencies in heat exchange systems, scheduled and unscheduled shutdowns, as well as increased maintenance, operation and capital costs (Piyadasa et al., 2017). Saline water can be purified or recycled by making use of various desalination techniques, namely distillation (thermal and crystallisation distillation) and non-thermal membrane techniques (nano-filtration and reverse osmosis) (Amjad, 1996).

2.2 Mineral Scale Formation

Scale forms in alkaline water and is caused by the presence of Ca^{2+} and/or Mg^{2+} and other ions of the solution, with calcium carbonate being one of the more common scale components (Zhang et al., 2001). Sub-micron size crystals are the main contributors to the scale layer on a metal surface during the initial stages of scale formation. Supersaturation of the water can be described as the main cause of scale formation (Chen et al., 2005). Process parameters also plays a role in scale formation – with temperature and flow rate being the most influential (Wildebrand et al., 2007). Other factors include the deposit (scale) structures, shape, size and composition. It is important to note that, when mineral constituents remain soluble, they have no negative effect on heat transfer efficiency (Kavitha et al., 2011).

2.3 Scale Formation Mechanisms

When assessing the fundamental processes involved in the formation of scale and mineral precipitation, it becomes apparent that there are multiple steps involved, and these will be briefly explained with the schematic representation in Figure 2-1.

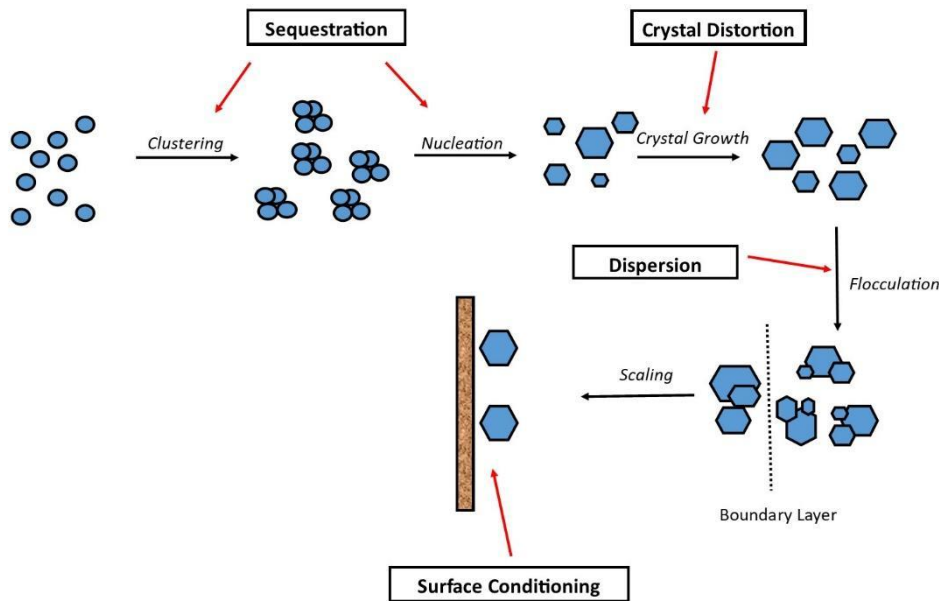


Figure 2-1: Schematic of processes involved with the formation of mineral scaling and scaling control by chemical anti-scaling agents

Reproduced from Antony et al. (2011)

When mineral ions are introduced to water, either artificially or through the continual concentrating of the ions present by decreasing the water volume, the ions will eventually become sufficiently concentrated to deem the water supersaturated. Mineral ions in solution under increasingly supersaturated conditions will, due to their polarity and random thermal motion, form clusters (Al-Roomi & Hussain, 2016). Once these clusters pass a critical size, nucleation will take place. As soon as nuclei are formed, spontaneous crystallisation will occur, forming larger particles. Subject to the surface properties and composition of the particles, they can either aggregate in order to create larger particles or remain suspended in the water for a period of time, after which these particles and present mineral ions will diffuse through the hydraulic boundary layer (Li, 2010) and form scale after depositing onto a solid surface.

2.3.1 Supersaturation/Clustering

Water containing ions of sparingly soluble salts, such as CaCO_3 , CaSO_4 or Mg(OH)_2 , has the potential to become supersaturated and/or allow mineral clustering to form under certain process conditions. Supersaturated conditions are achieved when the solution containing these salts is concentrated beyond the solubility limits of one or more of the constituents. This can occur by either separation of pure water (membrane processes such as RO) or water evaporation (usually present in thermal desalination systems or water cooling towers) (Hasson et al., 2011).

Supersaturated conditions can also be achieved by a change in temperature. The majority of generally encountered scaling salts exhibit inverse solubility characteristics with regard to temperature. When a solution containing an inverted-solubility salt comes into contact with a hot surface, supersaturation by this inverse-solubility effect can cause scale to deposit on the hot surface, even when the bulk of the solution is undersaturated (Hasson et al., 2011).

2.3.2 Nucleation

Once supersaturation conditions are achieved, the mineral ions present continuously adopt different configurations for solid mineral formation (Yang et al., 2002). The clustering that occurs can be deemed random, as it is caused by ionic thermal motion that is easily reversible. Mineral clusters consist of a broad size range, starting at dimers, trimers and continuing to i-mers ($i > 100$, where i is the number of ions) and stopping at the critical number, which can be denoted as number j . These clusters constantly form, break up and disappear. Once a cluster reaches the critical j -number/size, the addition of a monomer leads to nucleation. The formation of clustering centres from which spontaneous crystal growth can proceed is also referred to as nucleation (Li, 2010).

To summarise classic nucleation theory, the free energy of the formation of a nucleus consists mainly of the energy gained from creating bonds paired with the work required to create the nucleus surface (Stumm et al., 1992).

$$\Delta G_j = \Delta G_{bulk} + \Delta G_{surface} \quad \text{Equation 2-1}$$

Equation 2-1

Bulk energy gain for a nucleus can be expressed as follows:

$$\Delta G_{bulk} = -jkT \ln S \quad \text{Equation 2-2}$$

With j being the number of monomers (ionic units) in the nucleus. “ j ” can be expressed using volume where V_{ion} is the ionic volume (m^3) and r being the radius of a spherical nucleus:

$$j = \frac{\left(\frac{4\pi r^3}{3}\right)}{V_{ion}} \quad \text{Equation 2-3}$$

S which is the saturation ratio can be expressed as:

$$S = \left(\frac{IAP}{K_{sp}}\right)^{\frac{1}{n}} \quad \text{Equation 2-4}$$

Where IAP represents the ionic activity product, K_{sp} the solubility product and n the number of ions. The number of ions is obtained from the formula unit of the mineral (i.e., $n = v + w$ where mineral formula unit is $AvBw$).

The energy cost/work required during surface formation can be expressed using interfacial energy (surface tension), which is assumed to be independent of nucleus size, has a spherical area, is measured in mJ/m² and is represented by the symbol γ in the following equation:

$$\Delta G_{surface} = 4\pi r^2 \gamma \quad \text{Equation 2-5}$$

Combining the relevant equation results in the nucleation energy is written as follows:

$$\Delta G_j = -\left(\frac{4\pi r^3}{3}\right) \frac{kT \ln\left(\frac{IAP}{K_{sp}}\right)^{\frac{1}{n}}}{V_{ion}} + 4\pi r^2 \gamma \quad \text{Equation 2-6}$$

Nucleation energy can be expressed as a function of temperature, saturation ratio and nucleus size. It is apparent that spontaneous nucleation will take place as soon as the solution is supersaturated and the size of the ion clusters present in the solution is sufficient. Additionally, temperature increases result in conditions favourable for nucleation.

2.3.3 Crystal growth

Upon the commencement of nucleation, microcrystals are present in the solution, and they can agglomerate and/or absorb onto surfaces exposed to the solution where the micro-crystals will grow into larger micro-crystals to eventually form macro-crystals by fusing together (Al-Roomi & Hussain, 2016). Dandekar and Doherty (2014) reported that crystal growth will occur under non-equilibrium conditions when the chemical potential of the growth medium (μ_{medium}) is more than the chemical potential of the present bulk crystal ($\mu_{crystal}$). The difference between these two chemical potentials is the impelling cause for crystal growth (Dandekar & Doherty, 2014).

$$\Delta\mu = \mu_{medium} - \mu_{crystal} \quad \text{Equation 2-7}$$

2.3.4 Deposition/agglomeration

According to Al-Roomi and Hussain (2016), the adsorption of additional ions from the solution will in turn cause the macro-crystals to continue growing until their size deems them colloidal particles, and ultimately form a scale film onto any susceptible surface, growing into a deposit. It is important to note, however, that should there be an availability of active sites, scale forming species can bypass the crystal forming stage and directly proceed to crystal growth onto these sites (Ferguson et al., 2013).

2.3.5 Kinetics of Sulphate Removal through Gypsum Crystallization

A solution will be deemed over saturated pertaining to gypsum in two cases (Maree, et al., 2004):

- i) When an effluent rich in MgSO_4 is treated with lime in order to precipitate Mg^{2+} as $\text{Mg}(\text{OH})_2$, an over saturated CaSO_4 solution will form. (This typically happens if $[\text{SO}_4^{2-}]$ is greater than 1500 mg/L).
- ii) When an acid solution with a high enough sulphate concentration is treated by dosing lime so much so that the solution is over saturated with respect to gypsum after neutralization.

The sulphate removal rate by gypsum crystallization can be predicted by equation 2 – 8 (Geldenhuy, et al., 2003):

$$\frac{d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]}{dt} = k[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)[C - CO]^2 \quad \text{Equation 2-8}$$

Where: $\frac{d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]}{dt}$ is the crystallization rate; k represents the reaction rate constant, $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)$ represents the surface area of the seed crystals, C represents the initial calcium sulphate concentration and CO represents the saturated calcium sulphate in solution concentration.

From this equation 2-8 it becomes apparent that the gypsum concentration and gypsum crystallization is proportional, as an increased gypsum concentration will result in an increased rate of gypsum crystallization (Geldenhuy, et al., 2003). This serves as motivation for sludge recirculation during lime dosing stages when sulphate removal is required, or if sulphate is required to stay in solution – no recirculation of sludge (Maree, et al., 2004).

When CO_2 is used for pH adjustment, the occurrence of CaCO_3 crystallization can be indicated by a decrease in the concentration of calcium (Maree, et al., 2004). The under saturation, super saturation and saturation states of CaCO_3 can theoretically be identified by the activity product of Ca^{2+} and CO_3^{2-} species that compares with the solubility product constant k_{sp} for CaCO_3 (Loewenthal & Marais, 1976). If above the solubility product, CaCO_3 will precipitate from the solution. If below, CaCO_3 will dissolve. Equation 2-9 describes the precipitation or dissolution rate (Geldenhuy, et al., 2003):

$$-\frac{d[\text{Ca}^{2+}]}{dt} = kS \left\{ (\text{Ca}^{2+})^{\frac{1}{2}} - k_{sp}^{\frac{1}{2}} \right\}^2 \quad \text{Equation 2-9}$$

Where k represents the precipitation rate constant and S represents the surface area of the CaCO_3 growth/dissolution as well as the activity in mol/L

The precipitation rate depends on k , S and the term inside the curled brackets. Although k is affected by crystal structure to an unknown extent, S depends on the mass, size and structure of the crystals. By controlling the term in curled brackets (the degree of supersaturation) as well as S (the surface area of the CaCO_3) – the rate of dissolution or precipitation of CaCO_3 can be determined (Geldenhuy, et al., 2003).

2.4 Scale Inhibition Mechanisms

Physical, chemical and biological methods can be used to inhibit the formation and treat formed scale with varying levels of effectiveness. Table 2-1 displays the effectiveness of various methods.

Table 2-1: Chemical, physical and biological methods and their effectiveness

Method	Reported Effectiveness	Mechanism
Ion Exchange Softening	Complete scale control	Removal of scale forming calcium species
Acid Dosing	Complete scale control (possible corrosion occurrence)	Alters calcium carbonate solubility
Chemical Inhibitors	Complete scale control possible, dosage type and water quality dependent	Block growth sites, stops crystal formation
Metal Ions	80% reduction	Blockage of growth sites/reacts with carbonate
Magnetic Conditioners	80% reduction	None agreed on
Electronic Conditioners	40% reduction	Preferential formation of particles in bulk
Electrolytic	30% reduction	Releases inhibitory metal ions into solution
Ultrasound	65% reduction	Induction of precipitation by changes to local pH
Surface Modification	90% achievable	Production of lower fouling surfaces

Reproduced from MacAdam and Parsons (2004)

The methods of control listed in Table 2-1 can be arranged into three categories. The first category includes the methods that change and influence the growth mechanisms of the crystals, the second those that influence the solubility, with the last being the methods that influence the potential of a surface to foul (MacAdam & Parsons, 2004).

The addition of chemical inhibitors to potentially scaling waters is deemed one of the most effective methods of controlling and inhibiting the formation of scale (MacAdam & Parsons, 2004). Anti-scaling chemicals are capable of preventing the formation of scale in numerous ways. Three of the foremost mechanisms used by the majority of common scale inhibitors, according to the Nalco Water Handbook, are threshold inhibition, crystal modification and sequestration (Flynn, 2009).

With referral to the schematic in Figure 2-1, certain anti-scaling agents can sequester (or “complex with”) cationic species with scale forming potential, thus raising the solubility of the potentially problematic mineral ions (Li, 2010), thus preventing clustering in order to inhibit scale formation. Anti-scaling agents can additionally act as crystal modifiers, and by modifying the crystallisation pathways, inhibit the growth of mineral particles (Zhang et al., 2001). Furthermore, certain anti-scaling agents can act as dispersants by

introducing a steric and/or electronic repulsion between present mineral particles, therefore inhibiting aggregation and flocculation (Li, 2010). Lastly, certain anti-scaling agents can be used as a surface conditioner to alter the deposition surface, resulting in the surface being unfavourable for scale formation. A desirable anti-scaling agent should preferably make use of multiple of the above-named mechanisms to effectively inhibit scaling (Amjad, 2002).

2.4.1 Sequestration

Various organic molecules have been reported to exhibit an ability to inhibit or retard mineral precipitation from a solution when present at very low (ppm) dosages (Anklam & Firoozabadi, 2005). The addition of these anti-scaling agents is equivalent to a supersaturation level reduction of the mineral solution (Oner et al., 1998).

2.4.2 Crystal distortion

Growth inhibition can be accomplished by particle stabilisation (Amjad, 2002). Mineral colloids' stability can be achieved by increasing inter-particle repulsive forces (e.g. electrostatic and steric forces) or by preserving them.

2.4.3 Dispersion and surface conditioning

Apart from the complexation action used in the sequestration and crystal distortion mechanisms, anti-scaling agents can also interact with nuclei, unsettling the crystallisation process (Shakkthivel & Vasudevan, 2006). This in turn implies the dispersion of crystal particles back into the aqueous solution, making them less prone to adhesion onto available surfaces. Certain ions present in anti-scaling agents have the ability to adsorb onto energetically favourable growth positions on the available surface to completely inhibit further precipitation (Meyer, 1984).

2.5 Characteristics of Anti-Scaling Agents

When referring to anti-scaling agents, it must be noted that these include only the active ingredients that form part of the anti-scaling agents. The manufacturers of anti-scaling agents conduct business in a secretive and “patented” nature. Anti-scaling agents do not entirely eliminate the possibility of scaling to occur; they do however (when correctly dosed) control and delay the formation of scale.

The most widely, commercially used anti-scaling agents are derived from three “chemical families,” namely organophosphates, condensed polyphosphates, and poly-electrolytes (or carboxylic polymers) (MacAdam & Parsons, 2004). Polyphosphate anti-scaling agents have been recently replaced with polymers

such as poly-acrylic and -maelic acid, as these have been proven stable at high operating temperatures as well as having an increased resistance to chemical and biological breakdown (Hasson et al., 2011).

The most notable advantage of using anti-scaling agents is that, when dosed correctly, very low doses can subdue scale formation. These dosages are far below the stoichiometric concentration of the species that will scale, thus making it a cost-effective solution (Hasson et al., 2011). The agents are generally composed of organic compounds, and the techniques are adaptable as they offer more possibilities for efficient water treatment over a wider range of parameters and technical specifications (Drela et al., 1998).

Table 2-2 details examples of the effects that specific compounds (organic and inorganic) can have on calcium carbonate scaling (i.e. scale formation, precipitation and crystal growth):

Table 2-2: Examples of the effect that certain compounds have on calcium carbonate scaling

Inhibitor	Effect	Concentration	Reference
<i>Organic agents</i>			
Citric/Maleic Acid	Effectuated crystal Morphology	0.1 – 1mg/l	Meldrum and Hyde (2001)
Polymaleic Acid	56% precipitation inhibition	10mg/l	Harris and Marshall (1981)
EDTA	20% precipitation inhibition	10 mg/l	Harris and Marshall (1981)
	Dissolution of existing calcite crystals	73,1 x 10 ³ mg/l	Fredd and Fogler (1998)
Chondroitin Sulphate	65% crystal growth rate reduction	100mg/l	Manoli and Dalas (2000)
Parvaalbumin	Chelated calcium solution from 100 ppm to below 1 ppm	1 mg/l	Chen and Chan (2000)
Polyacrylate (PAA)	60% scale formation reduction	5 mg/l	Ravichandran and Sankara Narayanan (2002)
	93% precipitation inhibition	10 mg/l	Harris and Marshall (1981)
	Scale coverage reduction from 20,7% to 6,8%	25 mg/l	Neville and Morizot (2000)
	Scale formation reduction by 76%	25 mg/l	Yang et al. (2001)
Polycarboxylic Acids	80% growth rate reduction	1 mg/l	Reddy and Hoch (2001)
	Inhibition of nucleation and reduction of crystal growth	0,1-200 mg/l	Verraest et al. (1996)
2-phosphonobutane-1,2,3-tricarboxylic acid (PBTCA)	Scale formation reduction by 96%	25 mg/l	Yang et al. (2001)
	Strongly Inhibited	270 mg/l	Compton and Brown (1995)
Sodium alginate	95% crystal growth rate reduction	17,9 x 10 ³ mg/l	Manoli and Dalas (2002)
Phosphonic Acids	Inhibits aragonite & calcite growth	20,6 x 10 ³ mg/l	Nancollas and Sawada (1982)

Inhibitor	Effect	Concentration	Reference
	Scale growth rate reduction	0,7 mg/l	Garcia et al. (2001)
	Inhibition of precipitation (Up to 94%)	10 mg/l	Harris and Marshall (1981)
Organophosphorus Compounds	Increases induction time from 38 to 288 minutes	18,2 x 10 ³ mg/l	Xyla et al. (1992)
Metallocene dichlorides	Growth rate reduction of 66%	9,96 mg/l	Malkaj and Dalas (2002)
<i>Inorganic agents</i>			
Phosphate	Calcite precipitation inhibition	1,9 mg/l	Plant and House (2002)
Polyphosphate	Complete precepitation inhibition	10 mg/l	Harris and Marshall (1981)
Iron	Complete calcite growth inhibition	55,8 x 10 ³ mg/l	Takasaki et al. (1994)
Magnesium	Precipitation induction time increases from 120 minutes to 200 minutes	13 mg/l	Tai and Chien (2002)
	Calcite formation inhibition	24 mg/l	Compton and Brown (1994)
	Preferential aragonite precipitation	37 mg/l	Meldrum and Hyde (2001)
	Induction time increase of 1 hour	240 mg/l	Wada et al. (1995)
	Precipitation inhibition	295 mg/l	Meldrum and Hyde (2001)
Manganese	No effect	2 mg/l	Pernot et al. (1998)
Copper	Complete inhibition	5 mg/l	Ledion et al. (2002)
	Induction time increase of 30 minutes	31,8 x 10 ³ mg/l	Wada et al. (1995)
Chromium	Induction time increase of 90 minutes	26 x 10 ³ mg/l	Wada et al. (1995)
Silver	Nucleation promotion of calcium carbonate	54 x 10 ³ mg/l	Wada et al. (1995)
Sodium	No effect		Tai and Chen
Aluminium	Induction time increase of 48 minutes	130 mg/l	Wada et al. (1998)
Zinc	Induction time increase of 30 minutes		Wada et al. (1998)
	80% calcite growth rate reduction	13,1 x 10 ³ mg/l	Meyer (1984)

Inhibitor	Effect	Concentration	Reference
	77% scale formation reduction	0,2 mg/l	Coetzee et al. (1996)
	Increase in number of particles in bulk solution	0,5 mg/l	Pernot et al. (1999)
	Calcite precipitate decrease and Zn/Ca ratio increased	0,98 mg/l	Glasner and Weiss (1980)

Due to water having such a unique nature in terms of its exact composition, various factors, including supersaturation level, pH, temperature, presence of other metal ions and flow velocity, all influence the effectiveness of the anti-scaling agents as well as the dosage required for the same results (Wildebrand et al., 2007). Thus, the water that needs treatment must be analysed with an inductively coupled plasma optical emission spectrometer (ICP-OES) scan before treatment to determine the concentration of the minerals present in the water, pH and alkalinity.

2.6 Principles of the different treatment methods:

2.6.1 Distillation

Distillation is the oldest type of desalination and is described as a process whereby the induction of a phase change to a feed stream separates the pure water fraction by physical means (Amjad, 1996).

Multi-effect distillation

The majority of multi-effect distillation evaporators makes use of a horizontal tube evaporation principle. This principle makes use of a distribution system that evenly distributes feed water on top of a bundle of heated horizontal tubing. The water then flows from one tube to another, partially evaporating on the tubes. A typical horizontal tubing network generally evaporates approximately 33.3% of the feed water (Greffrath, 2002), as illustrated in Figure 2-2.

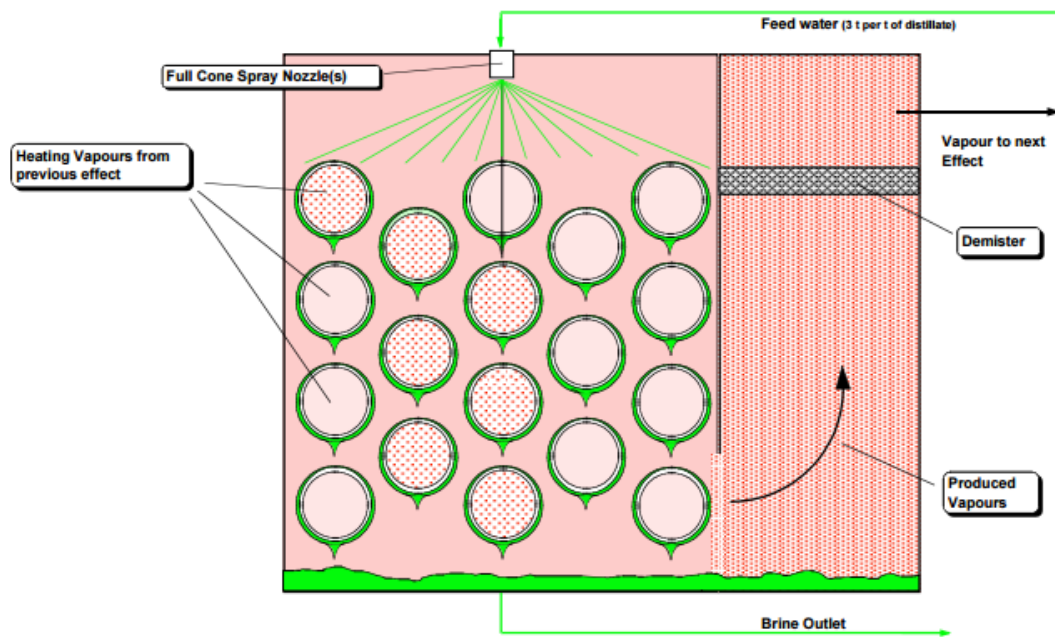


Figure 2-2: Principle of horizontal tube evaporation

(Greffrath, 2002).

This method of evaporation has been successfully applied to desalinate seawater and when making use of multiple chambers that are in sequence; it ensures the effective application of the principle. Each following chamber operates at a lower pressure than the preceding one, as illustrated in Figure 2-3. This can be repeated for eight to sixteen chambers to ensure that a high percentage of fresh water is removed from the feed and that a brine is produced that has a high percentage of total dissolved solids (Kennedy & Bremere, 2009). Depending on the application of this technology and the scaling properties of the feed water, the parameters and operating conditions should be adjusted accordingly to result in optimal evaporation by evaluating characteristics of the scaling properties of the scale forming minerals present (Wildebrand et al., 2007).

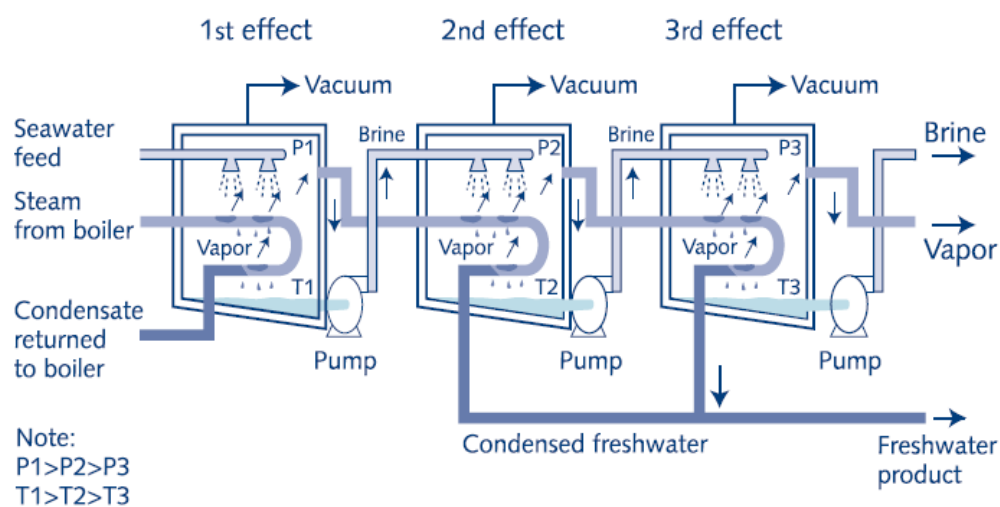


Figure 2-3: MED schematic

(Kennedy & Bremere, 2009)

Multi-stage flash distillation

Process water is heated to a temperature between 105°C and 115°C as the water flows through stages/chambers of decreasing pressure (Khoshrou et al., 2017). Water vapour is produced as the water flashes off from the heat exchange surfaces. In an attempt to decrease the energy usage of the plant, the vapour is used to heat the incoming feed water; more recently solar power as a source of heat energy has been incorporated to lower the energy requirements even further. Figure 2-4 demonstrates the process schematically. It is important to take into account the nature of the feed water (e.g. scaling potential at certain temperatures) (Khoshrou et al., 2017) when assessing the feasibility of using this technology at power generation plants.

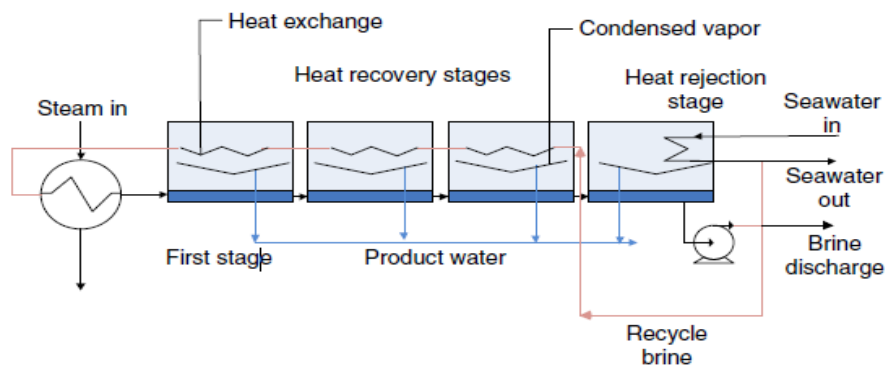


Figure 2-4: Multi-stage flash distillation (MSF) schematic diagram

(Khoshrou et al., 2017)

2.6.2 Eutectic freeze distillation

Sea-ice has a much lower salt content than seawater (Ahmad et al., 2018). Eutectic freeze distillation has been proven to be a successful method by which liquids can be concentrated and purified on a pilot scale. This process can be described in three simplified stages: Firstly, the water/liquid is frozen, secondly the ice crystals generated are separated from the remaining liquids, and thirdly the ice crystals are melted (producing clean water), whilst the brine is disposed of or dried to produce salts (Ahmad et al., 2018). Theoretically, the production of pure salts is possible due to the difference in salt crystallisation temperatures (Randall et al., 2011).

More recently, this technology has been used for desalination purposes, yielding a few important advantages, as described by Williams et al. (2015) and Randall and Nathoo (2015), including removing the need for chemical pre-treatment, therefore eliminating the discharge of toxic chemicals, a high separation factor, and high energy efficiency due to the latent heat of freezing (33.5 kJ/kg) being lower than the latent heat of evaporation (2256.7 kJ/kg), leading to a lower energy requirement in comparison to other processes (Rogers and Mayhew, 1994). Further advantages include fouling, scaling and corrosion resistance due to the lower operating temperature (lowering maintenance costs), and finally, less expensive construction materials (Randall & Nathoo, 2015 and Williams et al., 2015). Due to the desalination ability of this

technology, the possibility of incorporating it as a final stage in a water treatment process is feasible and attractive to various industries as a result of the following advantages (Ahmad et al., 2018):

- No need for chemical pre-treatment, eliminating the discharge of toxic chemicals
- A very high and desirable separation factor
- A high and desirable energy efficiency due to the latent heat of freezing (333.5 kJ/kg) being lower than the latent heat of evaporation (2256.7 kJ/kg), leading to a lower energy requirement in comparison to other processes (Rogers & Mayhew, 1994)
- Fouling, scaling and corrosion resistance due to low operating temperature (lower maintenance costs)
- Less expensive construction materials can be used at low temperatures (lowering capital cost)

2.6.3 Membrane technology

Membrane technology and techniques are a reliable means by which high quality water can be produced (Greenlee et al., 2009). Typically, membrane technology applications include, amongst others, ultra-filtration, forward osmosis, nano-filtration and reverse osmosis (Jiang et al., 2017).

Nano-filtration

Nano-filtration is usually used as a pre-treatment to RO, and is a method that rejects specific multivalent ions from feed water through the use of a membrane or filter. This filtration produces a retentate, concentrate or brine that can be treated elsewhere, which in turn lowers the load of the feed to the RO and increases the performance of RO modules (Pramanik et al., 2016). Figure 2-5 depicts a schematic of the basic principle on which this process functions.

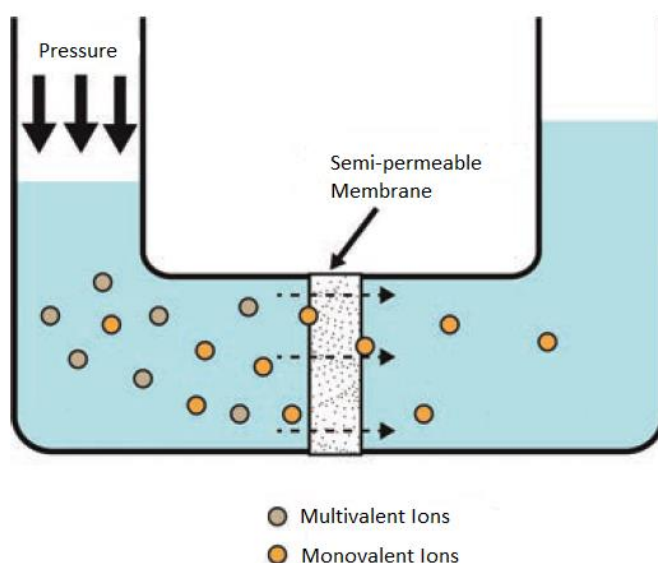


Figure 2-5: Nano-filtration schematic

(Pramanik et al., 2016)

Reverse osmosis

Semi-permeable membranes are the principle component in an reverse osmosis plant. This membrane is permeable to certain smaller particles, such as water molecules, but prevents solutes from passing through the membrane. In order to reverse the osmotic process by forcing pure water through the semi-permeable membranes, away from the low water potential, the dynamic pressure difference needs to exceed the osmotic pressure. The pressure difference and permeability coefficient of these membranes has an effect on the water passage through the membrane. Furthermore, the pre-treatment prior to the RO process, such ultra-filtration, nano-filtration and the use of anti-scaling agents, can increase the efficiency of the process (Jiang et al., 2017). This process is illustrated in Figure 2-6.

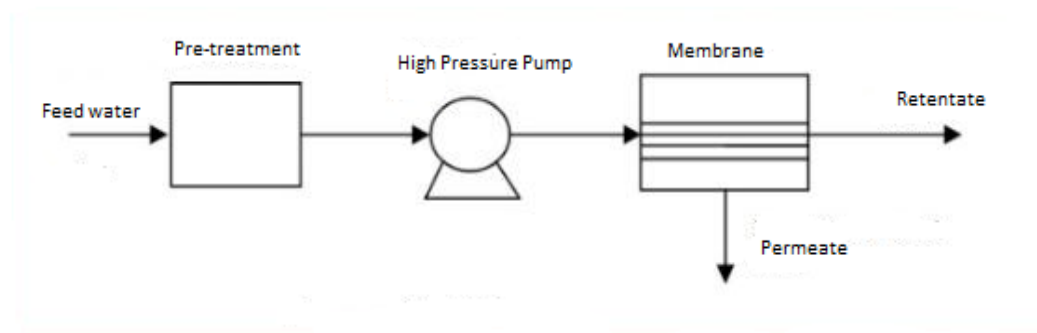


Figure 2-6: Reverse osmosis process diagram

(reproduced from Jiang et al., 2017)

Reverse osmosis has been extensively investigated and deemed the most energy efficient desalination technology with an energy consumption of approximately 1.8 kWh/m³ (Jiang et al., 2017). Fouling is the main challenge opposing reliable membrane performance and is influenced by the condition of the water being treated as well as its pre-treatment (Perez-Gonzalez et al., 2012). Reverse osmosis produces a retentate, concentrate or brine that is mineral rich and requires disposal similar to the retentate produced by nano-filtration.

Forward osmosis

The movement of a substance from a solution with a low osmotic pressure to a solution with a higher osmotic pressure through a semi-permeable membrane is known as forward osmosis (Boo et al., 2012). In this water treatment process, a draw solution needs to be created, which can be either an organic or inorganic substance with a high osmotic pressure that will draw the water from the saline stream with the lower osmotic pressure (Boo et al., 2012). Colloidal fouling can occur should the draw solution or cross flow velocities be inadequate, adding emphasis to the intricate cleaning methods required by this technology (Boo et al., 2012). This process is illustrated in Figure 2-7.

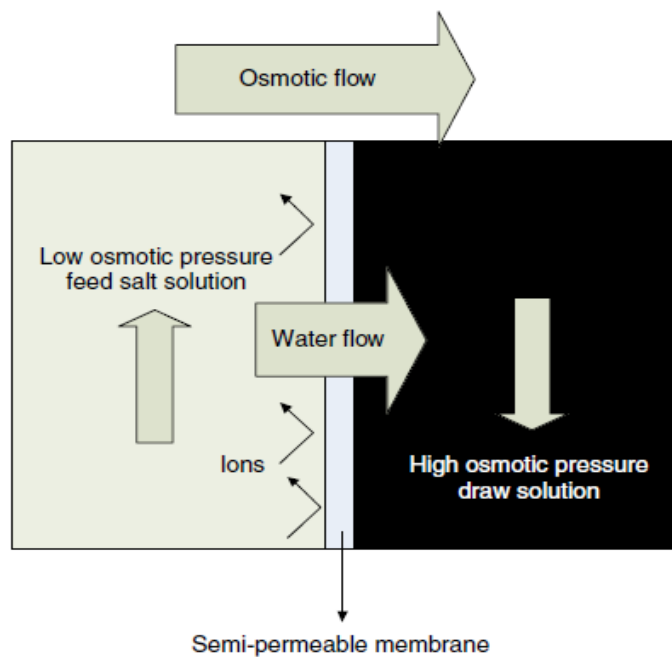


Figure 2-7: Schematic illustration of forward osmosis process

(Boo et al., 2012)

2.6.4 Comparison of different technologies

When comparing different desalination technologies, energy consumption, scaling and maximum brine salinity achievable are the main and most relevant terms by which to compare the technologies and specifically keeping in mind the abundant heat/energy available on power plants in the form of steam to be cooled. The combination of various technologies has the potential to provide the most efficient water treatment and waste disposal (Ahmad et al., 2018).

Scaling

When examining these technologies, fouling and scaling are the common problems that desalination industries encounter, as indicated by Chen et al. (2005). This is the result of the water characteristics being altered as the water being treated becomes increasingly concentrated. Multi-stage flash (MSF) and multi-effect distillation (MED) encounter scaling on heat exchange surfaces, negatively affecting heat exchange efficiencies. Reverse osmosis (RO) and nano-filtration (NF) encounter scaling and fouling with the main contributing compounds usually being, but not limited to, calcium carbonate, calcium sulphate and silica (El-Dessouky & Ettouney, 2002). Using NF as pre-treatment to remove bivalent ions prior to the primary desalination process has been a successful method by which scaling risk can be decreased as the process progresses. This allows RO to proceed with less risk of scale forming and also allowing MSF the ability to

operate at more effective temperatures when operated in series (Hassan et al., 1998); and similar conclusions can be drawn with the use of MED post-RO. The retentate and saline waste stream produced from the desalination processes, or a similar sequence of water treating technologies can be theoretically treated using Eutectic freeze crystallisation (EFC) to increase water recovery even more whilst producing

salts as a by-product. A 99.9% conversion of a waste stream generated using an RO plant to viable products has been reported (Randall et al., 2011).

Salinity limitations

The largest pressure difference that an RO membrane can support before rupture has been reported to be 55-75 bar (Fichtner, 2011), with a maximum salinity of 70 000 ppm in order to keep the osmotic pressure beneath this limiting salinity value. Additionally, the scale forming species' concentration must be kept below their respective supersaturation concentrations. MED and MSF salinity limitations are driven purely by the scale forming ions' concentrations and not by salinity itself (Roos et al., 2017), as the presence of non-scale forming ions in suspension will not negatively influence the efficiency of these technologies. This theory, having been tested as a pilot scale 3-effect MED system in California, reportedly achieved an evaporated water salinity of 80 000 ppm, demonstrating that when the scaling risk is addressed, using MED does not conform to the salinity limitations experienced by membrane processes. The use of anti-scaling agents at the correct dosage can increase the performance of all of the above-named technologies by preventing fouling on membranes, in pipes and on surfaces. When used in MED and MSF technologies, it could additionally lead to the optimisation of heat transfer efficiencies by preventing scale formation on heat exchange surfaces. Eutectic freeze crystallisation processes can operate right up to the salt saturation limits to produce precipitated salt crystals as a product (Ahmad et al., 2018).

Energy consumption

Reverse osmosis electric energy consumption is dependent on the osmotic pressure (i.e. salinity) of the feed water as well as the retentate/brine, as this influences the amount of pressure needed for the RO process. Reverse osmosis specific consumption of electricity for Eskom mine water with a salinity of 2000 ppm and a retentate of 8000 ppm has been recorded at 1.9 kWh/m³ (Roos et al., 2017). Power consumption for desalinating seawater with salinities of 39 000 ppm and 49 000 ppm has been reported to be 3.5 kWh/m³ and 4.25 kWh/m³ respectively (Fichtner, 2011). The main energy requirement for thermal desalination processes such as MED and MSF is the thermal heat required to evaporate the feed water, with the electrical requirements (such as pumping and to overcome pressure drops) contributing to a lesser extent. Reported electrical consumption of MED technology is between 1.5 kWh/m³ and 2.5 kWh/m³ (Fichtner, 2011), and for MSF processes between 3 kWh/m³ and 5 kWh/m³. When using EFC for seawater desalination, power consumption of 12.5 kWh/m³ has been reported (Lewis et al., 2010); however, varying values have been reported by different publications.

2.7 Conclusion

Eskom currently has nano-filtration as well as reverse osmosis as water reclamation and purification technologies present at some of its plants, such as Grootvlei and Lethabo, producing saline RO-retentate that needs to be disposed of to adhere to the zero liquid effluent discharge stipulations in its water usage

licenses. Due to the abundant heat present at Eskom's power plants and the versatility of multi-effect distillation, the possibility exists to implement a sequence of membrane and thermal technologies to approach a zero waste water reclamation process. An example of such a sequence is as follows: The use of nano-filtration to remove bivalent scaling ions from feed water before treating nano-filtration permeate using RO. The treatment of nano-filtration retentate to precipitate scaling ions. The combination of treated nano-filtration retentate with RO-retentate and treatment using multi-effect distillation –a method of heating that harnesses some of the abundant heat that needs to be dissipated at the power plant, as well as the correct selection and dosage of anti-scaling agents. The last step in such a sequence could be making use of Eutectic freeze crystallisation to separate the reject from the multi-effect distillation into fresh water and dry salt.

In this study, a bench scale single effect evaporator (using the same principles and conditions produced in multi-effect distillation) is proposed to examine the possibility of water recovery from waste water streams produced at Eskom's power plants while using correctly selected anti-scaling agents. Reverse osmosis retentate from the Lethabo Power Plant will be treated in the bench scale single effect evaporator with and without the use of scale-inhibiting agents.

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CHAPTER 3: Design, Configuration and Construction of Bench Scale MED

Abstract— An investigation into the potential scale formation during the application of multi-effect distillation (MED) technology for the treatment of reverse osmosis (RO) retentate was performed. An improved bench scale single effect evaporation unit was designed using the Solidworks Simulation Package and appropriate materials. Operating conditions were determined to be 80°C and 0.48 bar with the design constructed to maximise evaporation. Once assembled, RO-retentate was introduced into the evaporator, with an evaporation rate of 4 L/h (22.3 L/m²/h), and the variation of the concentrations of scale forming elements was determined – the evaporation translates to 34.5% water recovery. Speciation using PHREEQ-C modelling software showed that the concentrations of scale forming ions increased during evaporation. Scale prediction and prevention were explored using French Creek software, with anti-scaling agents used to minimise scaling.

The dosage and type of the anti-scalant, as predicted by the French Creek software, yielded the desired results by preventing scaling on the heat exchanger surface and keeping ions in suspension. When measuring the performance of the anti-scaling agents on this basis, AMPS fared better than PBTC, whilst HEDP yielded concentrations of scale forming ions lower than when no anti-scaling agent was dosed. This may be attributed to complexation of the scale forming ions with the HEDP.

Keywords—MED, scale formation, RO-retentate, PHREEQ-C, French Creek.

3.1 Introduction

South Africa is a water-scarce country. Therefore, water consumers are forced to explore the utilisation of all available water sources, and the water scarcity is being worsened by climate change. Despite this water shortage, the demand for water usage in industry and for human consumption remains high, creating an ever-increasing dependence on seasonal rainfall (Fosso-Kankeu et al., 2016).

Waste water effluent is becoming more valuable as advances in technology make the recovery, treatment and re-use of waste water more attractive (Fosso-Kankeu et al., 2011). Scale formation is a common occurrence when water is being treated and re-used, as treatment methods such as heat exchange and membrane processes increase the concentration of the initial minerals present in the feed water (Roos et al., 2017).

Eskom, South Africa's national power utility, is allocated 2-3% of the national available fresh water to generate electricity. Eskom, however, is under pressure to minimise its water usage and has set a target of lowering its usage to 1.34 L of water per kilowatt hour electricity produced by 2020, from the 1.39 L/kWh presently (Fosso-Kankeu et al., 2016). Of the total water intake, 98% is lost via evaporation in the cooling towers of wet cooled power plants (Surenda, 2014). Therefore, the re-usage of certain water streams may potentially decrease the freshwater intake needed to replenish the amount of water lost due to evaporation. Eskom has thus initiated an investigation towards water management and proper usage of all available water sources. Reject from the primary RO module is high in salinity (depending on the feed water), and has been identified as a possible source from which to abstract usable water.

Sea water has been treated using multi-effect distillation (MED) systems, encouraging the usage of this technology for this application (Wildebrand et al., 2007). The majority of multi-effect distillation evaporators makes use of a horizontal tube evaporation principle. This principle makes use of a distribution system that evenly distributes feed water on top of a bundle of heated horizontal tubing. The water then flows from one tube to another, partially evaporating on the tubes. A typical horizontal tubing network generally evaporates approximately 33.3% of the feed water (Greffrath, 2002). A limitation of such a system is the scale formed on the heat exchange surfaces due to the quality of the water, therefore negatively affecting the efficiency of the MED (Wildebrand et al., 2007).

This problem is amplified when treating concentrated and saline waters that are prone to scaling on heat exchange surfaces, especially at elevated temperatures. Reducing the temperature of the heat exchange surfaces to minimise scaling causes the evaporation rate of the clean water to decrease. The lower evaporation rate can be countered by reducing the pressure of the entire chamber for the water to evaporate at an adequate or even a higher rate. The reduction of the heat exchange surface temperature requires the steam supply pressure to be decreased as well. This can be accomplished by introducing vacuum pumps to the system, while maintaining the steam in the vapour phase to ensure efficient heat exchange.

These evaporation favouring, scale avoiding conditions indicate that MED technology could potentially be incorporated into the existing water treatment system at Eskom. This technology will aid Eskom in adhering to its zero liquid effluent discharge (ZLED) policy, stipulated in the utility's water use licences (Roos et al., 2017), by treating relatively saline solutions for reuse. The primary purpose of MED is to serve as a water producing/recycling technology that can treat saline/brine solutions. The potential secondary purpose of the technology when applied to a power plant could be to dissipate some of the abundant heat that would otherwise have to be dissipated in the cooling towers, thus decreasing the amount of cooling water needed (Drela et al., 1998).

Scaling is caused by concentrated minerals in water when they become insoluble. When the mineral constituents remain soluble, they have no negative effect on heat transfer efficiency (Kavitha et al., 2011), and this should be considered when exposing mineral-rich waters to heat exchange surfaces. Scale formation occurs in alkaline water and is attributed to the presence of scale forming ions such as Ca^{2+} and Mg^{2+} and calcium carbonate (Li, 2010). Process parameters also plays a role in scale formation – with temperature and flow rate being the most influential (Wildebrand et al., 2007), as these parameters can influence deposit (scale) structures, shape, size and composition.

Scaling potential can be determined by using PHREEQ-C, an open-source modelling package developed by the US Geological Survey (USGS, 2016). French Creek software can additionally be used, as it combines multiple saturation and stability indices to accurately predict the scaling potentials of the minerals present in the water. This is similar to the capabilities of PHREEQ-C, with the additional capability of predicting which anti-scaling agent will yield the best results and the simulation of addition (French Creek Software, 2017).

When mineral ions are present in water, they may become more concentrated over time and eventually cause the water to become supersaturated. Mineral ions under increasingly supersaturated conditions will, due to their polarity and random thermal motion, form clusters. Once these clusters pass a critical size, nucleation will take place. As soon as nuclei are formed, spontaneous crystallisation will take place, forming larger particles. Subject to the surface properties and composition of these particles, the particles can either aggregate to create larger particles, or remain suspended in the water for a period. After sufficient time, these articles and mineral ions will diffuse through the hydraulic boundary layer (Li, 2010) and form scale after depositing onto a solid surface. The scaling process is illustrated in Figure 3-1.

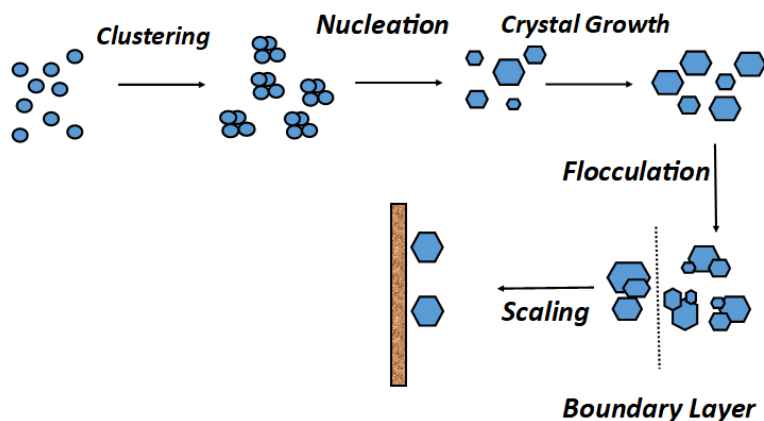


Figure 3-1: Schematic of processes involved with the formation of mineral
Reproduced from MacAdam and Parsons (2004)

In the present study, reverse osmosis (RO) retentate from the Lethabo Power Plant was evaporated in an improved bench-top single effect evaporator and the variation in the concentration of scale forming elements was evaluated.

3.2 Operating Conditions

3.2.1 Temperature

A steam generator was used as the evaporator's heat source; it supplied steam through the heat exchange surface. The temperature of the steam was a concern when using the steam generator, as the steam had a higher temperature than the critical temperature for scale formation. It has been reported that, at a temperature above 80°C, the rate of scale formation is substantially increased (Wildebrand et al., 2007). The temperature set point target is consequently 80 °C.

3.2.2 Pressure

Saturation pressure and operating parameter targets were determined using Thermosolver software (Koretsky, 2014), specifically the Saturation Pressure Calculator and Antoine Equation of state. The ambient pressure of Potchefstroom (0.875 bar) (Everson et al., 2013) was considered during vacuum calculations at different temperatures. These results are detailed in Table 3-1.

Table 3-1: Operating parameter targets of evaporation chamber

Temperature (° C)	Solver Saturation Pressure (bar)	Size of Vacuum Required (bar)
60	0,1992	0,6758
65	0,2502	0,6249
70	0,3117	0.5633

75	0,3856	0.4894
80	0,4737	0.4013

According to the thermodynamic principle, when a temperature target of 80°C is achieved, the pressure inside the evaporation chamber of the MED needs to be as close to 0.47 bar as possible for optimal evaporation to take place, as this is the saturation pressure of water at 80°C.

3.3 Materials

Before the evaporator could be built, the scale forming properties as well as the strength and temperature effects of the materials had to be evaluated. These materials were to be exposed to pressure reduction, high temperatures and mineral rich water with increasing scaling potential. The design of the evaporator can be divided into three main components: The evaporation chamber, the dual heat exchange surface running through the evaporation chamber, and drip tray that dispenses the water onto the heat exchange surface inside the evaporation chamber.

Polymers and certain polyvinyl chlorides were deemed appropriate materials for the construction of the evaporation chamber of the evaporator as well as the drip tray. These materials are scaling resistant and would therefore not influence the concentrated water (RO-retentate) that was used in the evaporator (The International Nickel Company, INC, 1963). Stainless steel was used inside the evaporation chamber to control the height of the drip tray above the heat exchange surface due to its unreactive nature, largely due to the unavailability of nucleation sites suitable for the scale to attach to (Copper Development Association, 2016).

The dual heat exchange surface inside the evaporator is metallic to provide the necessary heat conductivity needed at the exchange surface. Cu-Ni and copper alloys have been used as heat exchanging surfaces successfully, particularly in sea-water cooled heat exchangers (Kirk & Tuthill, 1992), with a mild corrosion resistance (Copper Development Association, 2016). When comparing the high salinity of sea water to RO-retentate, copper will perform as a sufficient heat exchange surface due to its mild corrosion resistance. Without proper pre-treatment, the copper heat exchange surfaces are mildly susceptible to scaling.

The material of the pump that recycles the brine from the evaporation chamber to the drip tray is exposed to the high scaling potential water and must thus be constructed with appropriate materials. A magnetically driven, single stage, centrifugal pump constructed using thermoplastics will suffice due to its chemical resistance.

These three key components are depicted in Figure 3-2:

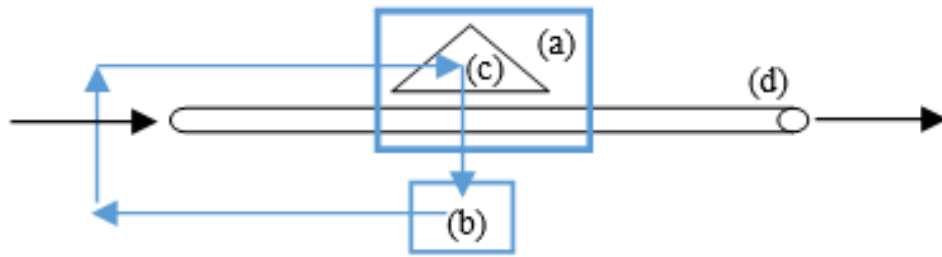


Figure 3-2: Main components in MED design: (a) evaporation vessel; (b) recycle pump; (c) drip-tray; (d) heat source/exchange surface

3.4 Design and Configuration

3.4.1 Evaporation chamber

The initially commissioned bench scale MED (Fosso-Kankeu et al., 2016) had to be improved to conduct more realistic and extensive experiments. Firstly, the structural integrity of the evaporation chamber was significantly improved to increase the vacuum applied to it without the structure failing (Fosso-Kankeu et al., 2016). Secondly, the initial bench scale MED could function with a pressure reduction of 0.09 bar before the risk of structural decomposition occurs.

A simulation on Solidworks (3D design and simulation software) on a range of polycarbonate thermoplastics resulted in a material selection and design consisting of multiple and extensive internal rib structures. The Solidworks Simulation Packet recommended a material thickness of 12 mm. Trial and error with the types, sizes and placement of the rib reinforcing structures resulted in the design displayed in Figure 3-3.

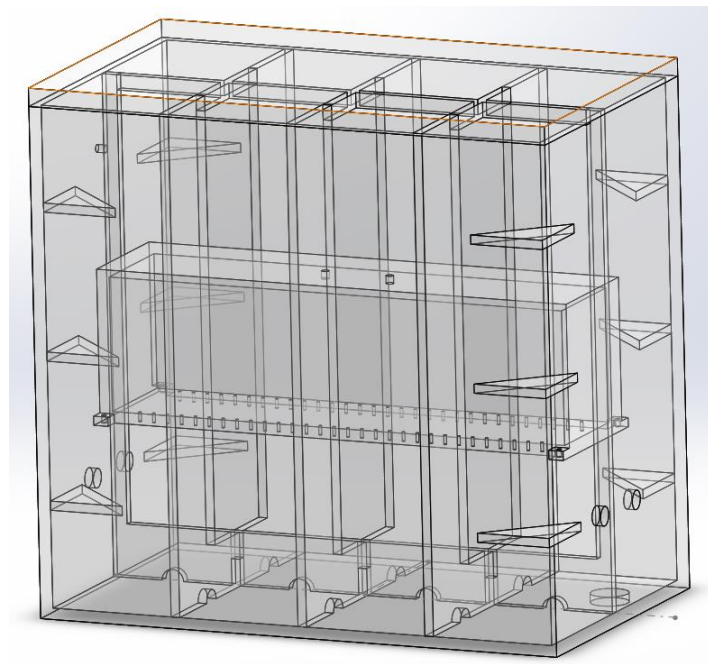


Figure 3-3: Three-dimensional visualization of improved evaporation chamber design

This design was simulated and is represented in Figures 3-4 and 3-5.

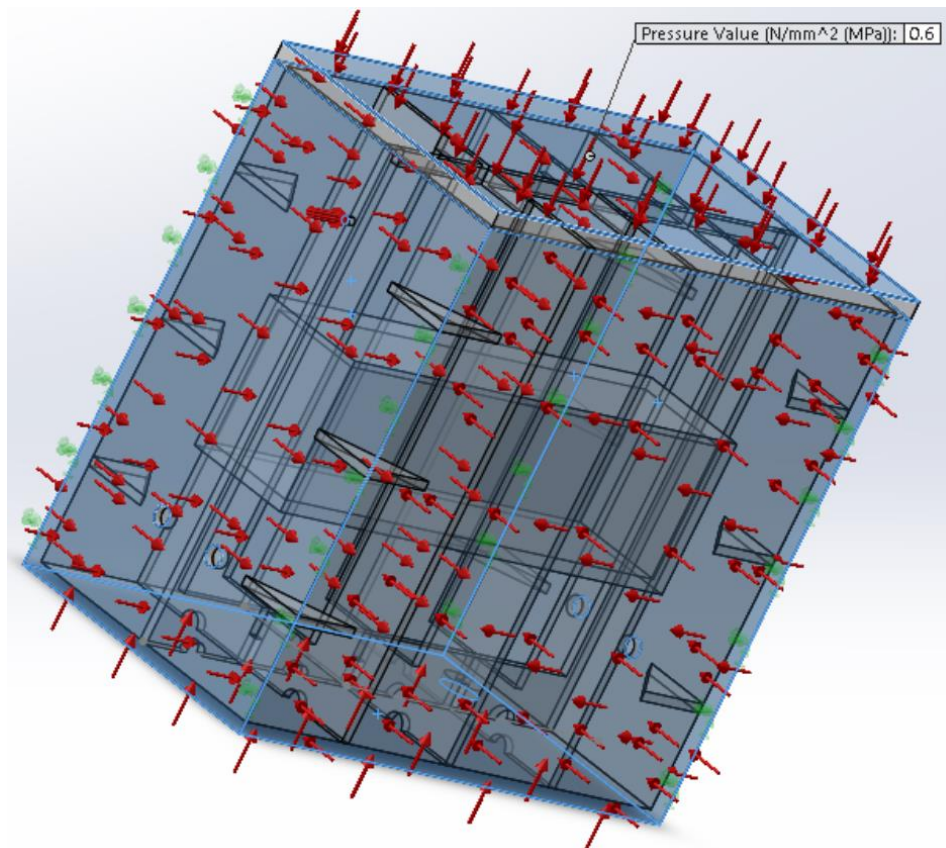


Figure 3-4: 0.6 MPa (6 bar) pressure difference applied to design in simulation program - visualization

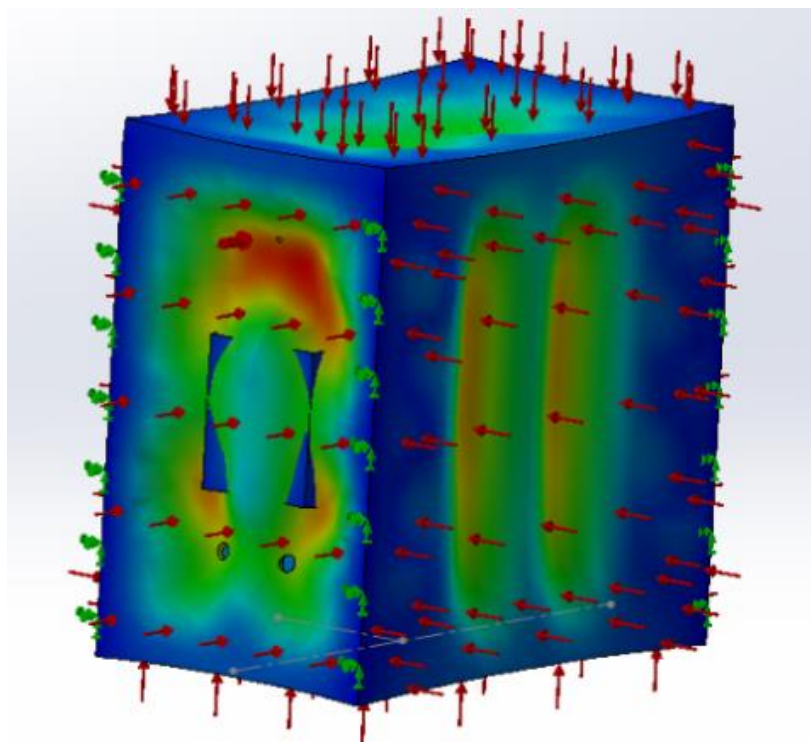


Figure 3-5: Solidworks simulation displaying a maximum displacement of 4 mm when 6 bar pressure difference is applied to evaporation chamber

Stratasys (2013) performed an investigation to evaluate the effects of time, temperature and environment on a polycarbonate (PC) thermoplastic. They evaluated the PC thermoplastic at temperatures ranging from -40°C to 140°C. The tensile strength of this PC thermoplastic at a temperature of 80°C remains above a pressure of 300 bar. The results of the investigation are displayed in Table 3-2.

Table 3-2: Tensile strength of polycarbonate and the effect of temperature Stratasys (2013)

Temperature (°C)	Wet (bar)	Dry (bar)	1 week (bar)	13 weeks (bar)	26 weeks (bar)	52 weeks (bar)
40	492	517	527	502	540	495
60	414	456	461	446	493	449
80	377	401	429	396	426	395
100	336	351	391	341	361	335

It is thus apparent when examining the material properties from literature and the Solidworks design simulation that PC thermoplastic yielded satisfactory results, indicating that the design's structural integrity will not be compromised when exposed to the target pressure reduction of 0.41 bar.

3.4.2 Vacuum pumps

The vacuum pump's cooling system needed to be altered from a recirculating system to a 'once through' system to run the pumps for a longer period whilst preventing the risk of overheating. This was due to the fact that they were operating near to or above recommended temperature ranges with the initial recycling closed circuit water configuration.

3.4.3 Drip tray

The drip tray had to fulfil a dual purpose. Firstly, the drip tray plays a key part in the structural integrity of the evaporation chamber and secondly, laminar flow of water onto the heat exchange surface. Multiple factors influence the latter, with the size and distance in between the apertures, and the distance heat exchange surfaces are below the drip tray being key factors when designing the evaporator.

Design of the drip tray for distributing the liquid on the heat exchanger tube was based on the equation for the flow rate, Q_{rec} , through an orifice with area A , using a water height h as driving force for flow:

$$Q_{rec} = 0.61A\sqrt{2gh} \quad \text{Equation 3-1}$$

This equation was derived from the Bernoulli flow equation, assuming that the fluid contracts after the orifice to an area 0.61 A as shown in Figure 3-6.

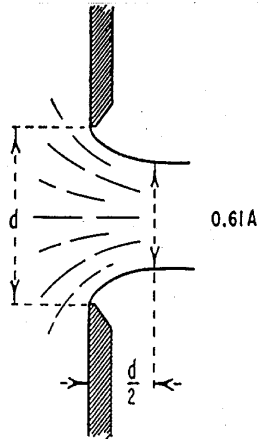


Figure 3-6: Flow contraction after an orifice with area A

The diameter of the N orifices in a drip tray of height h to generate a total recycle liquid flow rate of Q_{rec} m³/s is then given by:

$$d = \sqrt{\frac{4\pi Q_{rec}}{0.61N\sqrt{2gh}}} \quad \text{Equation 3-2}$$

The feed flow rate for falling film evaporators, Γ , can be expressed as the mass flow rate per length of tube, L , in kg/m/s. For horizontal films, this is usually expressed per tube side:

$$\Gamma = \frac{\rho Q_{rec}}{2L} \quad \text{Equation 3-3}$$

Where Q_{rec} is the volumetric flow rate of the feed water recycled via the drip tray over the heat exchanger tube and ρ is the water density.

The falling film Reynolds number is then, according to Ouldhadda et al. (2002), defined as:

$$Re = \frac{4\Gamma}{\mu} = \frac{2\rho Q_{rec}}{\mu L} \quad \text{Equation 3-4}$$

Flow can be considered to be laminar when the Reynolds number ranges between 400 and 4000 (Ouldhadda et al., 2002), whilst typical MED conditions range from 500 to 2000, according to Shausberger et al. (2009), with the significance of the Reynolds number being displayed in Figure 3-7. Table 3-3 displays the approximate ranges for the film Reynolds number with respect to the flow pattern – the hydrodynamic regime.

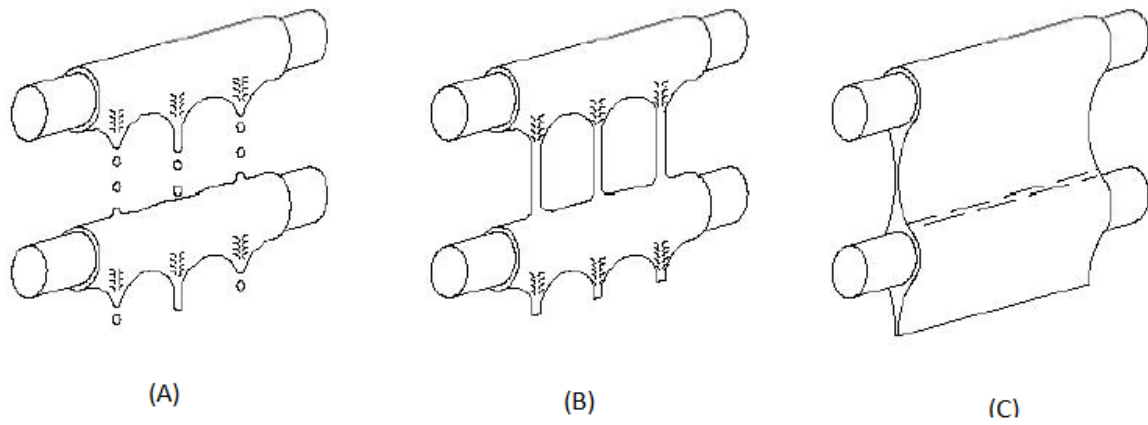


Figure 3-7: Inter tube falling-film modes: (A) droplet mode, (B) jet mode, (C) sheet mode
(Schausberger et al., 2009)

Table 3-3: Ranges for the film patterns and corresponding flow regimes

Scenario	Reynolds Number
Flow Pattern (A)-(B)	150-200
Flow Pattern (B)-(C)	315-600
Flow regime Laminar – Turbulent	1000-2000
Typical MED Re range	500-2000

Other factors that influence the flow of liquid over the heat exchange surface that should be kept in mind include flow rate of the water moving through the drip tray, turbulence of flow inside the drip tray and the length of the heat exchange surface. Consequences when not designed correctly include decreased heat exchange efficiency and increased scale formation.

Equations 1 - 4, in conjunction with the two heat exchange surfaces running through the chamber as well as the need for additional structural integrity, resulted in the design depicted in Figures 3-8 to 3-10. The two holes on top of the drip tray were meant for the inlet of water to be dripped onto the heat exchange surfaces as well as an air vent to control the liquid level inside the drip tray. The four anchoring holes allowed for the attachment of the stainless steel adjustable legs.



Figure 3-8: Drip tray prior to installation inside evaporation chamber

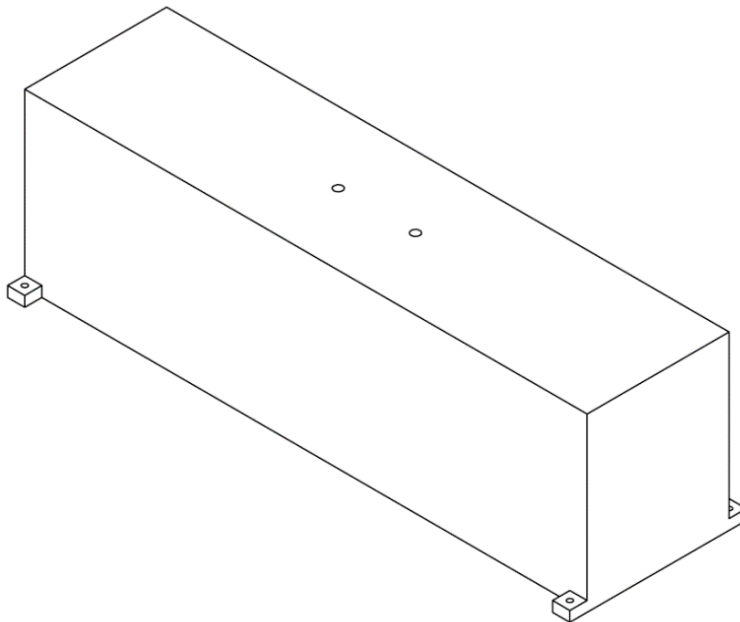


Figure 3-9: 3-D view of drip tray

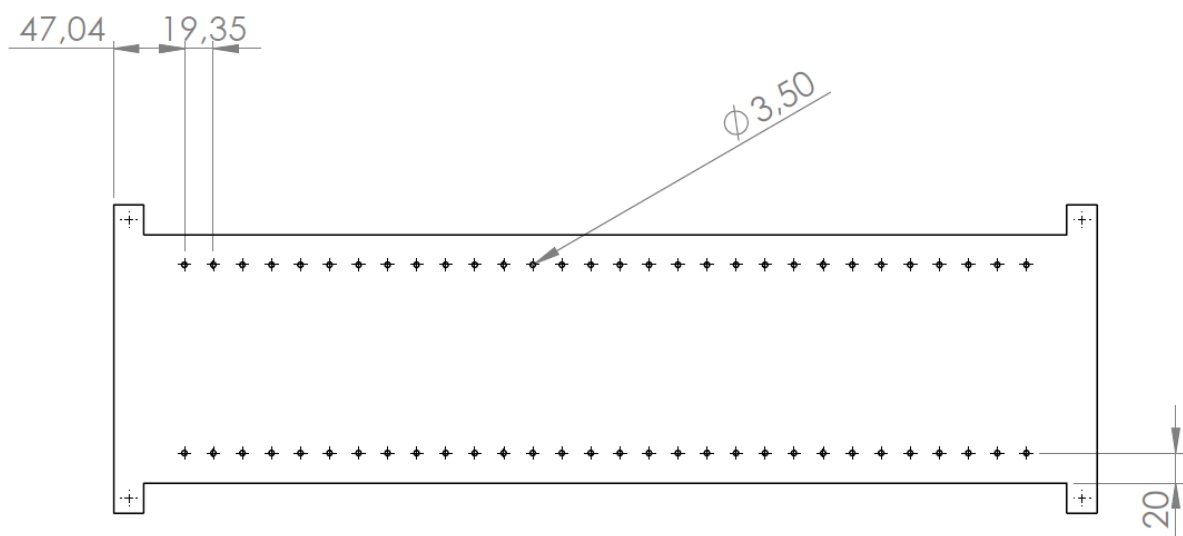


Figure 3-10: View of aperture sizing and spacing of drip tray

3.4.4 Operation

The previously determined ideal operating conditions (Section 3.2) were initiated with the incorporation of two Busch LX 0030-0430 B Vacuum Pumps. One was introduced to the evaporation chamber to lower the pressure inside and to increase the rate of evaporation, whilst the other was introduced to lower the heat exchange surface temperature by lowering the pressure of the steam flowing through the heat exchange surface. It was determined that the temperature of the steam providing the heat needed to be lowered to 80°C, and a vacuum of 0.41 bar needed to be created inside the evaporation chamber.

3.4.5 Method of evaluating MED performance

An accurate measurement of the amount of water evaporated was challenging to obtain due to the once-through cooling of the vacuum pump that removed the vapour from the evaporation chamber. PHREEQ-C software and the PITZER database were used to verify the volumetric calculations and level differences inside the MED to determine the amount of water evaporated.

3.5 Methodology

3.5.1 Assembly

Once the design was finalised and materials obtained, the assembly entailed milling the polycarbonate to the right sizes, after which they were glued together (Figures 3-11 to 3-13).



Figure 3-11: Milled polycarbonate



Figure 3-12: Gluing of polycarbonate to form evaporation chamber.



Figure 3-13: Evaporation chamber assembly

Stainless steel fittings and unreactive reinforced plastic piping were used to assemble the closed water circuit running from the evaporation chamber to the recycling pump and to the drip tray. The recirculation piping was further reinforced with stainless steel springs to ensure the vacuum would not influence the flow of the brine/water. The available steam supply piping had to be adapted and positioned to the inlet of the MED with valves to control the supply and pressure with pressure and temperature gauges before, inside, and after MED. A frame to house the different components (evaporation chamber, recirculation chamber, recirculation pump, vacuum pumps, vacuum pump cooling and effluent tanks) was also designed and constructed. A silicon sheet lining was used as a sealant beneath the lid of the MED to ensure an airtight seal. The start-up of the evaporator (filling up and recirculation of RO brine) proved challenging due to the closed and airtight nature of the evaporator. Various air vent valves were introduced to speed up and improve the control during the start-up and initial stabilisation of the evaporator. A continuous cooling liquid supply with buffer tank was incorporated into the design to ensure adequate vacuum pump operating temperatures.

3.5.2 Water sampling and analysis

Water/RO-retentate was sampled directly from the Lethabo Power Plant's RO-retentate stream using clean and dry 25 L containers. Samples were sent for analysis to the Midvaal Water Company, as its Scientific Services division and laboratory are SANAS (South African National Accreditation System) accredited. The results from this analysis were used for scale formation modelling.

3.5.3 Operation and control of MED

The control of the MED utilised the manipulation of various valves. The pressure valve on the steam supply line was used to alter the temperature of the steam entering the MED, as the steam supply was placed under a vacuum. A pressure regulating valve on the MED was used to manipulate the pressure in the MED. A valve regulating the flow from the recirculation pump was used to influence the flow to the drip tray – ultimately the flow of water onto the heat exchange surface.

3.5.4 Determination of anti-scaling agents by manual calculations

Accurate calculation included manual calculations, which mainly involved the Langelier saturation and Ryznar stability indices, as well as the developing Puckorius equilibrium index. These indices usually produced conflicting results, and thus simulation software was used to verify the exact calculations.

3.5.5 Determination of anti-scaling agents with modelling software

Scaling potential can be viewed by using PHREEQ-C, an open-source modelling package developed by the US Geological Survey. This software was initially created for the simulation and modelling of water chemistry with regard to hydrogeology and geochemical modelling, but when using thermochemical equilibrium calculations, the scaling potential of aqueous solutions can be accurately identified (USGS, 2016).

French Creek software is applicable in this study, as it combines the Langelier saturation and Ryznar stability indices, the Puckorius equilibrium index, the calculation of saturation levels based on an extensive free ion association/exchange model, as well as Momentary Excess and Larson-Skold indices, which are deemed appropriate and realistic by the programme authors to accurately predict the scaling potential of the minerals present in the water. This is similar to PHREEQ-C's capabilities, but with the additional capabilities of predicting which anti-scaling agent will yield the best performance. Furthermore, the French Creek WaterCycle software was developed specifically to allow the user to view these popular and lesser known indicators in order to display problems and potential problems specifically inside a cooling water treatment system. This software incorporates more than 18 different relevant scales (such as calcium carbonate, calcite, aragonite, barite, tricalcium phosphate, etc.), yielding accurate results and predictions. It functions as a system simulator taking water chemistry and operating conditions into consideration and also provides treatment plans and anti-scaling agent limitations and preferences (French Creek Software, 2017).

3.5.6 Anti-scaling agent dosage

The data obtained from the RO-retentate to be used in the MED were plugged into French Creek to determine which anti-scaling agents and dosages were to be used (Table 3-4).

Table 3-4: Anti-scaling agent active ingredient dosages

Anti-Scaling Agent	Dosage (ppm)
100% HEDP	0.169
100% PBTC	0.210
100% AMPS	0.369

Simulation results are displayed in Figures 3-14 to 3-16.

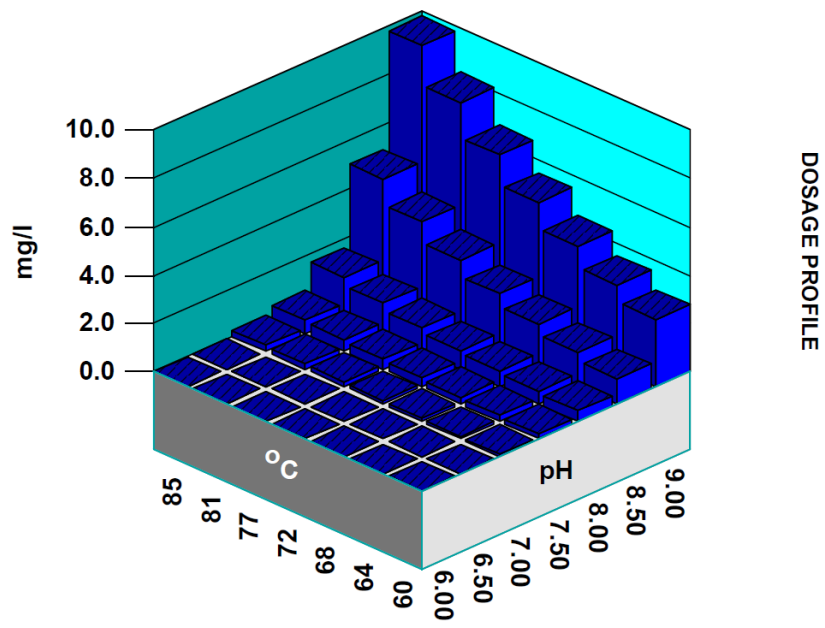


Figure 3-14: AMP dosage profile

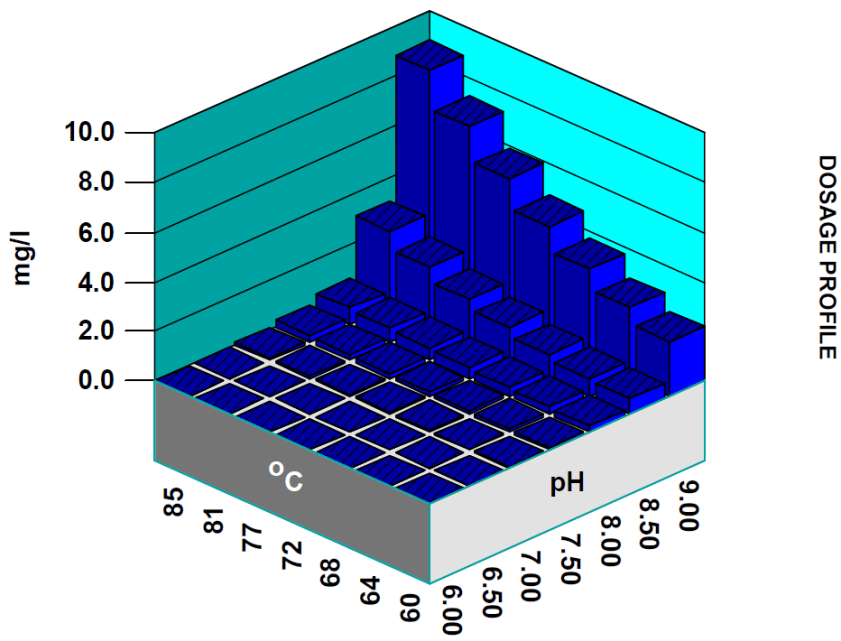


Figure 3-15: HEDP dosage profile

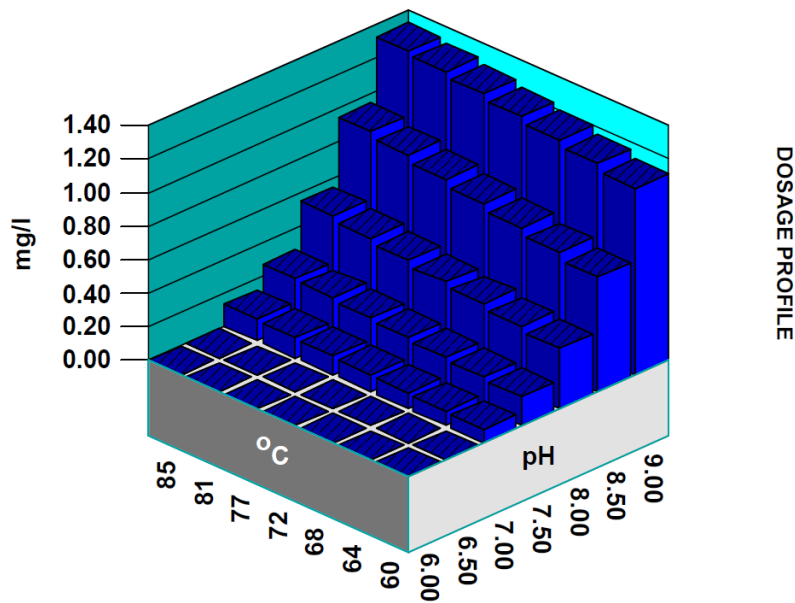


Figure 3-16: PBTC dosage profile

3.6 Results

3.6.1 Performance of MED

Parameters

The targeted parameters were obtained. A steam supply temperature varying between 78°C and 80°C (Figure 3-17), paired with a vacuum varying between 0.40 and 0.44 bar inside the evaporation chamber (Figure 3-18) of the MED ensured rapid evaporation. The temperature inside the MED stabilised at 60°C (Figure 3-19) with the steam exit temperature stabilising around 50°C.



Figure 3-17: Temperature gauge displaying the temperature of steam entering the evaporation chamber inside the heat exchange piping



Figure 3-18: Vacuum gauge displaying vacuum inside evaporation chamber



Figure 3-19: Temperature gauge displaying temperature inside evaporation chamber

The assembled and functioning single effect evaporator is displayed in Figure 3-20.

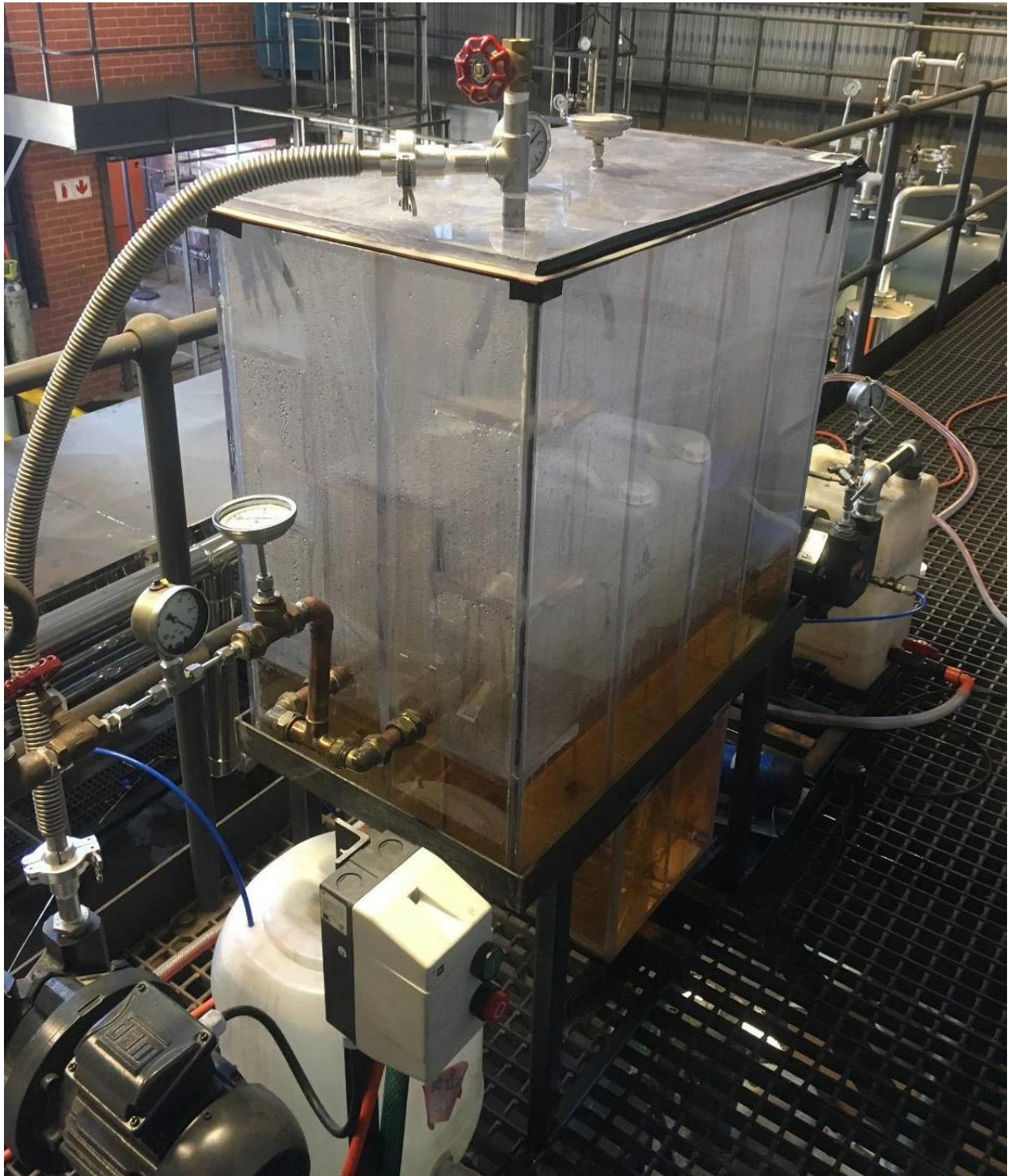


Figure 3-20: Assembled, functioning single effect bench scale evaporator

Evaporation rate

When evaluating the water level pre-and post-evaporation, an 8 cm level difference translated into 24 L of water being evaporated from the initial 70 L over a 6-hour run time. Displayed in Figure 3-21 is the water flow onto the heat exchange surfaces.



Figure 3-21: Drip tray's laminar water flow distribution onto heat exchange surfaces

The trial runs were performed and tabulated below in Table 3-5. It was the clear increase in the concentrations of certain elements, portraying adequate functioning of the evaporator, that prompted further and more in-depth investigation.

Table 3-5: Concentration in mg/L of a) RO-retentate before MED-evaporation and b) after MED-evaporation

	ICP-OES RO-Retentate	ICP-OES MED Reject	PHREEQ-C Simulation-Theoretical MED Reject
Ca	2830	3310	4304,38
K	10100	13400	15357,81
Mg	174,92	231,83	265,90

Anti-scaling agents were not used during trial runs, and the influence can be clearly seen in Table 3-5 when comparing ICP-OES analysis of the MED reject with the PHREEQ-C simulation theoretical MED reject concentrations. It is palpably clear that scaling and precipitation took place during the trial runs inside the MED.

Analysis of water

The water both prior to and after the evaporation were analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) to determine the elements present and to determine the increase in concentration. These analyses were then used for scale prediction and modelling. Displayed in Table 3-6 is the increase in concentration of certain scale influencing and forming elements:

Table 3-6: Speciation of certain elements present in MED reject

Speciation of MED Reject without anti-scaling agents					
Ba	Ba ²⁺	92,41%	K	K ⁺	99,36%
	BaSO ₄	7,60%		KSO ₄ ⁻	0,65%
	BaOH ⁺	0,00%	Li	Li ⁺	99,81%
Ca	Ca ²⁺	95,83%		LiSO ₄ ⁻	0,19%
	CaSO ₄	4,19%	Mg	Mg ²⁺	87,52%
Cu(1)	Cu ⁺	100,00%		MgSO ₄	12,15%
Cu(2)	Cu(OH) ₂	80,29%		MgOH ⁺	0,34%
	Cu ²⁺	9,88%	Mn(2)	Mn ²⁺	91,33%
	Cu ₂ (OH) ₂ ²⁺	3,87%		MnSO ₄	7,03%
	CuOH ⁺	1,63%		MnOH ⁺	1,68%
	CuSO ₄	0,50%	Mn(3)	Mn ³⁺	100,00%
	Cu(OH) ₃ ⁻	0,00%	Na	Na ⁺	99,72%
	Cu(OH) ₄ ²⁻	0,00%		NaSO ₄ ⁻	0,28%
Fe(2)	Fe ²⁺	80,56%	S(6)	SO ₄ ²⁻	48,72%
	FeOH ⁺	13,30%		CaSO ₄	22,91%
	FeSO ₄	5,98%		MgSO ₄	19,75%
	Fe(OH) ₂	0,15%		NaSO ₄ ⁻	6,04%
	Fe(OH) ₃ ⁻	0,00%		KSO ₄ ⁻	2,49%
	FeHSO ₄ ⁺	0,00%		SrSO ₄	0,06%
	Fe(HS) ₂	0,00%		BaSO ₄	0,01%
	Fe(HS) ₃ ⁻	0,00%		MnSO ₄	0,01%
Fe(3)	Fe(OH) ₃	78,82%		LiSO ₄ ⁻	0,01%
	Fe(OH) ₄ ⁻	17,82%	Sr	Sr ²⁺	94,45%
	Fe(OH) ₂ ⁺	3,36%		SrSO ₄	5,57%

It is very clear that, when the water is concentrated, the use of PHREEQ-C modelling software displays the abundance of scale forming ions present in the water (Ca⁺² and Mg⁺² for example) when the amount of volumetrically determined water is evaporated from of the RO-retentate inside the MED.

Prediction of scale formation and modelling

Using the initial water analysis from Midvaal Water Company as input parameters combined with the operating conditions inside the MED, Figures 3-22, 3-23 and 3-24 display the temperatures and pH-values at which aragonite and calcite are supersaturated and the Langelier Saturation Index. These graphs were generated using French Creek modelling software.

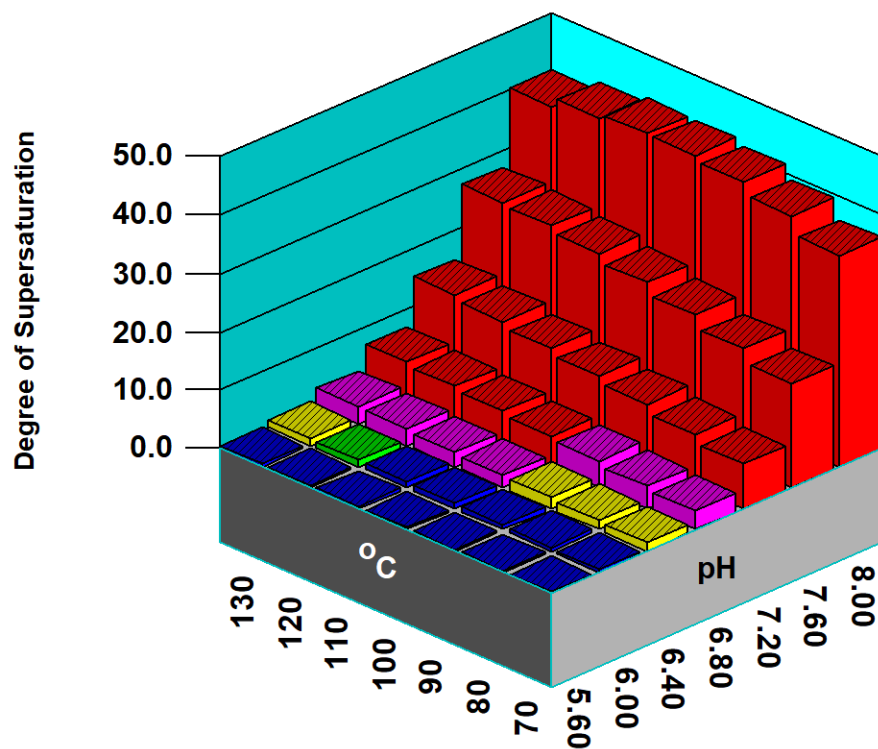


Figure 3-22: Aragonite saturation level vs. temperature vs. pH

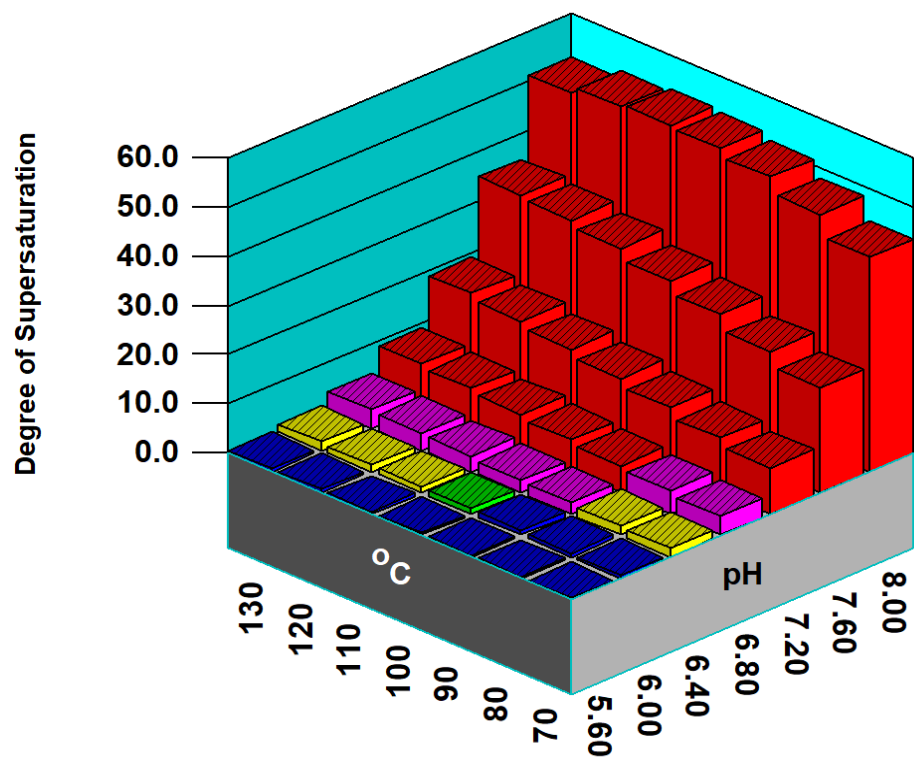


Figure 3-23: Calcite saturation level vs. temperature vs. pH

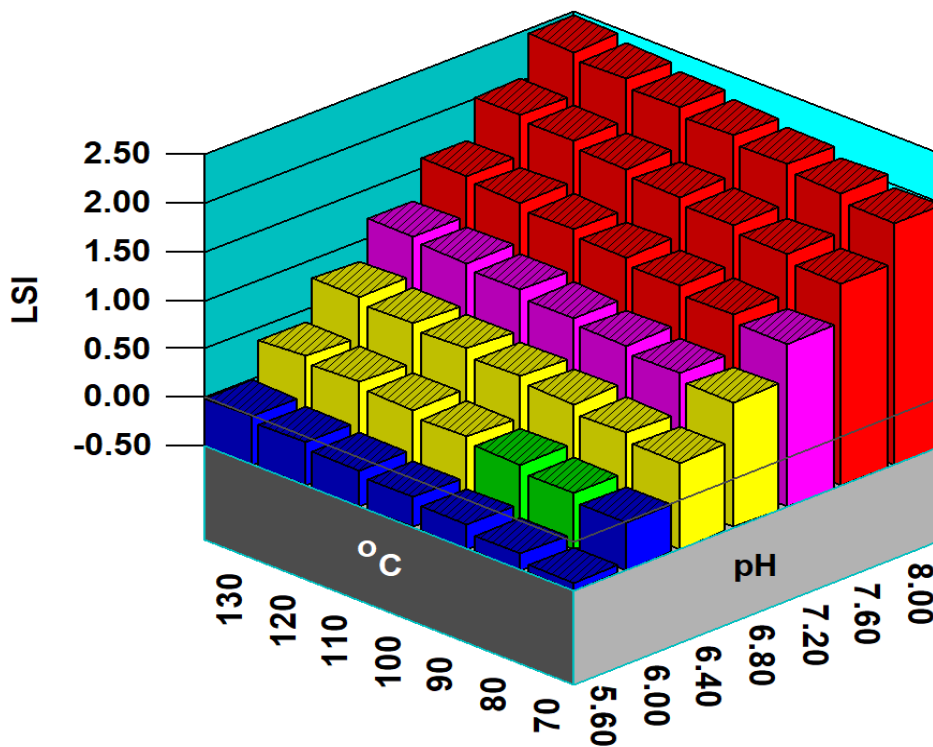


Figure 3-24: Langelier saturation index

French Creek software confirmed that scale will form and that various elements will become oversaturated at 80°C, 0.48 bar pressure and a residence time of 6 hours.

When using the PHREEQ-C modelling software, the amount of water that evaporated was less than the volumetrically determined amount, depending on which element's balance was used. When evaporating 24 L of water with this modelling software, the results differed from the ICP-OES analysis, as displayed in Table 3-5. The reason for this difference is that PHREEQ-C did not take the scale formed on the heat exchange surface into account. According to the PHREEQ-C modelling, roughly 13 L of water should be evaporated to obtain an identical calcium concentration to the ICP-OES analyses during the trial runs. When taking the scale formation on the heat exchange surface into account and evaluating the increase of other non-scaling elements, 24 L of water evaporated is confirmed to be a realistic and accurate measurement. Furthermore, the speciation of elements before and after evaporation shows that more scale forming ions such as Ca^{+2} and Mg^{+2} are likely to occur after evaporation of the feed water; implying that scale formation will take place should the necessary precautions not be taken. Refer to Table 3-7 to compare the performance of the MED with and without anti-scaling agents.

Table 3-7: PPM concentration of certain elements prior and post MED evaporation, with and without anti-scaling agents

Before MED	RO- Retentate to be used inside MED (ppm)	ICP-OES MED Reject with PBTC (ppm)	ICP-OES MED Reject with AMPS (ppm)	ICP-OES MED Reject with HEDP (ppm)	After MED Evaporation No Dosage (ppm)	PHREEQC Simulation theoretical MED reject (ppm)
Ba	0,27	0,39	0,37	0,36	0,35	0,41
Ca	309,46	451,48	457,62	399,37	447,32	470,42
Cu	0,09	33,35	18,92	18,60	0,68	0,14
Fe	0,85	0,63	0,42	0,67	0,95	1,29
K	212,26	288,57	297,47	260,66	295,18	322,76
Li	0,27	0,35	0,36	0,32	0,37	0,41
Mg	55,85	65,08	65,82	57,99	79,25	84,92
Mn	0,07	0,20	0,09	0,11	0,32	0,11
Na	695,19	884,78	925,87	797,17	986,78	1057,03
S	136,00	112,29	97,93	97,93	197,89	206,69
Sr	1,35	1,96	1,97	1,72	1,90	2,05
pH	7,4					7,48

When the performance of the MED combined with the three anti-scaling agents was evaluated, it was determined AMPS worked the best. When evaluating the performance of the MED paired with the three anti-scaling agents as prescribed by French Creek software, it becomes apparent how well which anti-scaling agent performed. The key to determine the best performance is to keep in mind that the purpose of the anti-scaling agent is to keep ions in suspension whilst increasing their concentration. AMPS fared best when specifically examining the amount of calcium present in suspension. The explanation as to why the calcium count when dosing HEDP is lower than when no anti-scaling agent is dosed, is ascribed to the manner in which it complexes with the precipitation prone ions in order to keep them in suspension not being accurately measured as calcium ions by ICP-OES techniques.

3.7 Conclusion and Recommendations

The designed bench-scale single effect vacuum evaporator exhibited a performance that complied with all the design requirements. The vacuum inside the vessel was maintained between 0.40 and 0.44 bar, with the steam temperature varying between 78°C and 80°C. The evaporation rate of the RO-retentate was volumetrically measured to be 4 L/h (22.3 L/m²/h), and this was verified by the PHREEQ-C modelling software. The improved structural integrity of the evaporator and vacuum pump cooling adaptations paired with the doubling of heat exchange surface area increased the evaporation rate from 1.25 L/h to 4 L/h. This implied that roughly 34.5% of the feed water/RO-retentate was evaporated and can then theoretically be recycled whilst absorbing some of the abundant heat present at the power station. This was more than the 33.3% reported when using MED to desalinate seawater, which may be attributed to the lower salinity of the RO-retentate.

The speciation using PHREEQ-C modelling software further showed that evaporation increased the concentration of scale forming agents. The dosage determined using the software showed that the anti-scaling agents inside the MED yielded confirmation of their capability of keeping ions in suspension and not allowing them to scale. When measuring the performance of the anti-scaling agents on this basis, AMPS fared better than PBTC whilst HEDP yielded concentrations of scale forming ions lower than when no anti-scaling agent was dosed. This may be ascribed to the complexes that HEDP forms with the scale forming ions. It is recommended that the evaluation of the anti-scaling agents be further investigated by means of heat transfer efficiencies, as the active ingredients of anti-scaling agents work with different anti-scaling mechanisms through various publications (Li, 2010). Furthermore, calcium carbonate scaling is a complex and poorly understood phenomenon, with the unique composition and nature of the water on which the anti-scaling agents are being tested (MacAdam & Parsons, 2004).

The application of MED technology paired with the use of anti-scaling agents to treat inland waste waters will see the MED-evaporator serving a dual purpose. Its primary purpose is to serve as water producing/recycling technology that can treat brine solutions. The MED reject will be suitable for further treatment using Eutectic Freeze Crystallisation technology to produce fresh water and salts. The secondary purpose of the MED technology when applied to a power plant will be to dissipate some of the abundant heat – alleviating the amount of heat energy the cooling towers must dissipate to some extent, and thus lowering the amount of cooling water needed. A combination of a thermal technology and membrane technology could be theoretically utilised to adhere to the zero liquid effluent discharge policy considered at Eskom, whilst lowering the amount of fresh water needed for cooling purposes.

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CHAPTER 4: Determination of Anti-Scaling Agent to be used inside Bench Scale MED

Abstract—Increasing pollution and scarcity of fresh water have prompted the need to develop and implement effective strategies to treat waste water and reduce water usage. One such a strategy is to recirculate waste water in a power plant; however, this strategy necessitates additional treatment. The considered water contains high levels of scale forming ions. Scale formation needs to be controlled to practically increase the feasibility of recirculation processes. The selected test method to determine anti-scaling agent induction times was found to be inefficient, and an improvement on the current method was proposed. The possible causes for the inefficiency of the selected induction time test method was mainly ascribed to an insufficient heating apparatus setup. The main finding in this study was observed at 75°C where the anti-scaling agent PBTC performed better than ATMP; the former exhibiting a longer induction time in reverse osmosis reject water.

Keywords—Anti-scaling agent, Scale, PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid), AMTP (Amino Trimethylene Phosphonic Acid), Cooling water.

4.1 Introduction

Water is one of the most important resources to sustain biological life. It is needed for various applications, including human consumption, power generation, industrial processes and agriculture. Thus, water conservation is critical. To further emphasise the need for water conservation, South Africa has recently experienced a severe drought that led to eight of the nine provinces in the country being declared disaster areas (Zhuwakinyu, 2016).

Effective water management has consequently become a priority. Power and processing plants are currently looking for methods that allow for water to be used more efficiently, thus optimising water use. The high concentrations of scale forming ions in certain waste water streams may pose significant problems when considering treatment through membrane or thermal technology. Scale formation and build-up in heat transfer units (heat exchangers) as well as membrane filters causes a decrease in treatment efficiency, which results in lower water reclamation/re-use. Furthermore, this causes high levels of maintenance, increased maintenance costs and more downtime to perform maintenance in order to restore efficiency.

Eskom, South Africa's national power utility, is allocated 2-3% of the national available fresh water to generate electricity (Surenda, 2014). Eskom is under pressure to minimise its water usage and has set a target of lowering its usage to 1.34 L of water per kilowatt hour electricity produced by 2020, from the 1.39 L/kWh presently (Fosso-Kankeu et al., 2016). Of the total water intake, 98% is lost via evaporation in the cooling towers of the power plants. The re-usage of certain streams may potentially reduce the amount of fresh water intake needed to replenish the amount of water lost due to evaporation. Eskom's water usage licences clearly stipulate that they have to adhere to a zero liquid effluent discharge policy. This results in Eskom investigating all potential methods to aid in adhering to this policy.

The use of multi-effect distillation, amongst various other technologies, is being investigated and thus the investigation of curbing the most common challenge facing these technologies, namely scaling (Wildebrand et al., 2007), needs to be better examined and explored.

Scale formation occurs due to changes occurring in the physical conditions of a system. Anti-scaling agents (a chemical and proven method of countering scale formation) inhibit scale formation by interfering with scale formation mechanisms. By adding an anti-scaling agent or a combination of more than one anti-scaling agent, industries in turn could decrease maintenance costs on affected equipment. Anti-scaling agent performance is limited thus more than one anti-scaling agent can be utilized to increase performance (MacAdam & Parsons, 2004).

The purpose of this study was to identify problems related to the induction time test method and to establish anti-scaling agent performance of PBTC and ATMP in terms of induction time for application in the treatment of waste waters such as reverse osmosis retentate and cooling water from Eskom's power plants.

4.2 Materials and Methods

4.2.1 Sampling and sample storage

Different water streams were sampled at the Grootvlei Power Plant. A cooling water blowdown/bleed off stream was sampled (concentrated water effluent from the power plant's cooling towers). The reason for sampling the cooling water blowdown/bleed off stream was due to its high scale forming ion/mineral content, hence the consideration of scale inhibition treatment on this stream. To further save costs and decrease usage of fresh make-up water, the RO-retentate stream was considered for treatment and sampling was also considered. Samples were stored in a cold environment, which aided in decreasing the sampled water's scaling ability as well as preserved the water chemistry.

The cooling water blowdown/bleed off stream (CW-blowdown) and reverse osmosis retentate (RO-retentate) stream conductivities and pH are displayed in Table 4-1 below and were established for the sample batch on which static induction tests were performed. Conductivity measurements were performed with the use of the Lovibond SensoDirect 150 (Lovibond, Germany). pH measurements were conducted with the Hanna HI8424 portable pH/ORP meter (HANNA instruments, USA).

Table 4-1: Table displaying conductivities and pH's of CW-blowdown and RO-retentate

Water Source:	Conductivity	pH
CW Blowdown	1.98 mS/cm	7.4
RO Retentate	1.08 mS/cm	7.8

4.2.2 Synthetic control water preparation

A synthetic water sample (control) was prepared by dissolving salts with a concentration of 0.005 mol/dm^3 CaCl_2 and 0.005 mol/dm^3 $\text{Ca}(\text{HCO}_3)_2$ in demineralised water. The pH of the control solution was 7.5. The purpose of the synthetic water was to compare the difference between the sampled cooling water blowdown, reverse osmosis reject stream and the synthetic water sample. This helped to note if any of the minerals, besides those associated with the scale forming mechanism in the sampled water, interacted with the scale forming mechanism. Each water sample was analysed for additional minerals not associated with scale formation.

4.2.3 Spiked sample preparation

500 mL of the RO-reject and CW-blowdown samples were spiked with 0.105 g $\text{Ca}(\text{HCO}_3)_2$ and 0.138 g CaCl_2 ; amounting to the same content as the control solution. Spiked solutions were analysed to investigate

the assumption that scale forming ions in the raw samples might have formed scale before static induction tests are performed.

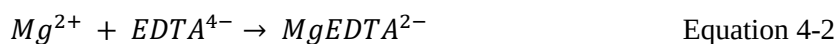
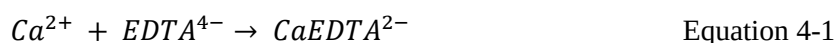
4.2.4 ICP-OES analysis

An ICP analysis using ICP Expert II, Agilent Technologies 720 ICP-OES (Agilent Technologies, USA) was performed to determine the concentration of calcium present in the two sampled waters.

4.2.5 EDTA titration

An EDTA (ethylene-diamine-tetra-acetic acid) titration was performed to determine the hardness of the CW-blowdown and RO-reject water samples. Two titrations were performed, one to determine the total hardness and the other to determine the calcium hardness. 25 mL of the samples were diluted to 50 mL for the total and calcium hardness titrations. 0.01 M EDTA solution was used as titrant. An ammonium buffer solution was used for the total hardness titration and was prepared by adding 16.9 g of ammonium chloride (NH₄Cl) to 143 mL of concentrated ammonium hydroxide (NH₄OH). The buffer solution used for calcium titration was 0.1 M sodium hydroxide (NaOH) solution.

Total hardness was established using an EDTA titration with the pH of the samples maintained at 10±0.1. 1 – 2 mL of ammonium buffer solution was added to the diluted samples. A pH of 10 allowed the EDTA to react with both calcium and magnesium:



Calmagite indicator was used, which changed from a red to a blue at the end point.

Calcium hardness determination was done by EDTA titration, with the pH of the sample maintained between 12 and 13. 1 - 2 mL of ammonium hydroxide (NH₄OH) buffer was added to the solution to maintain a pH of 12 - 13. The pH was maintained at 13 so that magnesium would not react with EDTA and precipitate from solution, so only the reaction using calcium would take place. Murexide indicator was used for calcium titration, which changed from a pink to a purple colour at the end point.

The difference between the total hardness and calcium hardness yielded the amount of magnesium hardness as:

$$\text{Total hardness} = \text{Ca hardness} + \text{Mg hardness} \quad \text{Equation 4-3}$$

The total hardness was calculated by using the following equation:

$$\text{Total or calcium hardness} = \frac{\text{EDTA Volume} \times 1000}{\text{Sample Volume}} \quad \text{Equation 4-4}$$

The EDTA volume was calculated by subtracting the volume of EDTA inside the burette before titration from the EDTA left inside the burette after titration.

4.2.6 Alkalinity test

As the measurement of the amount of carbonates and bicarbonates of the water was necessary to determine the scaling potential of the water, an alkalinity test was performed. Alkalinity is a measurement of the concentration of carbonates and bicarbonates in the water as well as a measurement of the buffer capability to resist changes in pH from the addition of acidic or basic solutions. The presence and concentration of bicarbonates were determined through the alkalinity test, by titrating water samples with 0.1 M sulphuric acid solution. The sample batch for which alkalinity was tested had a pH of 8.6 for both CW-blowdown and RO-reject. A volume of 25 mL was used for the alkalinity titration. First, the sulphuric acid was added to a titration point of pH 8.3, which represented the elimination of hydroxyl ions (OH^-). The volume of acid in the burette was noted. Sulphuric acid was further added to the water sample until an end point of pH 4.5 was reached. The volume left in the burette was noted and the volume of acid added from 8.3 to 4.5 was calculated. The total alkalinity was calculated by using the following equation:

$$\text{Alkalinity} = \frac{\text{Sulphuric acid volume} \times 1000}{\text{Sample volume}} \quad \text{Equation 4-5}$$

4.2.7 Sulphate content in samples

Sulphate content was analysed with the use of the HANNA instruments HI 83099 COD and multi-parameter photometer. The sulphate content was analysed three times for both the CW-blowdown and RO-reject samples, of which the mean was reported.

4.2.8 Scale potential modelling

The MineSat™ application of French Creek software® was used to model the scaling potential of the water samples. The model aided in selecting a dosage for which the performance of anti-scaling agents in terms of induction times could be evaluated within a reasonable time. The software calculated the degree of supersaturation for a range of pH and temperatures. The model was additionally used for comparison and interpretation of static induction tests, as well as to draw a thermodynamic result of scaling.

4.2.9 Jar heating system

Jars were heated to temperatures of 25, 40 and 75°C respectively, using a water bath comprised of a heating element and temperature control. These temperatures were selected to determine the performance of anti-scaling agents at room temperature (25°), at slightly elevated temperature (40°) and a temperature mimicking conditions that would occur in the constructed bench scale single effect evaporator (75°). The

heated water was then circulated using a pump and recirculation piping to maintain the temperature surrounding the jars (Figure 4-1 and 4-2).



Figure 4-1: Jar test apparatus with a tray



Figure 4-2: Jar heating system

A jar test apparatus was used to allow for stirring the contents of the glass jars. A tray was filled with the heated water provided by a water heating bath and placed under the impellers of the jar test apparatus in which jars were placed. Warm water flowed around the jars, which allowed transfer of heat to the contents of the glass jar. The circulation maintained a constant temperature inside the tray, and thus the glass jars once the required temperature was reached.

4.2.10 Data logging method

An Arduino Uno micro-controller was used as a data logging and measurement tool for the measurement of the resistivity of the samples. The Arduino Uno measured the voltage drop over the water sample, from which a resistivity can be determined according to a voltage divider calculation:

$$R_{water} = \frac{V_{out} R_1}{V_s - V_{out}} \quad \text{Equation 4-6}$$

V_s was the voltage of the source, which was 5 V (in this case the output voltage of the Arduino Uno); R_1 was a resistance chosen such that the voltage over the water remained within the range of 0-5 V, in order for the Arduino to have the capability to read a resistivity for the water. R_1 was chosen as 1740 Ω .

V_{out} , the output voltage, was a variable voltage value, which varied according to the change in resistivity of the water sample. Having known V_{out} , R_1 and V_s values, R_{water} , which was the resistivity of the water ($\Omega \cdot \text{cm}$), was calculated. Conductivity is the inverse of resistivity, which was the measurement of consideration for the static induction test.

Two copper wires were placed in the water samples, with the objective of measuring the resistivity of the water. The copper wires were placed 1 cm apart. The measured resistivity was converted to conductivity, then data was treated with a Savitzky–Golay smoothing algorithm to eliminate noise.

4.2.11 Static induction test procedure

A static induction test was performed in order to determine the difference in time induction performance of two anti-scaling agents.

Anti-scaling agents were selected according to their effectivity after simulation and evaluation of dosage profiles using French Creek software. The resulting anti-scalants differ from those used in Chapter 3, as the water sampled and used to complete Chapter 4 originated from the Grootvlei Power Plant, as opposed to the Lethabo Power Plant for Chapter 3.

- PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid)
- Belclene 640 (Amino Trimethylene Phosphonic Acid)

The kinetics of scale formation of the synthetic water sample (control solution), CW-blowdown and RO-reject samples (in the presence as well as absence of ATMP and PBTC) and the spiked CW-blowdown and RO-reject sample (in the presence as well as absence of ATMP and PBTC) were tested using the static induction test. The procedure was initiated by heating the bath and was allowed to stabilise at a temperature such that the temperature inside the tray was either 25, 40 or 75°C respectively.

After experimentation of the modelled dosage, a final dosage of 0.2 ppm of PBTC and ATMP was chosen for the RO-reject sample and 0.1 ppm dosage of PBTC and ATMP for the cooling water blowdown sample as well as the control solution, as these dosages indicated a drop in conductivity within a reasonable time.

Glass jars were filled with 500 mL of the water sample and placed in the heating tray. The samples were dosed with anti-scaling agent while being stirred at a speed of 60 rpm using the jar test apparatus. Two samples were dosed with ATMP, two with PBTC and two samples were left blank, which amounts to six samples per experimental. Logging was initiated and allowed to continue for 30 seconds, after which the pump was switched on and heated water allowed to circulate around the jars. Resistivity was logged every

1 minute in the case of 25°C and every 10 seconds for the case of 40°C and 75°C. Experimental runs of 12 hours were performed for 25°C, 6 hours for 40°C and 2 hours for 75°C.

4.3 Results and Discussion

4.3.1 Sample pre-analysis

ICP-OES

The calcium content of the samples was determined using ICP-OES, the value of 83.61 ppm was recorded in the CW-blowdown sample and 170.4 ppm in the RO-reject sample. The high ion concentration and hardness of the CW blowdown will potentially cause fouling/scaling, and this is then treated to a certain extent with RO keeping this in mind. The RO reject generated from the CW Blowdown has a higher fouling/scaling potential than the CW blowdown and will potentially lead to extensive fouling of membranes and heat exchange surfaces if it comes in contact when being treated further in downstream processes. This will effect the choice and complexity of downstream processes. The concentration of other metals was also determined using ICP-OES and is summarised in Table 4-2:

Table 4-2: Concentration of metals contained in samples

Element	CW-blowdown (ppm)	RO-reject (ppm)
Al	0.11	0.15
Ba	0.21	0.45
Ca	83.61	170.40
Co	0.01	0.00
Cu	0.14	0.27
K	26.84	53.78
Li	0.15	0.35
Mg	37.95	76.32
Mo	0.10	0.15
Na	87.63	159.76
Pb (220.353 nm)	0.00	0.20
Pb (283.305 nm)	0.05	0.34
Se	1.75	0.04
Sr	0.60	1.27
Tl	1.14	0.01
Zn	0.15	0.20

Water hardness determined by EDTA titration

The results of the EDTA titrations for the CW-blowdown and RO-reject are summarised in Table 4-3, where the results are given as CaCO₃ concentration equivalent. The CW blowdown is treated with RO hence an increase in hardness is observed. This hardness potentially can cause fouling and scaling when

treated further and complicate downstream processes; the impact of hardness on scale formation has been reported in previous studies (Ben Amor et al., 2004).

Table 4-3: Hardness of water samples

Sample	Ca Hardness (mg CaCO ₃ /L)	Mg Hardness (mg CaCO ₃ /L)	Total hardness (mg CaCO ₃ /L)
CW-blowdown	160	115	275
RO-reject	348	210	558

4.3.2 Bicarbonate and carbonate content from alkalinity test

The alkalinity was reported as a concentration equivalent to CaCO₃ and determined by means of an alkalinity test. The concentration of bicarbonates in the CW-blowdown stream was found to be 124.4 mg CaCO₃/L and 60 mg CaCO₃/L for the RO-reject sample.

4.3.3 Sulphate content

The sulphate content of the RO-reject was determined to be 400 mg/L, while the sulphate content of the CW-blowdown was 208 mg/L.

4.3.4 Scaling potential model

The French Creek MineSat™ modelling application was used for scale potential modelling. Scaling potential models were calculated for a temperature range of 15 - 85°C. The pH ranged from 7 - 9 for the calculation of the scaling potential models. Scaling potential is proportionally related to the degree of supersaturation.

(Note: For descriptive purposes, the following colour codes of Figures 4-3 and 4-4 are assigned for scaling potential: blue - low, green - moderate, yellow - moderately high, pink - high and red - severe)

CW-blowdown stream

Figure 4-3 depicts the scaling potential of the CW-blowdown stream calculated at 25°C.

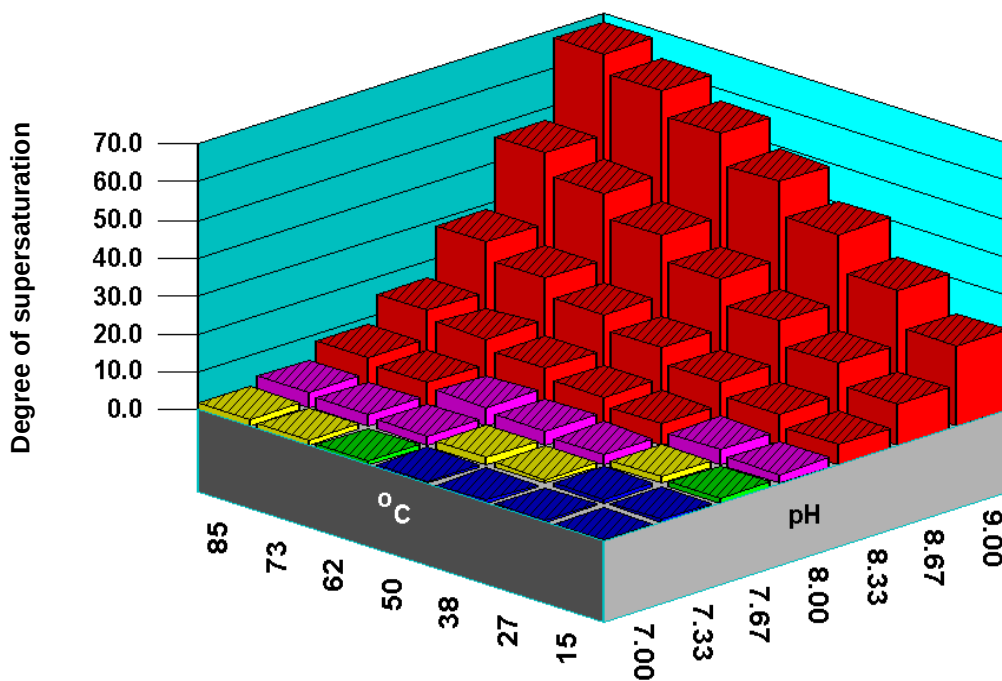


Figure 4-3: French Creek MineSat® model, degree of supersaturation for CW

The expected low degree of supersaturation at low temperatures and low pH-values was evident from Figure 4-3. Below a pH of 7.67, the scaling potential was low. Between a pH of 7.67 and 8, scaling was moderately low. Above pH 8.33, scaling was excessively bad for a temperature range of 15°C - 85°C.

1 CW-blowdown at 25°C:

At a temperature of 25°C and pH 7.4, scaling should not form easily as the scaling potential was low according to the MineSat™ model, and scaling was kinetically and thermodynamically unfavored in this case, as scaling could take long and the driving force to form scale was found to be low. The concentration of Ca^{2+} and HCO_3^- was too low to indicate signs of CaCO_3 formation.

2 CW-blowdown at 40°C:

The scaling potential of the CW-blowdown stream was moderate at a temperature of 40°C and a pH of 7.4, according to Figure 4-3. Although, according to the MineSat®, the scaling potential was not severe; the potential for scaling in the cooling water system could occur from a thermodynamic perspective, as it was still moderately high.

3 CW-blowdown at 75°C:

According to the model, scaling became severe when calculated at 75°C and pH 7.4. The considered severe scaling potential was indicative of scaling being most likely. The solubility of Ca^{2+} ions and carbonate ions was decreased with temperature, as was indicated by the increase in scale potential with temperature in Figure 4-3. The driving force for scale formation was high in this case, hence favourable from the thermodynamic and kinetic perspective.

RO-reject stream

The scale potential model for the RO-reject stream is displayed in Figure 4-4.

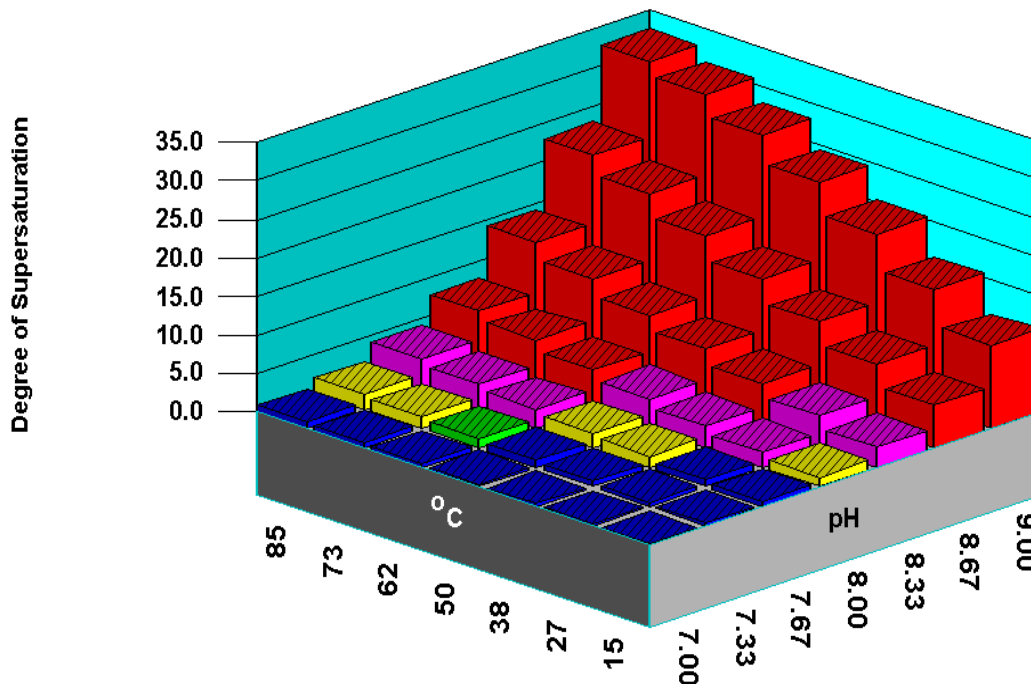


Figure 4-4: French Creek MineSat® model, degree of supersaturation for RO

Similar to the CW-blowdown stream, Figure 4-4 indicated a low scaling potential at low temperatures and low pH-values. The degree of supersaturation was low, below a 7.67 pH and high above a pH of 8.67. Scaling was moderate below 27°C and between a pH of 7.8 and 8.

4 RO-reject at 25°C:

At a pH of 7.8 and at a temperature of 25°C, scaling potential was low and unlikely to occur, therefore thermodynamically and kinetically unfavoured. The concentration of Ca^{2+} and HCO_3^- was too low to show signs of CaCO_3 formation at this temperature.

5 RO-reject at 40°C:

The RO-reject stream showed a moderate potential to form CaCO_3 scale at 40°C with a pH of 7.8, although not severe; yet a high scaling potential was considered, as there was a thermodynamic drive to form scale according to the French Creek simulation model shown in Figure 4-4.

6 RO-reject at 75°C:

Evaluation of the scaling potential viewed in Figure 4-4 at 75°C and pH 7.8 showed a severe tendency to scale according to the high degree of supersaturation. As a result, the stream should be considered as highly thermodynamic and kinetically favourable.

Summary of scaling potential

The description of scaling potential and degree of supersaturation are summarised in Table 4-4:

Table 4-4: Scaling potential and degree of supersaturation for CaCO₃ for CW-blowdown and RO-reject streams

Temperature (°C)	Scaling potential		Degree of supersaturation (Calcite)	
	CW-blowdown	RO-reject	CW-blowdown	RO-reject
25	Low	low	0.98	1.2
40	Moderately high	high	1.59	1.93
75	Severe	severe	3.79	4.36
<i>* Note: For descriptive purposes in Table 4-4, the following colour codes of Figures 4-3 and 4-4 are assigned for scaling potential: blue - low, green - moderate, yellow - moderately high, pink - high and red - severe.</i>				

The degree of supersaturation was determined using the French Creek MineSat™ application. The scaling tendency for the RO-reject stream was determined to be higher than the CW-blowdown at all three temperatures according to the degree of supersaturation; this was due to the concentration of the calcium ions being greater in the RO-reject stream. The calcium ion concentration was determined by ICP-OES as 170.40 ppm present in the RO-reject stream and 83.61 ppm present in the CW-blowdown stream.

4.3.5 Dosage profile modelling for ATMP and PBTC anti-scaling agents

In addition to the scaling potential model, a dosage profile model was generated by French Creek's software MineSat™ application and illustrated in Figures 4-5 and 4-6. The dosage profile gave a general idea of the dosage that was needed for the static induction tests. The dosage was considered at the highest temperature of experimentation.

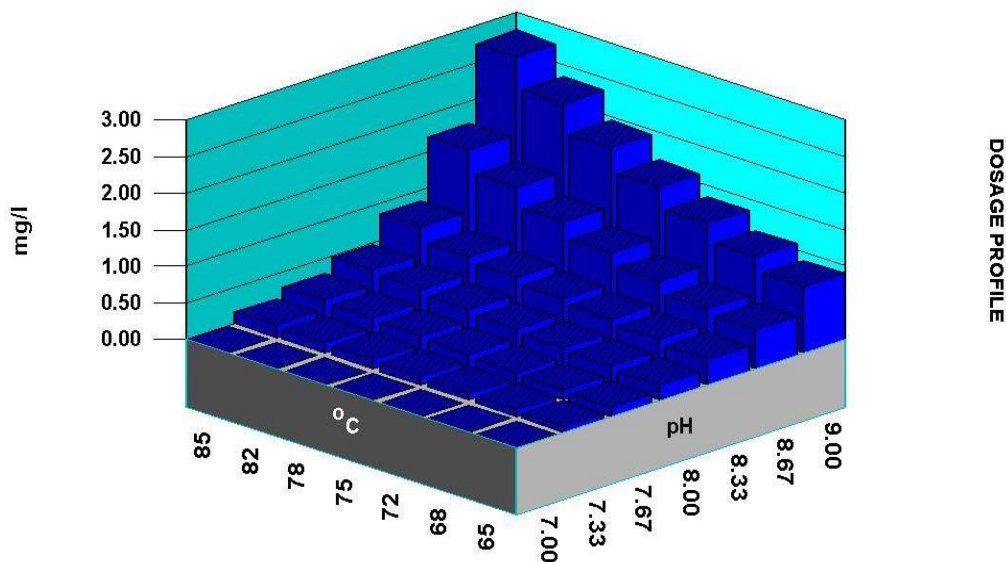


Figure 4-5: French Creek MineSat® model, dosage profile of ATMP for RO, calculated at 75°C

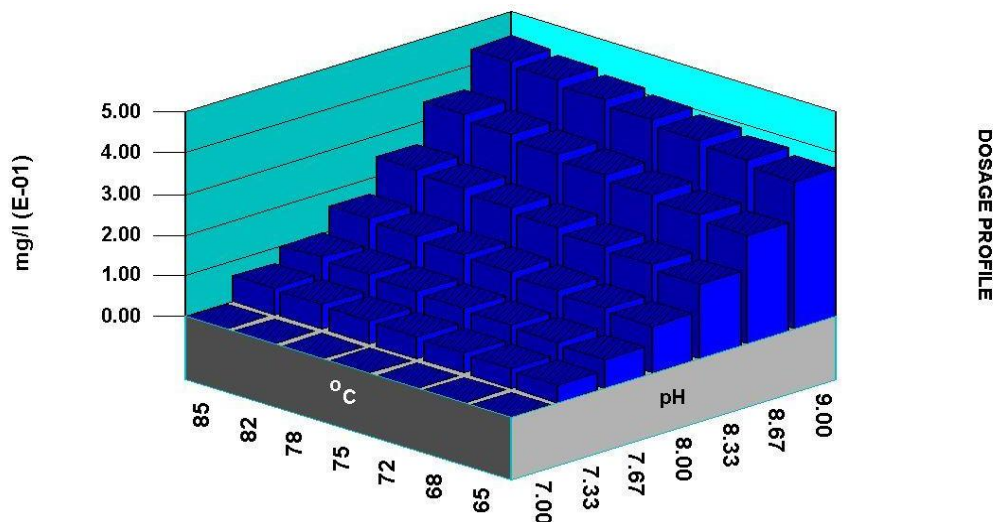


Figure 4-6: French Creek MineSat® model, dosage profile of PBTC for RO, calculated at 75°C

4.3.6 Static induction test:

Anti-scaling agents (PBTC & ATMP) were evaluated at 25°C, 40°C and 75°C respectively, to determine the difference in performance in terms of induction time. Each of the samples was divided into three batches, a blank (without anti-scaling agent dosage), ATMP dosed, and a PBTC dosed batch.

The first gradual increase in conductivity was due to the increase in energy in the form of heat, whereby the samples were heated from ambient temperature to the considered temperature of either 25°C, 40°C, or 75°, as observed in Figure 4-7 to Figure 4-21. Ions moved more readily upon elevated temperatures, thereby increasing conductivity. In some cases, the induction test at 25°C showed no initial rise in conductivity; this was due to the ambient temperature varying with time and in the case where no initial rise in conductivity was observed; the ambient temperature was much closer to 25°C than in other cases. A decrease in

conductivity occurred when the ion content of the water decreased, which was the case when scale precipitated from the water.

The compositions of potential scale forming waters and the methods of testing anti-scaling agent performance vary greatly throughout the literature (MacAdam & Parsons, 2004). As a result, comparison to the scaling potential model generated by French Creek's MineSat™ application provided valuable insight. The general trend of what was expected can be related to the plot of conductivity over time given by Muryanto et al. (2014). The difference observed is that an initial rise in conductivity was not observed in the study done by Muryanto et al. (2014), although the trend after the rise became similar to the study. There was a sudden rise of conductivity which eventually stabilised and then dropped due to the precipitation of CaCO_3 scale.

Note: Conductivities are not as accurate due to noise, polarisation on the wire probes and electro-magnetic induction present from the use of an Arduino set-up; the changes in conductivity can however be considered for determining an induction time in the case of this experiment.

4.3.7 Static induction test at 25°C

Figure 4-7 represents an induction test of the control solution at 25°C.

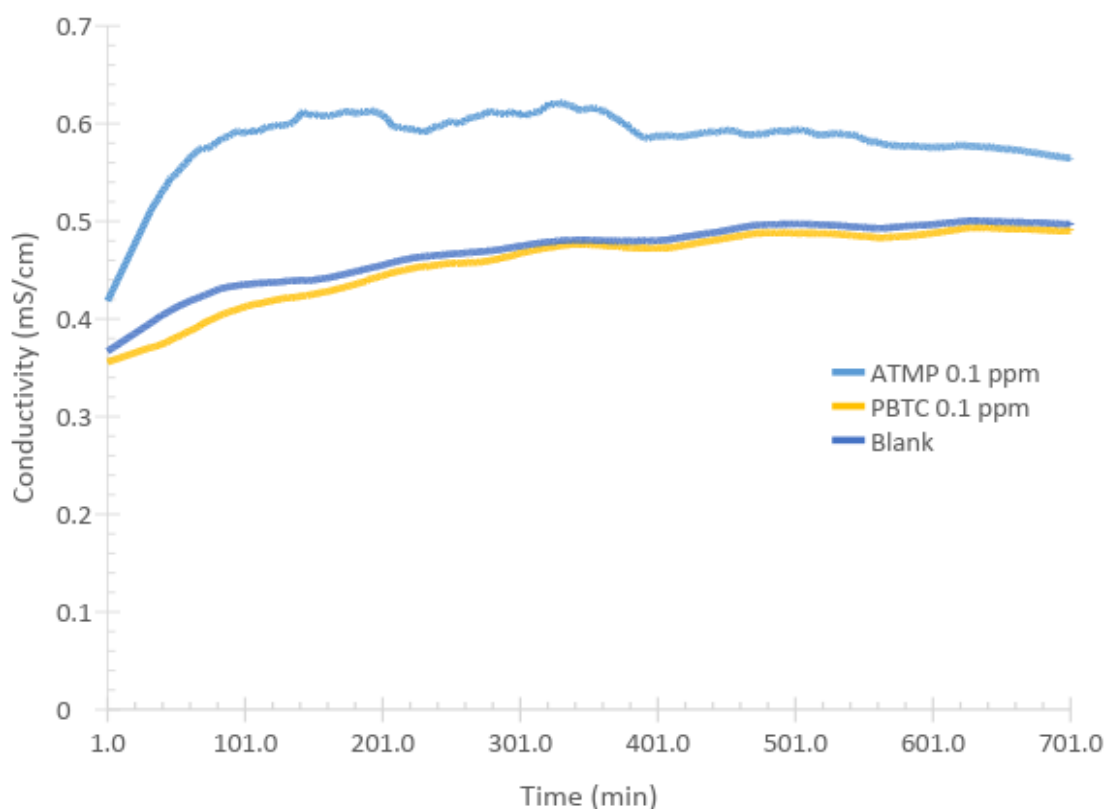


Figure 4-7: Conductivity over time (control solution 25°C)

The induction time test showed no drop in conductivity for the synthetic water control solution; this was due to the low scaling potential of the control solution at 25°C and a moderately low initial pH of 7.5, which further added to a low scaling potential.

In Figure 4-8, the induction test performed on the CW-blowdown sample at 25°C is given.

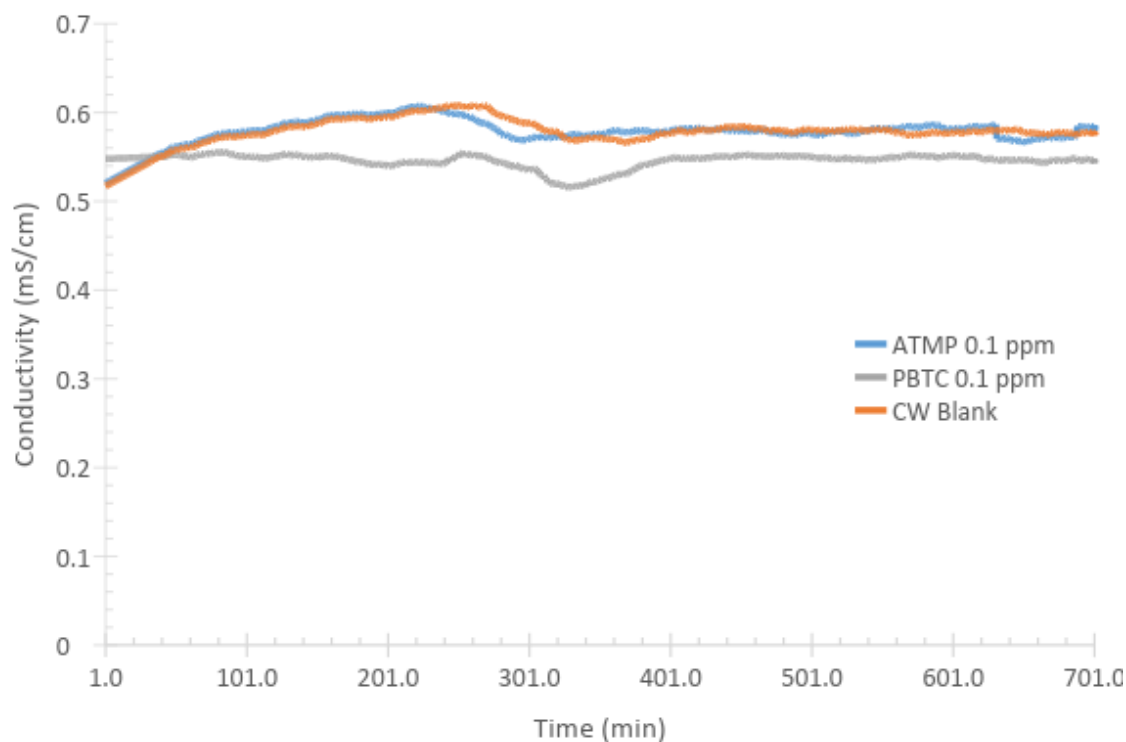


Figure 4-8: Conductivity over time (CW sample 25°C)

As depicted in Figure 4-8, a slight drop in conductivity was observed between 226 min and 351 min, and although this had occurred, it was not large enough to draw a concrete conclusion in terms of CaCO_3 precipitation. The drop in conductivity was due to indeterminable external influences in this case. In comparison to Figure 4-10, which represents the induction test for the spiked CW-blowdown sample; it had a higher scaling potential than that of the standard CW-blowdown sample, and no drop in conductivity occurred. Furthermore, Figure 4-3 showed that, according to the scale potential model for the CW-blowdown stream, the scaling potential was low; therefore no precipitation occurred for the CW-blowdown stream at 25°C.

An induction test performed on the RO-reject sample at 25°C is given in Figure 4-9:

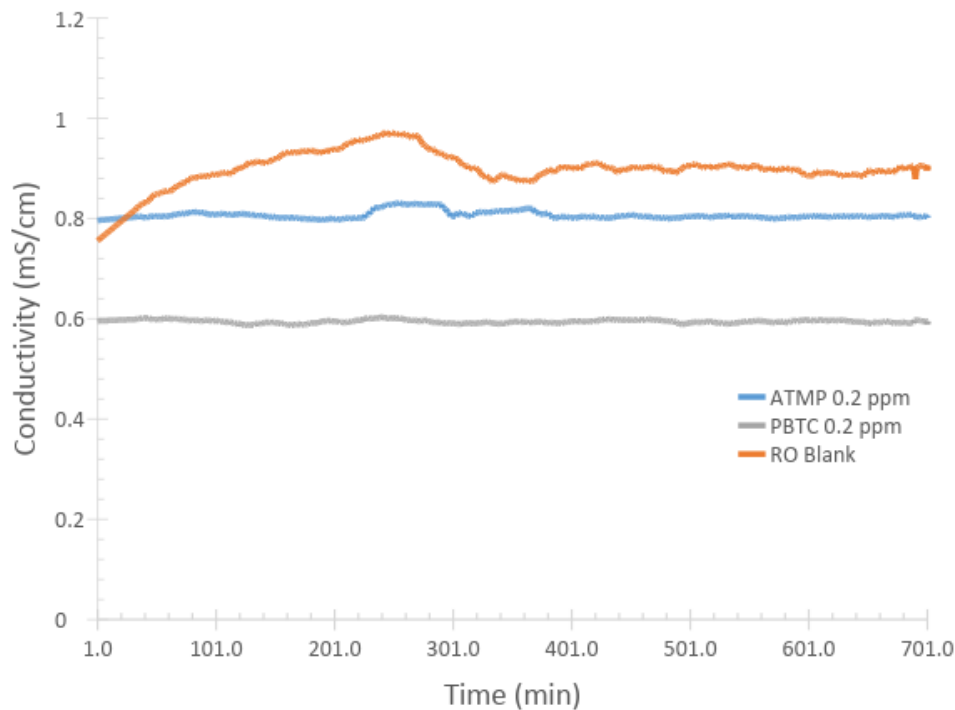


Figure 4-9: Conductivity over time (RO sample 25°C)

The drop in conductivity observed in Figure 4-9 exists only for the blank batch. The drop in conductivity was not accredited to the precipitation, as compared to Figure 4-11, which represents the spike RO-reject sample, which had a higher concentration of calcium and carbonate ions. Hence, a higher scaling potential than the standard RO-reject sample showed no drop in conductivity for the non-dosed blank batch. The scale potential model depicted in Figure 4-4 showed a low potential for scale formation, which further infers that the conductivity drop was not accredited to the formation of CaCO_3 , but rather to indeterminable external influences in this case.

Figure 4-10 represents the induction test for the spiked CW-blowdown sample at 25°C.

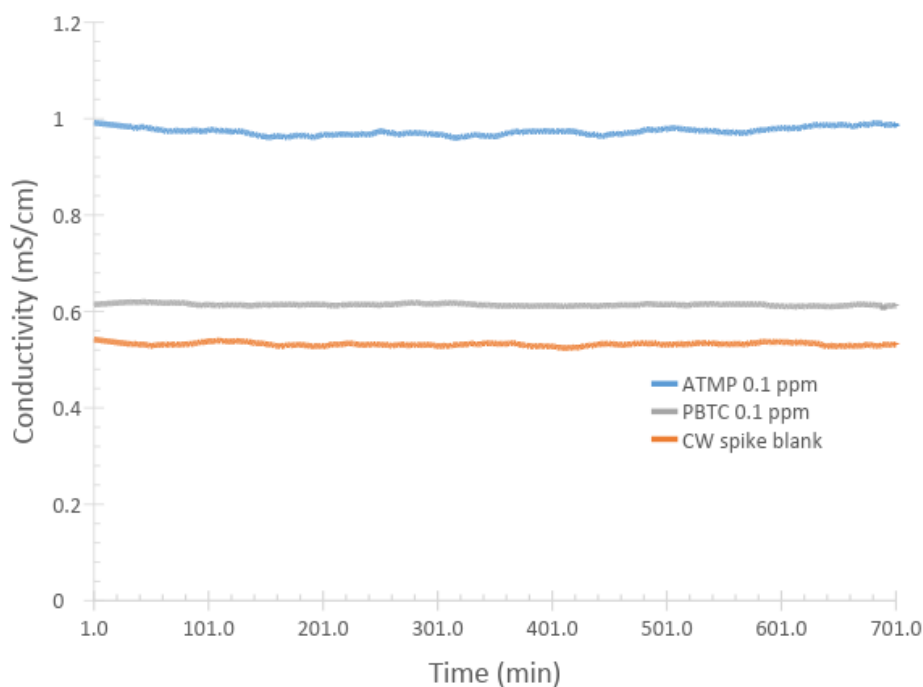


Figure 4-10: Conductivity over time (CW spiked sample 25°C)

Figure 4-11 represents the induction test for the spiked RO-reject sample at 25°C.

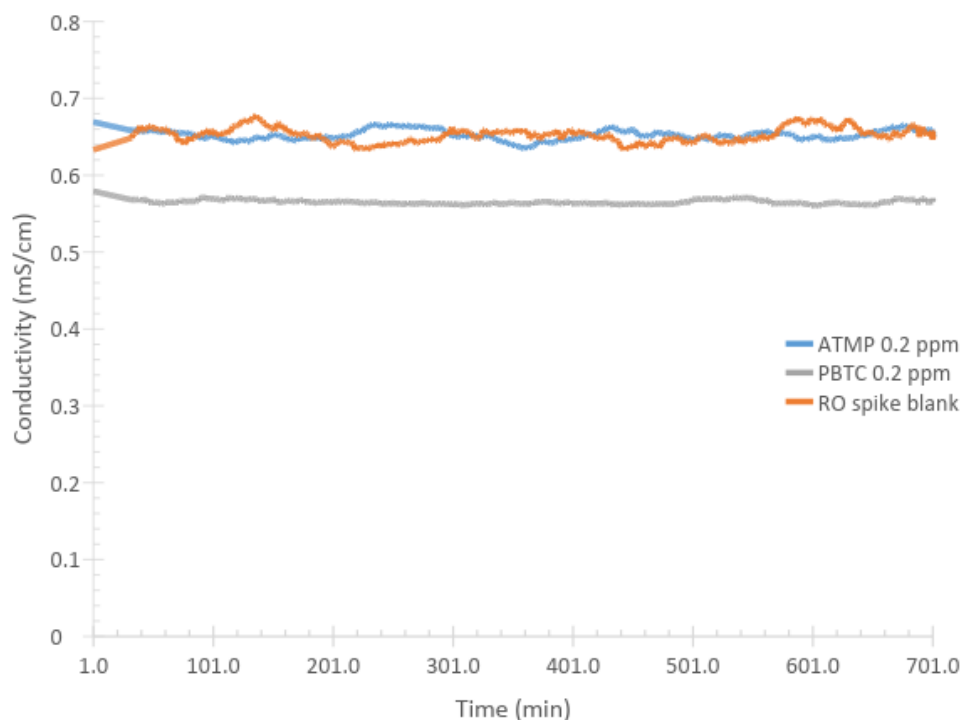


Figure 4-11: Conductivity over time (RO spike sample 25°C)

There was no significant change in conductivity for either the CW-blowdown or RO-reject samples and blank batches at a temperature of 25°C (Figures 4-10 and 4-11). At 25°C and for the considered time, all samples (control solution, CW-blowdown, RO-reject, spiked CW-blowdown and spiked RO-reject) were undersaturated with potential scale forming ions (Ca^{2+} and CO_3^{2-}).

For each sample, the blank, PBTC dosed and ATMP dosed batches were duplicated. In some cases, spikes associated with the electronics of the data logging method occurred, and in these cases, the duplicate where the electronic spike did not occur was selected for representation. The trends were similar for most cases, except in the case of electronic spikes. However, this trend remained similar prior to and after a spike had occurred for the duration of the experimental run time.

pH and actual conductivity and summary of results for 25°C

Table 4-5 details the results of the pH and actual conductivity measurements before the start of the induction test as well as directly after the induction test was completed.

Table 4-5: Initial and final measurements of pH and actual conductivity at 25°C

Samples at 25°C	pH		Conductivity (mS/cm)	
	Initial	Final	Initial	Final
Control solution	7.5	7.6	0.6	0.8
ATMP dosed control solution	7.4	7.5	0.7	0.8
PBTC dosed control solution	7.5	7.5	0.7	0.8
CW-blowdown	7.4	7.5	1.9	2.0
ATMP dosed CW-blowdown	7.5	7.5	2.0	2.0
PBTC dosed CW-blowdown	7.4	7.4	1.9	1.9
RO-reject	7.8	7.8	1.1	1.2
ATMP dosed RO-reject	7.7	7.8	1.0	1.0
PBTC dosed RO-reject	7.7	7.8	1.0	1.0
Spiked CW-blowdown	7.7	7.6	2.5	2.5
ATMP dosed spiked CW-blowdown	7.7	7.7	2.5	2.5
PBTC dosed spiked CW-blowdown	7.8	7.6	2.5	2.5
Spiked RO-reject	7.8	7.7	1.7	1.7
ATMP dosed spiked RO-reject	7.8	7.8	1.8	1.8
PBTC dosed spiked RO-reject	7.8	7.8	1.7	1.7
* Note: pH accuracy within ± 0.1 and conductivity accuracy was determined within ± 0.1 mS/cm				

The pH and conductivity remained relatively similar before and after the duration of the induction test. This is indicative that no change in conditions of any of the samples occurred throughout the duration (12 hours) of the induction test in the case of 25°C.

4.3.8 Static induction test at 40°C

The initial increase in conductivity observed at 40°C was higher than that observed at 25°C. Figure 4-12 represents an induction test of the control solution at 40°C.

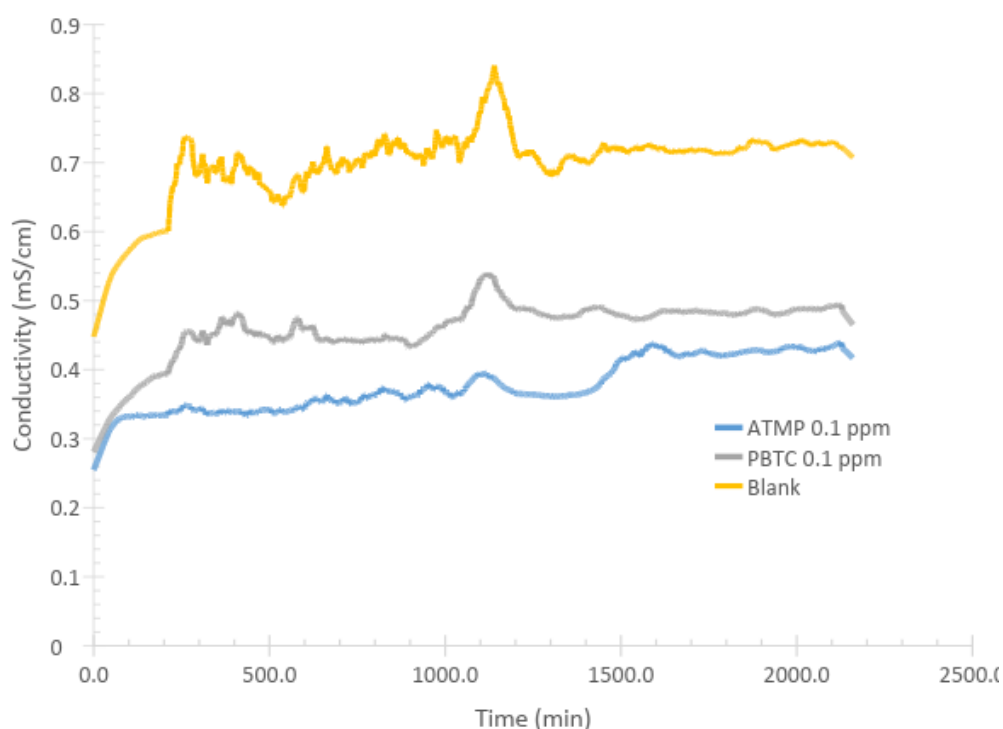


Figure 4-12: Conductivity over time (control solution 40°C)

The control solution showed no signs of CaCO_3 formation, as a drop in conductivity was absent. The amount of calcium and carbonate ions was too low for the temperature and pH conditions during an experimental run time of 6 hours.

A representation of the induction test performed on the CW-blowdown sample at 40°C is given in Figure 4-13.

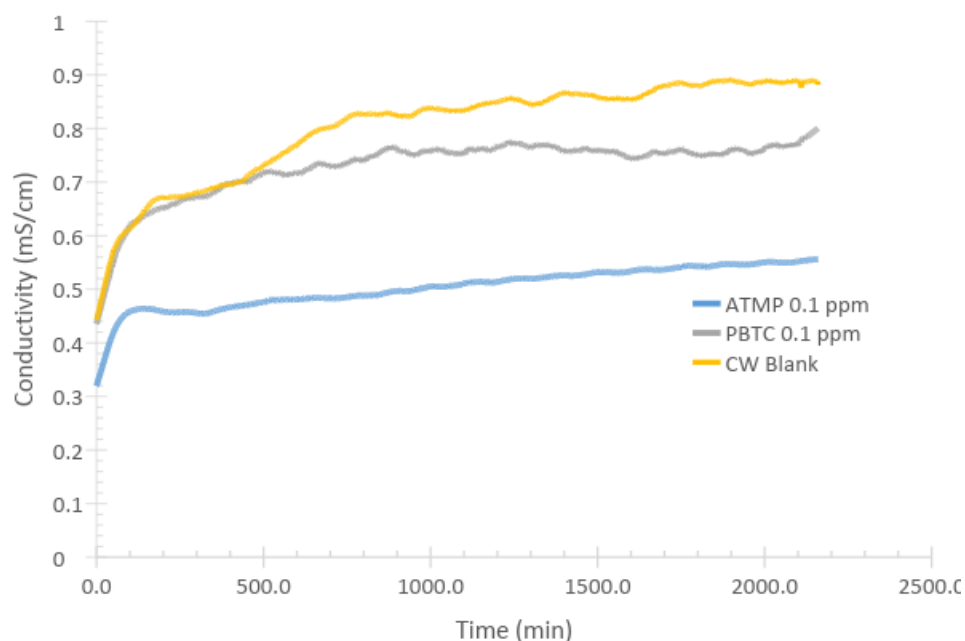


Figure 4-13: Conductivity over time (CW sample 40°C)

Figure 4-14 represents an induction test of the RO-reject sample at 40°C.

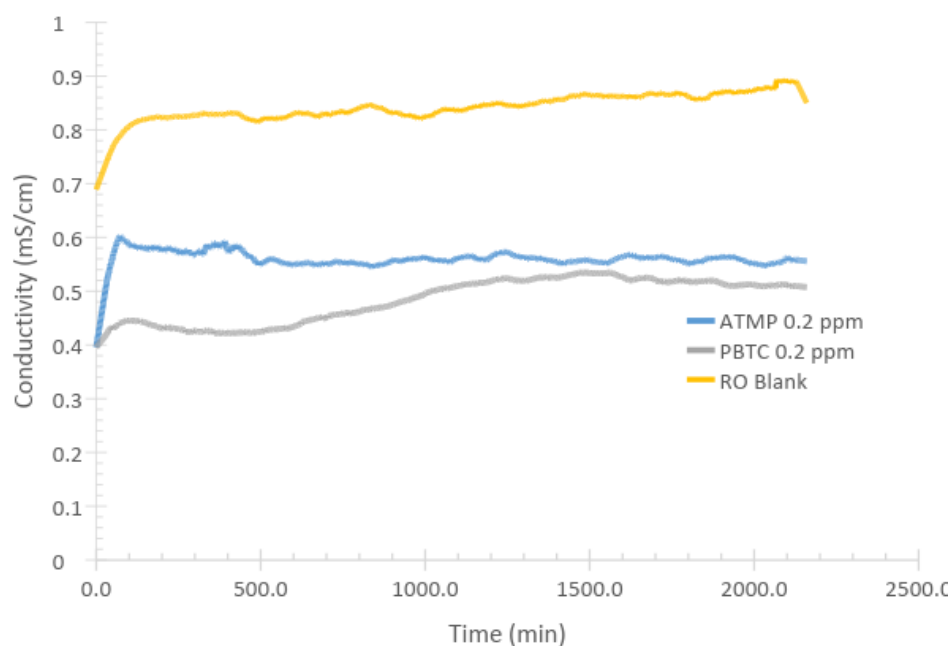


Figure 4-14: Conductivity over time (RO sample 40°C)

In Figure 4-13 and Figure 4-14, the rate of change in conductivity decreased during the initial increase in temperature of the water, which could be indicative of the occurrence of precipitation, and could be the case for the CW-blowdown sample (Figure 4-13). This behaviour occurred in the blank batch. In contrast, in the RO-reject sample (Figure 4-14), this behaviour occurred in the PBTC dosed batch and not in the blank batch, which was inconsistent and contradicted the idea that anti-scaling agents increase induction time.

Figure 4-3 (scaling potential model for CW-blowdown stream) and Figure 4-4 (scaling potential model for RO-reject stream) showed a moderately high and high potential to form scale. The spiked samples for the CW-blowdown (Figure 4-15) and RO-reject (Figure 4-16) had a higher potential to form scale than the standard samples due to the additional spiked amounts of calcium and bicarbonates, which showed no signs of scale formation, as there existed no observed drop in conductivity. Although the potential to form scale existed according to the scale potential models, a solid conclusion that scale forms could not be drawn due to the inconsistency between the spiked and standard samples in both CW-blowdown and RO-reject cases. Figure 4-15 represents an induction test of the spiked CW-blowdown sample at 40°C.

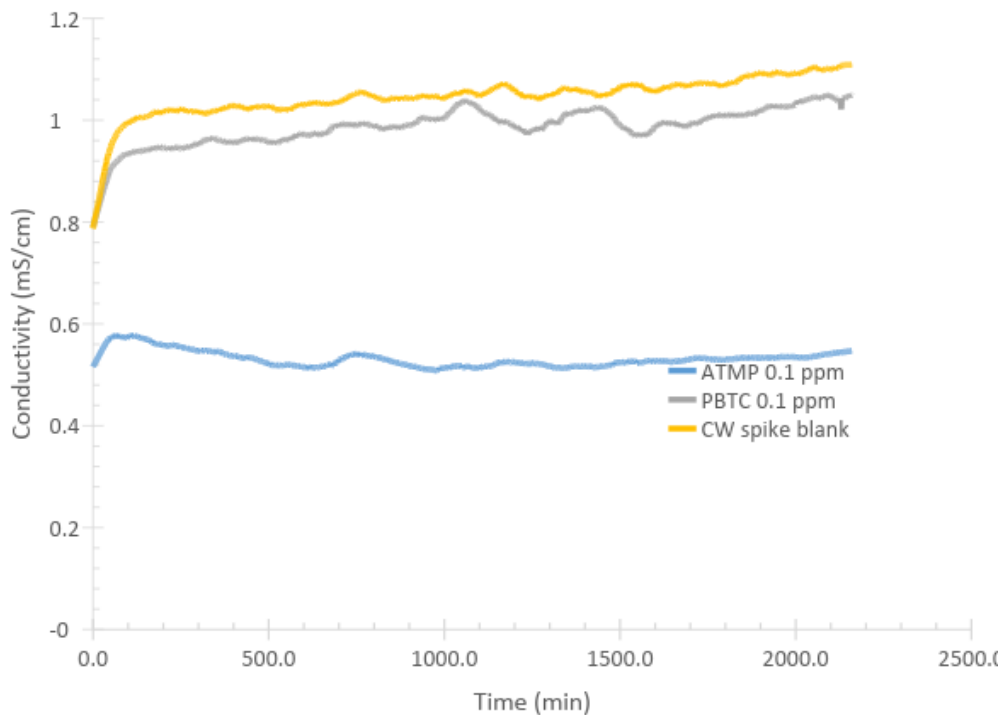


Figure 4-15: Conductivity over time (CW spike sample 40°C)

Figure 4-16 represents an induction test of the spiked RO-reject sample at 40°C.

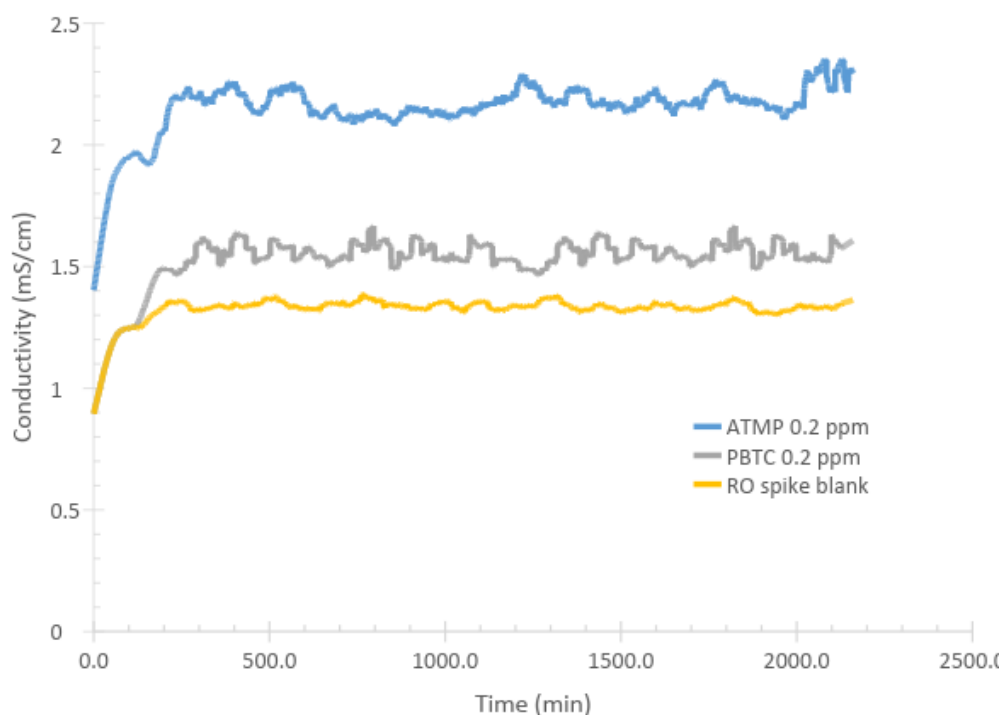


Figure 4-16: Conductivity over time (RO spike sample 40°C)

No signs of CaCO_3 formation existed in the spiked CW-blowdown or RO-reject samples, as there was no drop in conductivity. The amount of calcium and carbonate ions was too low for the temperature and pH conditions during an experimental run time of 6 hours. At 40°C, there was no observable change in conductivity after temperature set point was reached, and given the same situation as for 25°C; the solution and samples were both below supersaturation at 40°C and unable to undergo precipitation of CaCO_3 for the considered time of 6 hours.

All samples were run in duplicate, and the results observed were in most cases similar in both replicates. In some cases, spikes and noise associated with the electronics of the data logging method occurred, and in these cases, the duplicate where the electronic spikes and electronic noise did not occur were selected for representation. The trends were similar for most cases, except in the case of electronic spikes, but the trend remained similar prior to and after a spike had occurred for the duration of the experimental run. Some trends did not show similarity, and in these cases the most representative trend of the theory of anti-scaling agent performance was considered.

pH and actual conductivity and summary of results for 40°C

The initial and final measurements of pH and actual conductivity for the induction time test at 40°C are detailed in Table 4-6.

Table 4-6: Initial and final measurements of pH and actual conductivity at 40°C

Samples at 40°C	pH		Conductivity (mS/cm)	
	Initial	Final	Initial	Final
Control solution	7.6	7.9	0.7	0.9
ATMP dosed control solution	7.5	7.7	0.7	0.9
PBTC dosed control solution	7.5	7.7	0.7	0.9
CW-blowdown	7.5	8.3	2.0	2.4
ATMP dosed CW-blowdown	7.4	7.7	1.9	2.2
PBTC dosed CW-blowdown	7.4	8.2	1.9	2.3
RO-reject	7.8	8.2	1.1	1.2
ATMP dosed RO-reject	7.7	8.3	1.0	1.2
PBTC dosed RO-reject	7.7	8.0	1.1	1.2
Spiked CW-blowdown	7.8	8.2	2.5	2.8
ATMP dosed spiked CW-blowdown	7.8	7.8	2.5	2.6
PBTC dosed spiked CW-blowdown	7.7	8.3	2.5	2.8
Spiked RO-reject	7.8	8.4	1.7	2.2
ATMP dosed spiked RO-reject	7.7	8.5	1.7	2.6
PBTC dosed spiked RO-reject	7.8	8.3	1.8	2.5
* Note: pH accuracy within ± 0.1 and conductivity accuracy was determined within ± 0.1 mS/cm				

Conductivity was determined to be higher for all samples after the experimental run relative to the start of the experimental run. The increase in conductivity was due to a temperature increase of the samples, as ions were able to move more freely with a temperature elevation; hence the conductivity increased.

The pH was noticeably increased after the induction test. Coetzee et al. (2017) claim that this was due to the release of CO₂ gas as temperature was increased. Coetzee et al. (2017) further explains that a decrease in the pH of the solution signified an onset of CaCO₃ precipitation, and in their experiment the pH dropped well below the initial level. Although the pH was lower than the initial value for the Coetzee et al. (2017)

experiments, a conclusion based on pH cannot be inferred, as the considered method did not entail intermediate logging of the pH, as the possibility of a rise and fall in pH may have existed. In terms of conductivity, no signs of precipitation had occurred at 40°C.

4.3.9 Static induction test at 75°C

Experimental induction tests on the samples and solutions at 75°C produced a diversity of results.

Figure 4-17 represents an induction test of the control solution at 75°C.

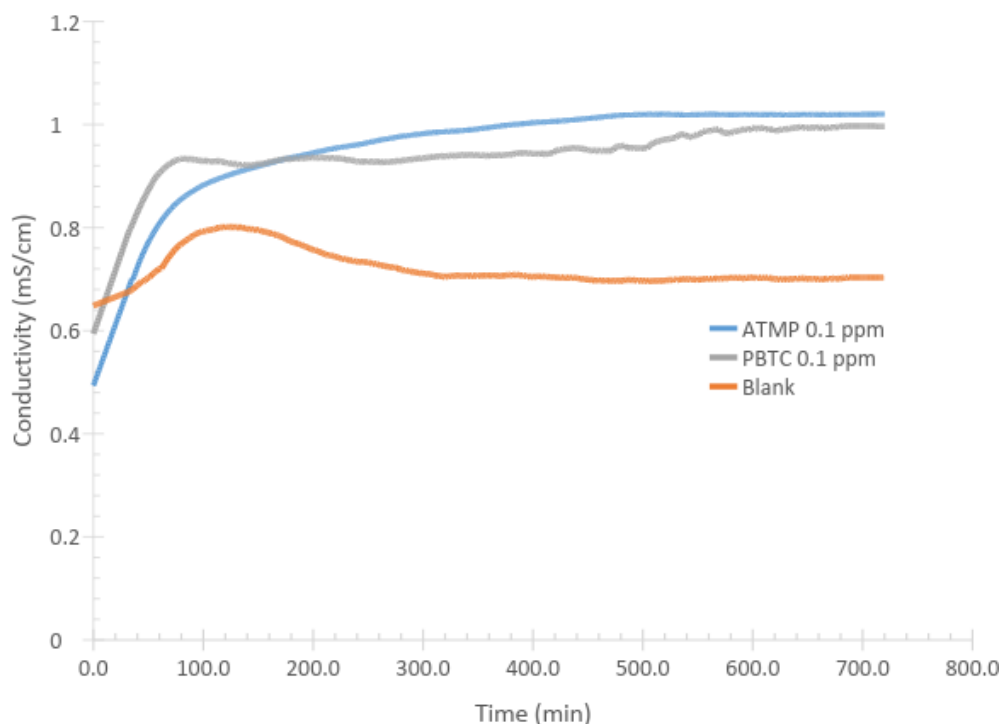


Figure 4-17: Conductivity over time (control solution 75°C)

As seen in Figure 4-17, ATMP performed better than PBTC in terms of induction time for the control solution, as no drop in conductivity occurred for ATMP. The sample containing PBTC showed a very slight decrease in conductivity, whereas the decrease in conductivity of the blank was steeper, starting at 25 min. The slight decrease in conductivity could be an indication of the occurrence of precipitation, but the drop was not large enough to draw a solid conclusion.

Figure 4-18 represents an induction test of the CW-blowdown at 75°C.

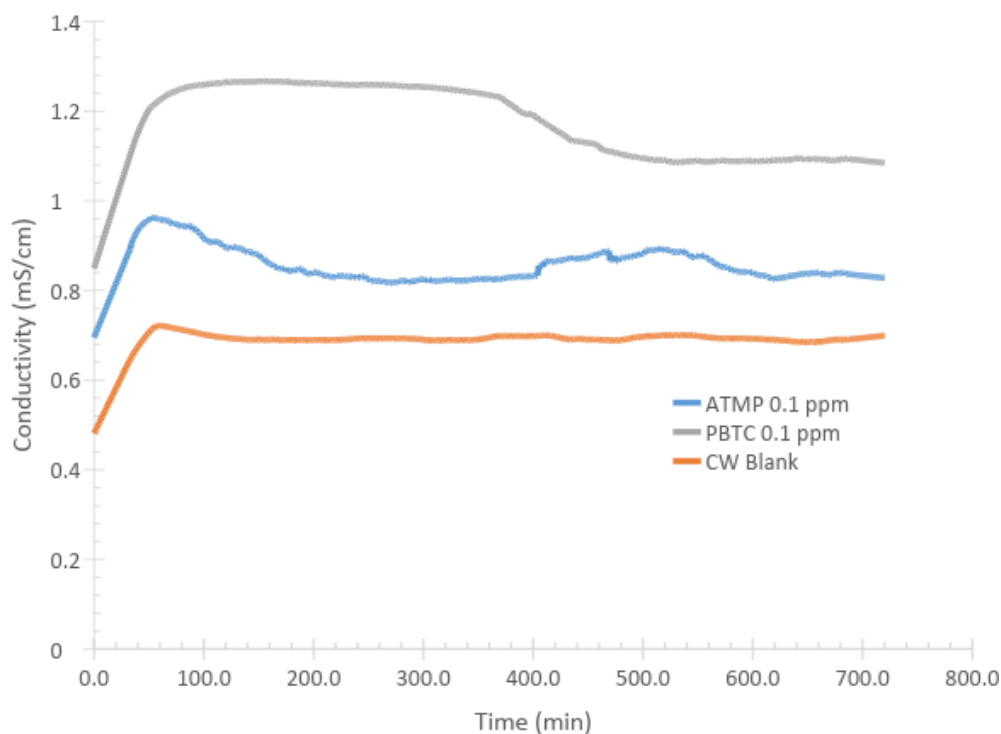


Figure 4-18: Conductivity over time (CW sample 75°C)

In the case of the CW-blowdown sample (Figure 4-18), it appeared that PBTC performed better than ATMP, as the conductivity dropped much later (62 mins) than that of the ATMP sample (12 mins), while an earlier drop (10 mins) was recorded for the blank batch, after which the conductivity remained constant for the rest of the experiment. However, there was no significant difference between the trend observed in the presence of ATMP and the one observed for the blank batch. PBTC performed better than ATMP in the case of the spiked CW-blowdown solution, further supporting the performance of PBTC over ATMP.

The scale potential model predicted that scaling was severe at 75°C and a pH of 7.4 (depicted in Figure 4-3), which was confirmed by the results of the induction test for the CW-blowdown sample at 75°C, as scaling was observed in all samples.

Figure 4-19 represents an induction test of the RO-reject at 75°C.

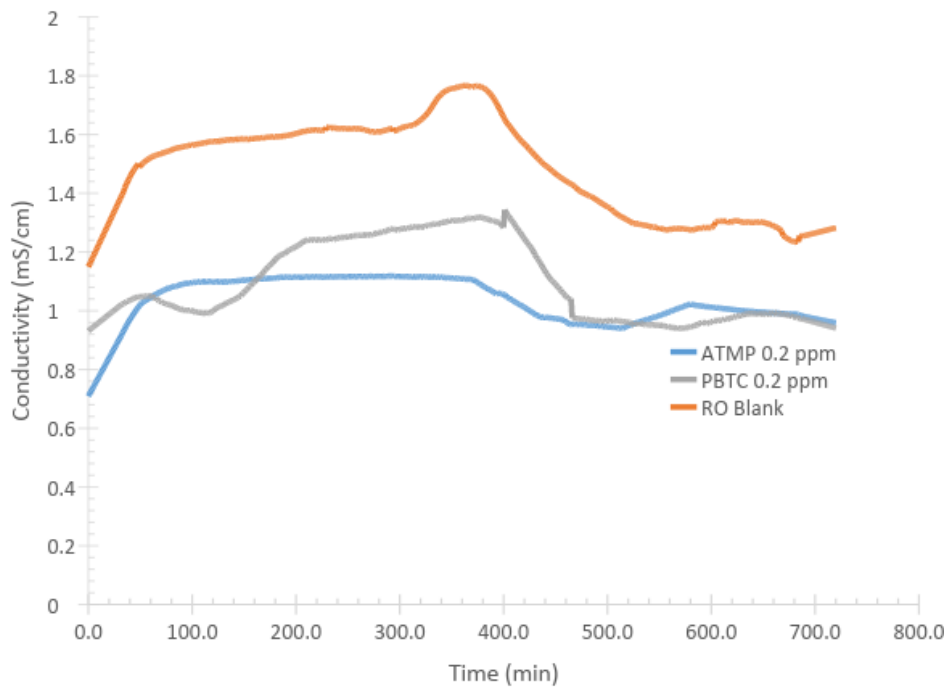


Figure 4-19: Conductivity over time (RO sample 75°C)

For the RO-reject sample (Figure 4-19), the conductivity decreased before the temperature reached 75°C. At high temperatures, scaling becomes significant, which was further supported by the scaling potential model at the conditions of pH 7.8 and 75°C (depicted in Figure 4-4). It can be observed in Figure 4-19 that all the major drops in conductivity were recorded almost simultaneously, although a slight delay by the PBTC could also be identified.

Figure 4-20 represents an induction test of the spiked CW-blowdown at 75°C.

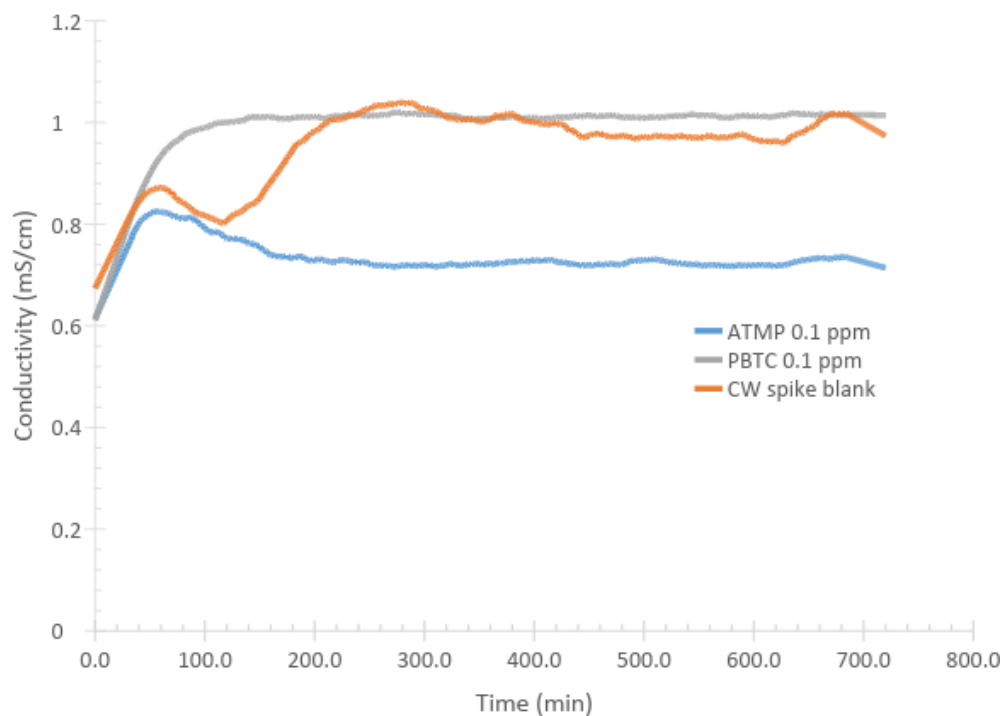


Figure 4-20: Conductivity over time (CW spike sample 75°C)

In Figure 4-20, the blank CW spiked solution showed precipitation at 62°C and 11 mins. In samples containing ATMP, conductivity drops started at 60°C and 12 mins, whereas samples containing PBTC showed no drop in conductivity throughout; hence there were no signs of precipitation.

Figure 4-21 represents an induction test of the spiked RO-reject at 75°C.

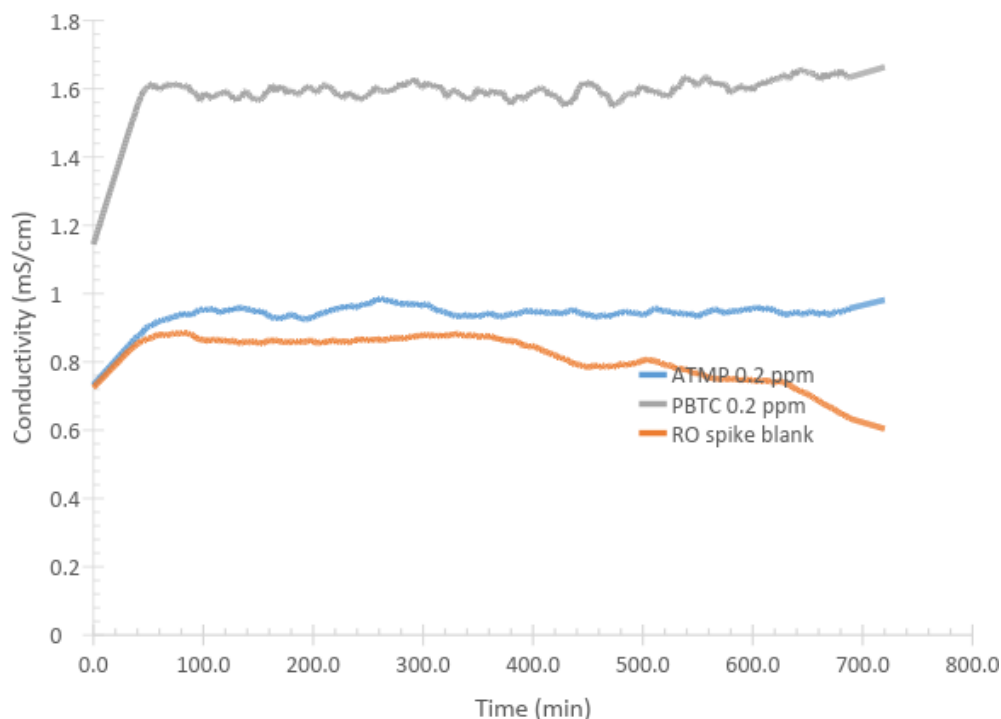


Figure 4-21: Conductivity over time (RO spike sample 75°C)

The spiked RO-reject sample showed no signs of drop in conductivity for the two considered anti-scaling agent dosed samples. The blank spiked RO-reject sample started to drop in conductivity at 65 mins.

Although the experiments were run in duplicate, in some cases, spikes and noise associated with the electronics of the data logging method occurred, and in these cases the duplicate where the electronic spikes and electronic noise did not occur were selected for representation. The trends were similar for most cases, except in the case of electronic spikes, but the trend remained similar before and after a spike had occurred for the duration of the experimental run.

pH and actual conductivity and summary of results for 75°C

The initial and final measurements of pH and actual conductivity for the induction time test at 75°C are given in Table 4-7.

Table 4-7: Initial and final measurements of pH and actual conductivity at 75°C

Samples at 75°C	pH		Conductivity (mS/cm)	
	Initial	Final	Initial	Final
Control solution	7.5	7.6	0.7	0.7
ATMP dosed control solution	7.5	8.1	0.7	1.2
PBTC dosed control solution	7.4	7.8	0.7	1.1
CW-blowdown	7.4	8.0	2.0	2.2
ATMP dosed CW-blowdown	7.3	7.9	2.0	2.1
PBTC dosed CW-blowdown	7.4	8.0	1.9	2.2
RO-reject	7.8	8.2	1.1	1.2
ATMP dosed RO-reject	7.8	8.4	1.1	1.3
PBTC dosed RO-reject	7.7	7.9	1.1	1.1
Spiked CW-blowdown	7.7	8.2	2.5	2.8
ATMP dosed spiked CW-blowdown	7.7	7.8	2.6	2.7
PBTC dosed spiked CW-blowdown	7.7	8.4	2.6	3.0
Spiked RO-reject	7.9	7.7	1.7	1.6
ATMP dosed spiked RO-reject	7.8	8.1	1.8	2.0
PBTC dosed spiked RO-reject	7.8	8.3	1.8	2.3

** Note: pH accuracy within ± 0.1 and conductivity accuracy was determined within ± 0.1 mS/cm*

Both the pH and actual conductivity were higher after the duration of the induction test at 75°C in relation to the initial conductivity and pH. As was the case for the induction test at 40°C, a rise in pH was due to the slow release of CO₂ during the heating stage of the induction test (Coetzee et al., 2017).

The final pH and conductivity were lower than the initial parameters for the spiked RO-reject, where the drop in pH of the solution signified an onset of CaCO₃ precipitation. In terms of conductivity, precipitation had occurred in the blank batches of all the samples for the case of 75°C, as can be seen in Figure 4-17 -

Figure 4-21. While in the presence of PBTC and ATMP, inhibition of precipitation was observed, with PBTC exhibiting an overall better performance in terms of longer induction time.

PBTC and ATMP are both phosphonate type scale inhibitors, and the mechanism/reason for PBTC outperforming ATMP is not clear, as research on the comparison between PBTC and ATMP is not widely available. Väisänen (2011) mentions that the smaller the molecular size of a phosphonate, the better its efficiency due to the adsorption of the inhibitor onto crystal growth sites. This could lead to a blockage for the adsorption of other molecules in the case of larger molecules.

The formula for density, the molecular size in terms of volume of one mole of ATMP and PBTC, is as follows:

$$\rho = \frac{m}{V} \quad \text{Equation 4-7}$$

Where ρ is density (kg/m³), m is mass (kg) and V is volume (m³). The density of ATMP is 1300 kg/m³ and has a molecular weight of 299 g/mol, which correlates to a volume of 2.3×10^{-3} m³. The density of PBTC is 1250 kg/m³ and has a molecular weight of 270.13 g/mol, which correlates to a volume of 2.16×10^{-3} m³. The volume of PBTC was smaller than ATMP, which means that PBTC performed better due to the ability of PBTC blocking more adsorption of other molecules onto the scale forming crystals.

4.3.10 General discussion of possible causes of results

The rate of heat transfer was not high enough, which affected the prediction of the performance of anti-scaling agents within reasonable time, as precipitation may have occurred before reaching the targeted temperature. Thus, an accurate evaluation of the performance of anti-scaling agents could not be achieved, as in the case of this study, precipitation occurred during the heating process.

4.4 Conclusions

Assessing the scaling potential of the different water streams, there was little change in water sample conditions when the temperature of the sample was changed from ambient temperature to 25°C. The conductivity remained constant for all samples, which indicated that the samples were below supersaturated conditions. When temperatures reached 40°C, conductivities remained fairly constant for all samples. Increasing the temperature to 75°C showed a diversity of trends. In some cases, conductivity dropped during the initial temperature increase phase, while in others a drop in conductivity was observed only when the targeted temperature was reached. However, in general the anti-scaling agent PBTC performed better than ATMP, both for RO-reject water and CW-blowdown. Overall, it is important to note that, in the context of a laboratory study aiming to compare the performance of anti-scaling agents, one must ensure that the solutions considered are supersaturated if results are to be obtained in a short time.

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CHAPTER 5: Conclusions and Recommendations

5.1 Conclusions

Eskom currently uses nano-filtration and reverse osmosis as water reclamation and purification technologies in its plants, producing saline water streams that need to be disposed of to adhere to the zero liquid effluent discharge stipulations in its water usage licenses. Due to the abundant heat present at Eskom's power plants and the versatility of Multi-Effect Distillation, a possible theoretical sequence of membrane and thermal technologies could be implemented to approach a zero waste water reclamation process: Firstly, the use of nano-filtration to remove bivalent scaling ions from feed water then treating nano-filtration permeate using RO; secondly, the treatment of nano-filtration retentate to precipitate scaling ions; thirdly, the combination of treated nano-filtration retentate with RO-retentate to be treated using Multi-Effect Distillation – using a method of heating that harnesses some of the abundant heat that needs to be dissipated on the power plant, as well as the correct selection and dosage of anti-scaling agents. The last step of this sequence would be to make use of Eutectic freeze crystallisation to separate the reject from the multi-effect distillation into fresh water and dry salt.

In this study, a bench scale single effect evaporator (using the same principles and conditions produced in multi-effect distillation) was designed and constructed to examine the water recovery potential from waste water streams produced at Eskom's power plants when using the correct anti-scaling agents. Reverse osmosis retentate from the Lethabo Power Plant was treated in the bench scale single effect evaporator with and without the use of scale inhibiting agents.

The bench scale single effect vacuum evaporator exhibited a performance that complied with all the design requirements. The vacuum inside the vessel was maintained between 0.4 and 0.44 bar, with the steam temperature varying between 78°C and 80°C. The evaporation rate of the RO-retentate was volumetrically measured to be 4l/h (22.3L/m²/h), and this was verified by PHREEQ-C modelling software. The improved structural integrity of the evaporator and vacuum pump cooling adaptations combined with the doubling of heat exchange surface area increased the evaporation rate from 1.25l/h to 4l/h. This implies that roughly 34.5% of the feed water/RO-retentate was evaporated that may theoretically be recycled while absorbing some of the abundant heat present at the power station to in turn lower the amount of cooling water needed. The speciation using PHREEQ-C modelling software further showed that evaporation increased the concentration of scale forming agents. The dosage of the software (French Creek) determined anti-scaling agents inside the MED yielded confirmation of their capability of keeping scale forming ions in suspension and not allowing them to scale. When measuring the performance of the anti-scaling agents on this basis, AMPS fared better than PBTC, while HEDP yielded concentrations of scale forming ions lower than when no anti-scaling agent was used. This may be ascribed to the nature of complexes that HEDP forms with the scale forming ions.

The MED reject will be suitable for further treatment using a technology such as Eutectic freeze crystallisation technology to produce fresh water and salts. Thus, based on the literature, a combination of a membrane technology and a thermal technology could be theoretically utilised in order to adhere to the zero liquid effluent discharge policy adopted by Eskom, whilst lowering the amount of fresh water needed for cooling purposes.

When evaluating selected anti-scaling agents in the laboratory, certain conclusions came to light, and these will be described according to the temperatures at which the experiments were performed:

There was little change in conditions when the temperature of the sample was changed from ambient temperature to 25°C. The conductivity remained constant for all samples, which indicated that the samples were below supersaturated conditions.

When the temperature reached 40°C, the conductivities remained fairly constant for all samples.

Increasing the temperature to 75°C showed a diversity of trends. In some cases, conductivity dropped during the initial temperature increasing phase, while in others a drop in conductivity was observed only when the targeted temperature was reached.

However, in general, the anti-scaling agent PBTC performed better than ATMP, both for RO-retentate and CW-blowdown. Overall, it is important to note that, in the context of laboratory study, aiming to compare the performance of anti-scaling agents, one must ensure that the solutions considered are supersaturated if results are to be obtained in a short time.

5.2 Recommendations

With regard to the MED paired with anti-scaling agents, it is recommended that the evaluation of the anti-scaling agents be further investigated by means of heat transfer efficiencies, as the active ingredients of anti-scaling agents remain poorly understood when considering the unique composition and nature of the water on which the anti-scaling agents are being tested.

An improved method of testing the anti-scaling agents is proposed, whereby the induction tests are performed using a closed jar cylinder. The water should be at the conditions required prior to dosing anti-scaling agents. A closed jar can better aid in controlling the temperature and pressure while keeping the contents constant by overcoming excessive evaporation of water. An accurate and reliable measuring device should be used, and more variables should be taken into consideration, such as pH, which can allow monitoring of the behaviour of critical elements or compounds in solution, such as bicarbonate, carbonate and carbon dioxide content. Increasing the rate of heat transfer could allow the prediction of the performance of anti-scaling agents within reasonable time, as precipitation may be occurring before reaching the targeted temperature. Accurate evaluation of the performance of anti-scaling agents could be achieved by designing a system that will shorten the heating time required to reach the targeted temperature,

as in the case of this study, precipitation occurred during the heating process, affecting proper evaluation of the performance of anti-scaling agents.

Appendix A: MED Designs

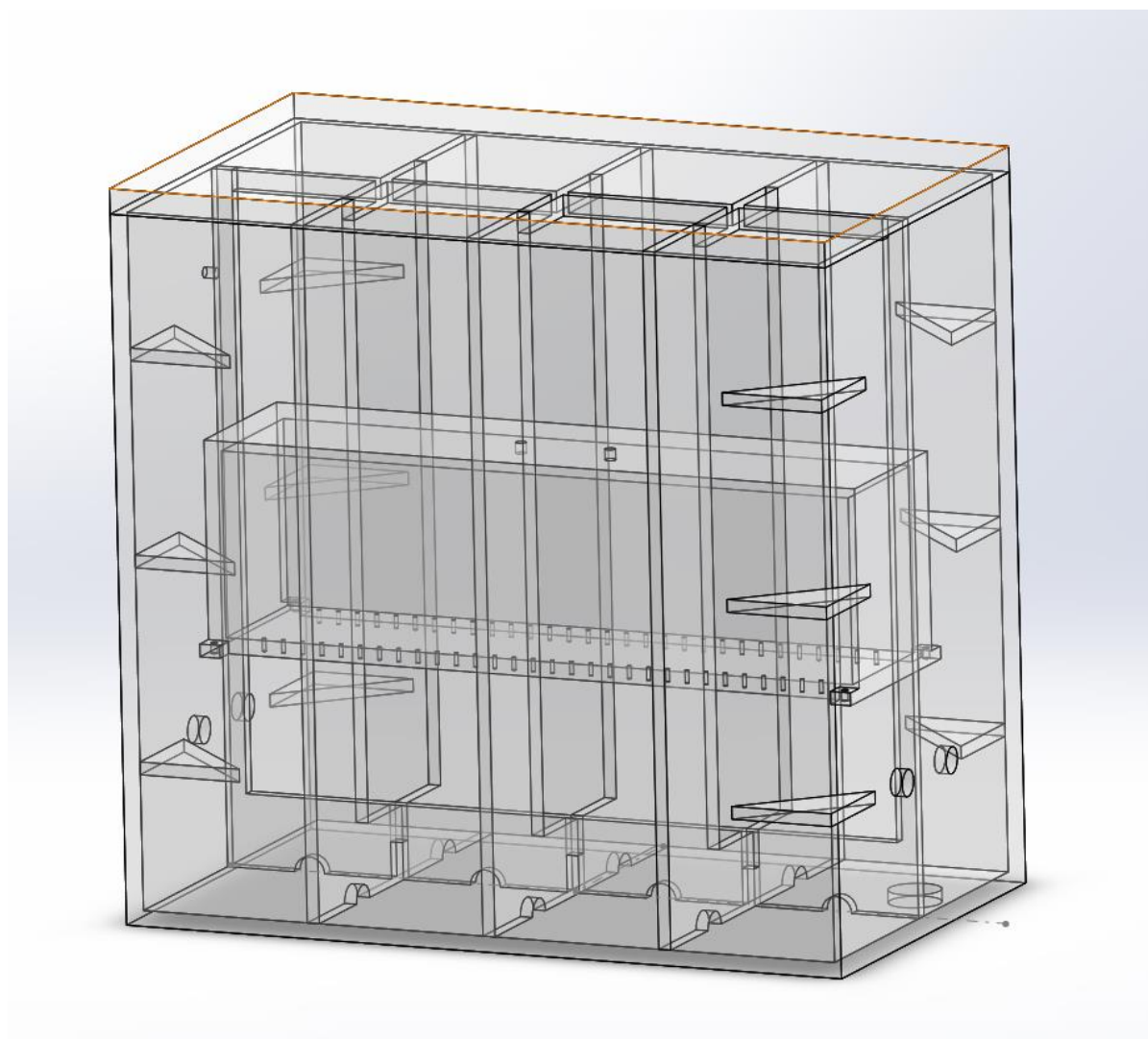
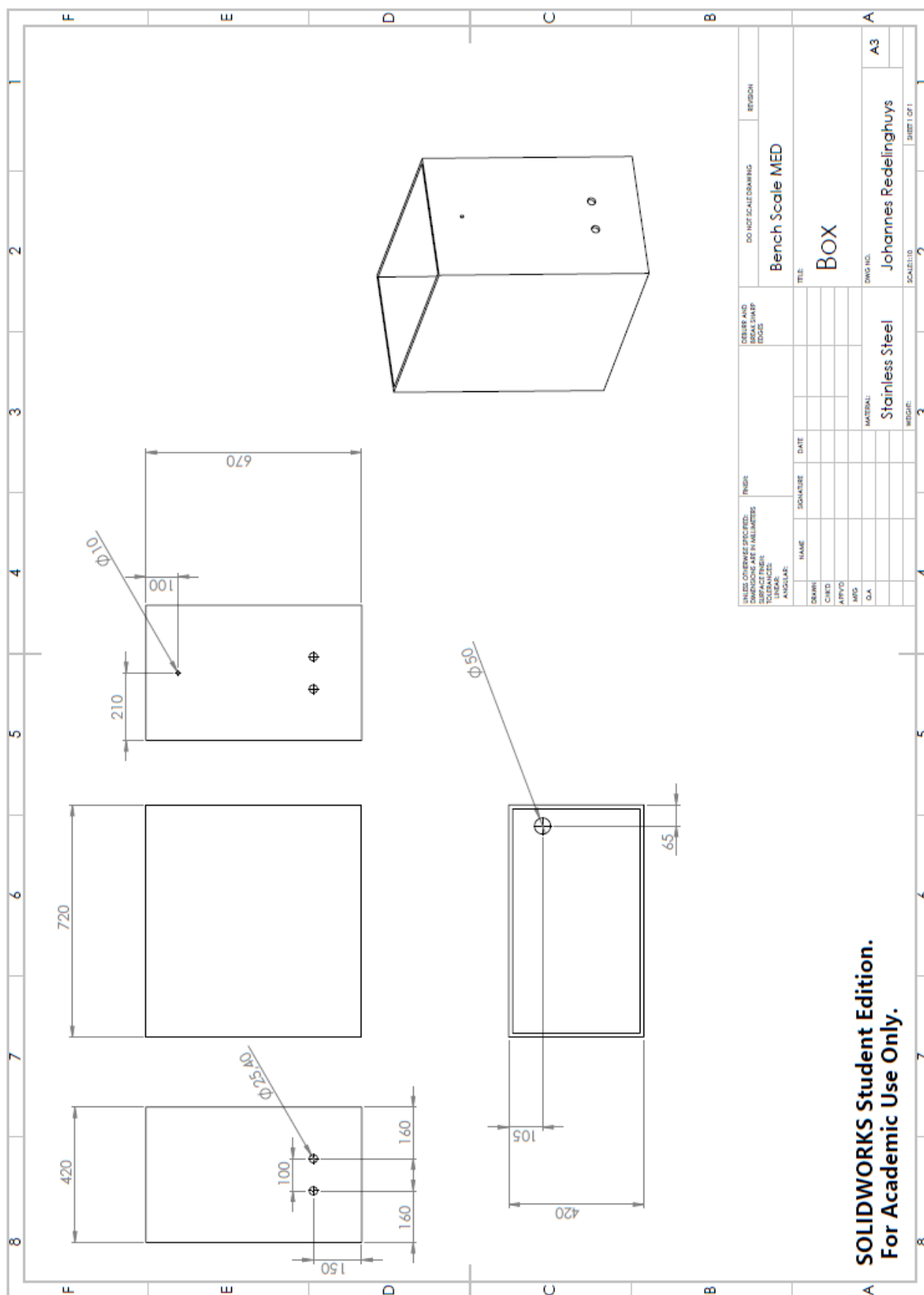
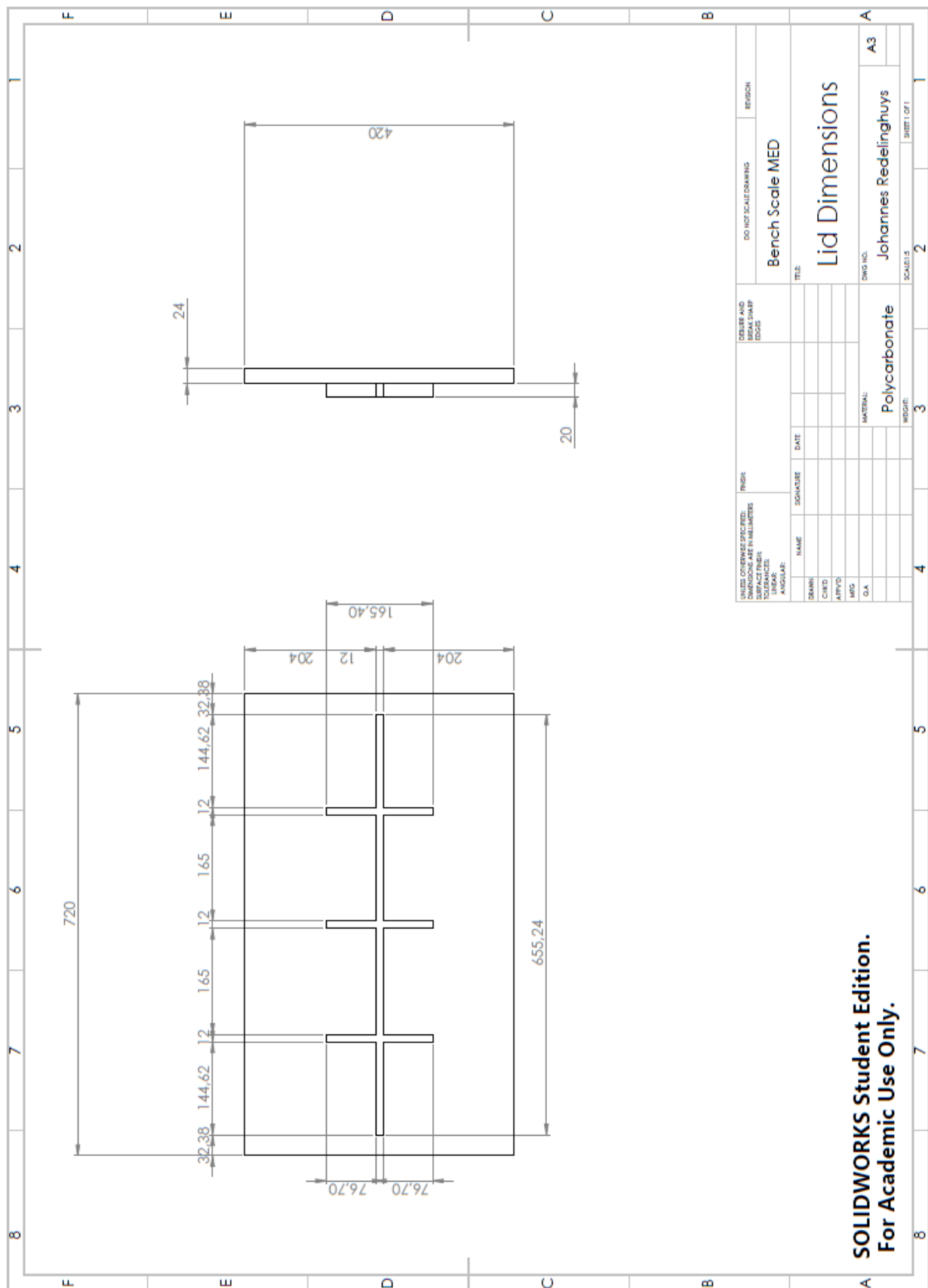
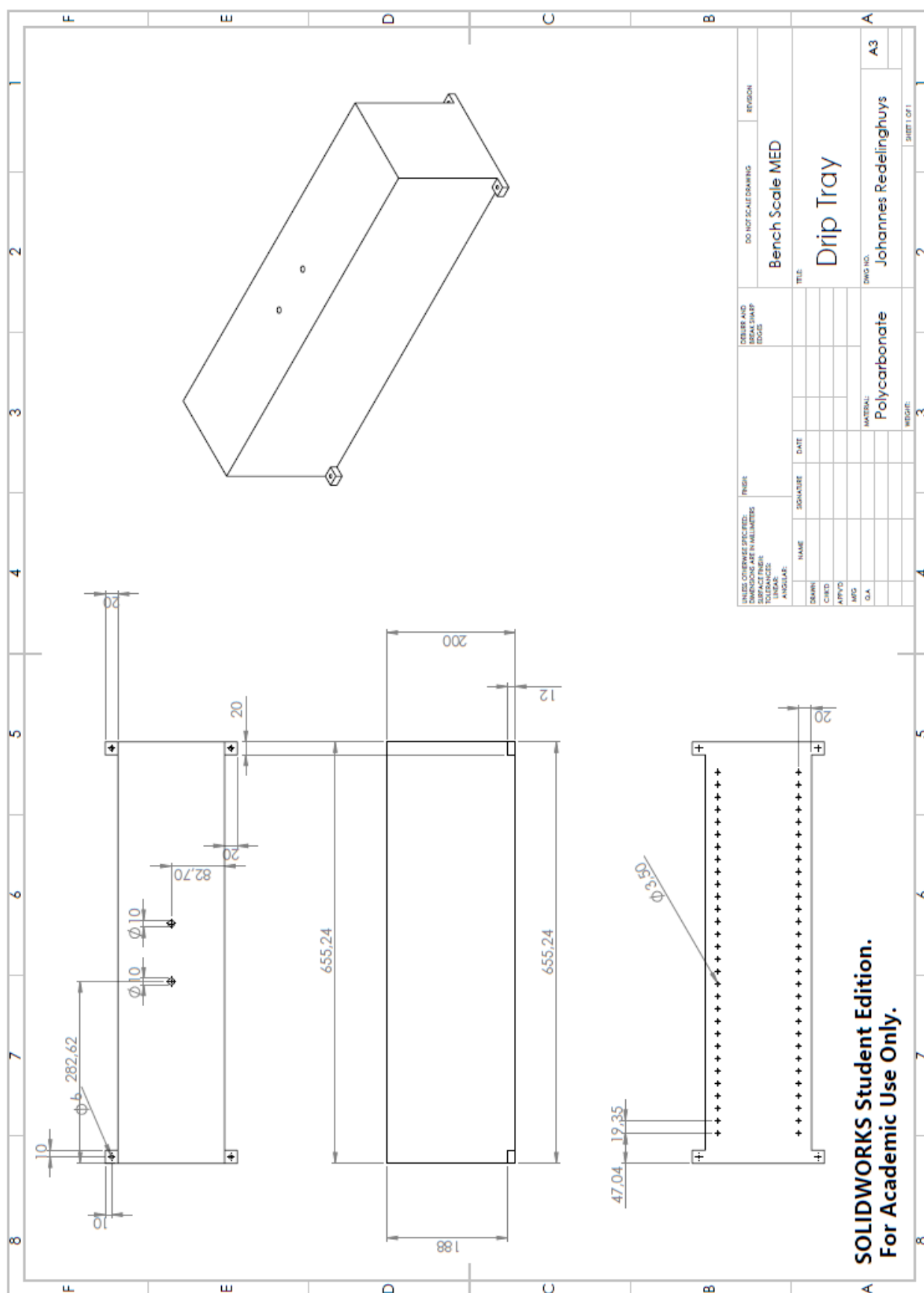
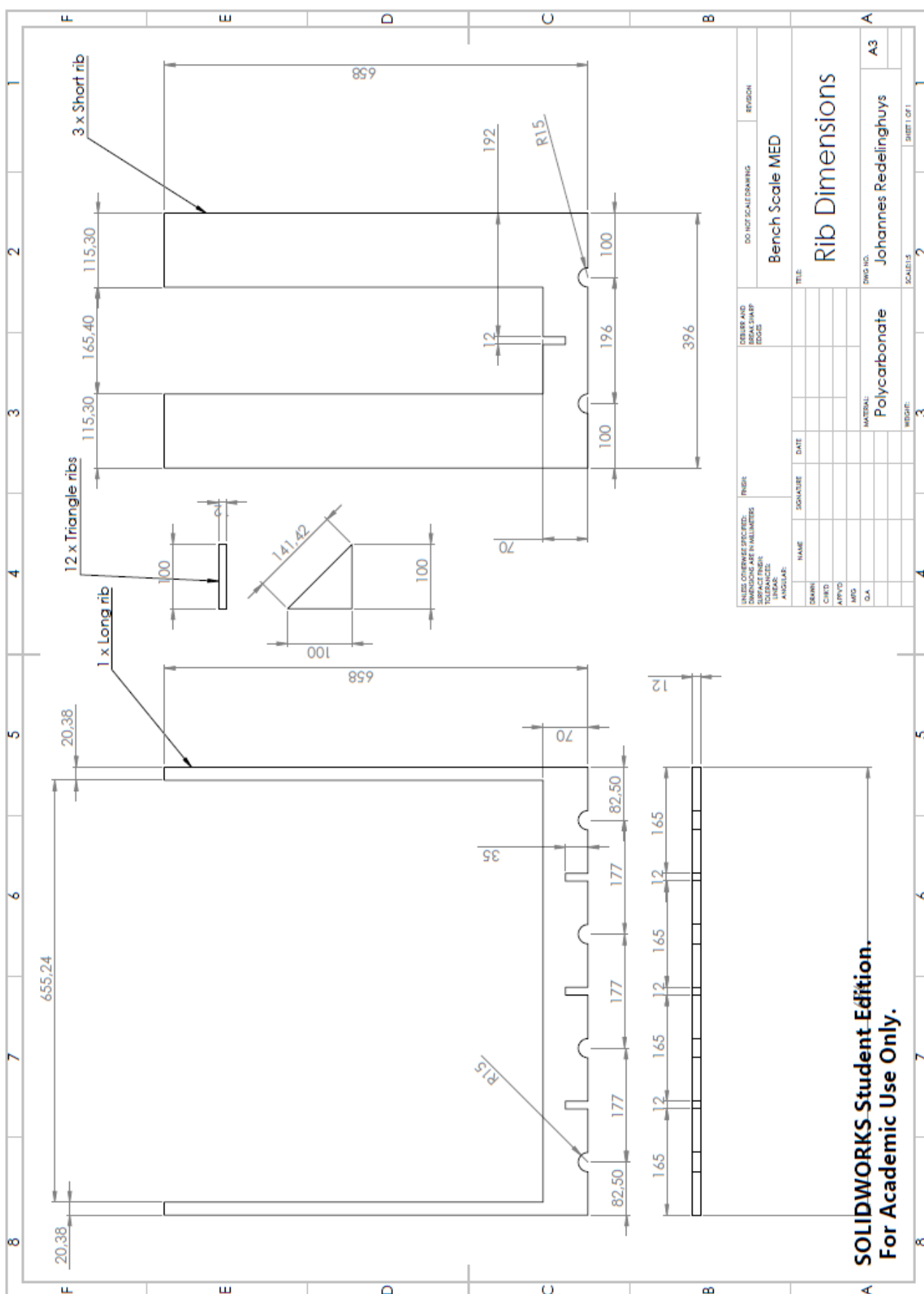


Figure A-1: 3D Assembly of designed MED









Appendix B: Academic and Technical Outputs

9th Int'l Conference on Advances in Science, Engineering, Technology & Waste Management (ASETWM-17) Nov. 27-28, 2017 Parys, South Africa

Scaling Conditions Inside Improved Bench-Scale Single Effect Vacuum Evaporator

Redelinghuys J, Fosso-Kankeu E, Waanders F, Rogers D, Gericke G

Abstract— An investigation into the potential of scale formation during the application of MED (Multi-Effect Distillation) technology for the treatment of Reverse Osmosis (RO) Retentate was carried out in this study. An improved bench scale single effect evaporation unit was designed using Solidworks Simulation Package and appropriate materials. Operating conditions were determined to be 80°C and 0.48 bar with the design constructed to maximize evaporation. Once assembled, RO Retentate was introduced to the evaporator and an evaporation rate of 4L/h (22.3L/m²/h) and the variation of the concentrations of scale forming elements determined – the evaporation translates to 34.5% water recovery. Speciation using PHREEQ-C modelling software showed that the concentrations of scale forming agents such as CaCO₃ and CaSO₄ increased after evaporation. Scale prediction was explored using French Creek software.

Keywords— MED, scale formation, RO retentate, PHREEQ-C, French Creek.

I. INTRODUCTION

South Africa is a water-scarce country. Water consumers are forced to explore the utilization of all available water sources, and the water scarcity is being worsened by climate change. Despite the water shortage the country is facing, the demand for water usage in industry and for human consumption stays high, creating an ever-increasing dependence on seasonal rainfall. Wastewater effluent is becoming more valuable as advances in technology makes the recovery, treat and re-use of waste water more attractive [1 – 11]. When water is being treated and re-used, a common occurrence whenever any form of heat exchange or membrane is used, scale is prone to form when not properly avoided [11]. Eskom, South Africa's National Power Utility, is allocated 2-3% of the national available fresh water to generate electricity. Eskom is however under pressure to minimize its water usage and has set a target of lowering its usage to 1.34L of water per kilowatt electricity produced by 2020, from the 1.39L/kW presently [12, 13]. Of

the total water intake, 98% is lost via evaporation in the cooling towers of the power plants. The re-usage of certain streams can potentially lower the amount of freshwater in-take needed to replenish the amount of water lost due to evaporation. Eskom, has thus initiated an investigation towards water management and proper usage of all available waters sources. Reject from the primary RO module is high in salinity and the recirculation through the RO system is not economically viable. Sea-water of high salt concentration has been treated using multi-effect distillation (MED) systems encouraging the usage of this technology for this application [4]. Most MED-Evaporators makes use of the horizontal tube evaporation principle. This principle makes use of a distribution system that evenly distributes water on top of a bundle of horizontal tubing. The water then flows from tube to tube partially evaporating on the tubes. A typical tubing network usually evaporates around 33.3% of the feed water [14]. A limitation of such a system is the scale formed on the heat exchange surfaces due to the quality of the water, therefore negatively affecting the efficiency of the MED [15]. This implies that MED technology could be hybridized to the existing water treatment system as it will help Eskom adhere to their zero liquid effluent discharge (ZLED) policy as stipulated in their water use licences [11]. The application of this technology to treat inland and waste waters will see the MED-evaporator possibly serving a dual-purpose. The primary purpose of MED is to serve as water producing/recycling technology that can treat brine solutions. The secondary purpose of the technology when applied to a power plant will be to dissipate some of the abundant heat present – alleviating the amount of heat energy the cooling towers must dissipate to some extent thus lowering the amount of cooling water needed [16]. Scaling potential can be determined by using PHREEQ-C, an open-source modeling package developed by the US Geological Survey [17]. French Creek software can also be used as it combines multiple saturation and stability indices to accurately predict the scaling potentials of the minerals present in the water. This is similar to PHREEQ-Cs capabilities but with the additional capability of predicting which anti-scalant will yield the best results and the simulation of the addition thereof [18].

Scaling is caused by concentrated minerals in water when they become insoluble. When mineral constituents remain soluble, they have no negative effect on heat transfer efficiency [19].

Scale formation occurs in alkaline water, and is attributed to the presence of scale forming ions such as Ca²⁺ and/or Mg²⁺. Calcium carbonate is one of the most common scale forming

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Figure B-1: Scaling conditions inside improved bench-scale single effect vacuum evaporator

minerals [20]. Process parameters however, do play a role in the scale formation within a pipe-system, especially temperature and flow rate [15], as these parameters can influence deposit (scale) structures, shape, size and composition.

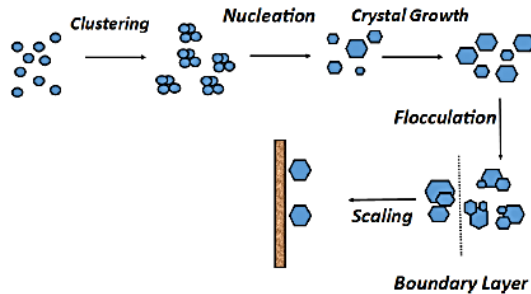


Fig 1: Schematic of processes involved with the formation of mineral (Reproduced from [21])

It is apparent that there are multiple steps involved in scaling, and these steps will be briefly explained with a schematic representation thereof in Figure 1.

When mineral ions are present in water, and if these ions become more concentrated over time, the ions present will eventually become abundant enough for the water to be supersaturated with these ions. Mineral ions under increasingly supersaturated conditions will, due to their polarity and random thermal motion, form clusters. Once these clusters pass a critical size, nucleation will take place. As soon as nuclei are formed, spontaneous crystallization will take place forming larger particles. Subject to the surface properties and composition of these particles, the particles can either aggregate to create larger particles, or stay suspended in the water for a period. After enough time these particles and present mineral ions will diffuse through the hydraulic boundary layer [21] and form scale after depositing onto a solid surface.

In this study, reverse osmosis (RO) retentate from Lethabo Power Plant was evaporated in an improved bench-top single effect evaporator and the variation of the concentration of scale forming elements evaluated.

A. Operating Conditions

1) Temperature

The evaporator's heat source is a steam generator that will supply steam through the heat exchange surface. There is one drawback regarding the steam generator as heat source – the temperature of the steam. The steam will have a temperature higher than the critical temperature where scaling is prone, as it has been reported that at a temperature above 80°C, the rate of scale formation is substantially increased [15].

2) Pressure

When evaluating pure water's saturation pressure as described by Milo Koretsky, and by making use of the software that accompanies the handbook "Engineering and

Chemical Thermodynamics" namely "Thermosolver" certain operating parameter targets can be determined [22]. The Saturation Pressure Calculator of the Thermosolver software package uses the Antoine Equation of state, and the results are displayed in Table 3. The ambient pressure of Potchefstroom is 0.875 bar, and this was considered when determining the vacuum needed at different temperatures.

TABLE 1: OPERATING PARAMETER TARGETS OF EVAPORATION CHAMBER

Temperature	Solver Saturation Pressure (bar)	Size of vacuum needed (bar)
75	0,38559	0.4013
80	0,4737	0.48941

Thermodynamically, when a temperature target of 80°C is achieved, the pressure inside the evaporation chamber of the MED needs to be as close to 0.47 bar as possible for optimal evaporation to take place as this is the saturation pressure of water at 80°C.

3) Materials

The scale forming properties of the materials combined with the strength and effect of temperature of the materials to be used had to be evaluated, as the material will be exposed to a pressure reduction, high temperature and water with an increasing scaling potential.

The design of the evaporator can be divided into three main components. The evaporation chamber, the dual heat exchange surface running through the evaporation chamber, and drip tray that dispenses the water onto the heat exchange surface inside the evaporation chamber.

Polymers and certain polyvinyl chlorides are deemed appropriate materials to be used when constructing the evaporation chamber of the evaporator as well as the drip tray as these polymers will not influence the concentrated water (RO retentate) that will be used in the evaporator, as these materials are scaling resistant [23]. Stainless steel has an unreactive nature with regards to scaling potential, largely due to the unavailability of nucleation sites available for the scale to attach to [24] and will be used inside the evaporation chamber to control the height of the drip tray above the heat exchange surface.

The dual heat exchange surface inside the evaporator is metallic to provide the necessary heat conductivity needed at the exchange surface. Cu-Ni as well as copper alloys have been used as successful heat exchanging surfaces especially in seawater cooled heat exchangers [25], with a mild corrosion resistance [20]. When comparing the high salinity of seawater to RO retentate, copper will perform as a sufficient heat exchange surface due to its mild corrosion resistance. Without proper pre-treatment, the copper heat exchange surfaces are mildly susceptible to scaling.

The material of the pump that recycles the brine from the evaporation chamber to the drip-tray is exposed to the high scaling potential water, and must thus be constructed with appropriate materials. A magnetically driven, single stage, centrifugal pump constructed using thermoplastics will suffice due to its chemical resistance.

These three key components are depicted in figure 2:

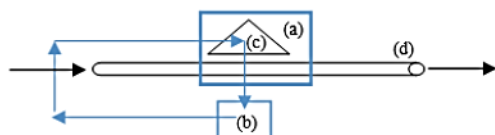


Fig 2:: Main components in MED design; (a), evaporation vessel; (b), recycle pump; (c), drip-tray; (d), heat source/exchange surface.

II. DESIGN & CONFIGURATION

A. Evaporation Chamber

The initially commissioned bench scale MED [26] had a few areas where it had to be improved to conduct more realistic and extensive experiments. Firstly, the structural integrity of the evaporation chamber had to be significantly improved to increase the vacuum applied to it without the structure failing [26]. The initial bench scale MED could function with a pressure reduction of 0.09 bar before the risk of structural decomposition occurs.

Simulation on Solidworks (3D design and simulation software whilst evaluating a range of polycarbonate thermoplastics resulted in a material selection and design consisting of multiple and extensive internal rib structures. The Solidworks Simulation Packet recommended a material thickness of 12 mm.

To characterize the effects of time, temperature and environment on polycarbonate thermoplastic, Loughborough University (UK) performed widespread testing on a polycarbonate (PC) thermoplastic over a year long period of time, the evaluation was conducted at temperatures ranging from -40 °C to 140 °C. The tensile strength of the material determined in this investigation is at 80°C stays well above 300 bar [27].

It is thus apparent when examining the material properties that the Solidworks design simulation yielded satisfactory results and that the design's structural integrity will not be compromised when exposed to the target pressure reduction of 0.41 bar.

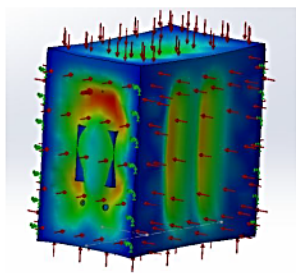


Fig 3: Solidworks simulation displaying a maximum displacement of 4 mm

B. Vacuum Pumps

The vacuum pumps' characteristics were of such a nature that changes had to be made to accommodate them. The problematic area being the operability of the current vacuum

pumps as they are operating very near to and above the recommended temperature ranges with the initial recycling closed circuit cooling water configuration.

The vacuum pump's cooling system needed to be altered to a 'once through' system from a recirculating system to run the pumps for a longer period whilst preventing the risk of overheating.

C. Drip-Tray

The drip-tray had to fulfill a dual-purpose. Firstly, the drip-tray plays a key part in the structural integrity of the evaporation chamber. Secondly, laminar flow of water onto the heat exchange surface. Multiple factors influence the latter named; namely the size and distance between the apertures, the distance the drip-tray is above the heat exchange surfaces being the factors carrying the most weight when designing the evaporator. Other factors include: flow rate of the water moving through the drip tray, turbulence of flow inside the drip tray, the conductivity of the heat exchange surface and the length of the heat exchange surface. Consequences when not designed correctly include decreased heat exchange efficiency and increased scale formation.

D. Operation

To achieve the ideal operating conditions, the temperature of the steam providing the heat needs to be lowered to below 80°C, and a vacuum of 0.41 bar needs to be created inside the evaporation chamber. This will be achieved with the incorporation of two Busch LX 0030-0430 B Vacuum Pumps. One creating a vacuum inside the evaporation chamber to increase evaporation at the lowered heat exchange surface temperature, and the other lowering the temperature of the steam flowing through the heat exchange surface.

E. Method of Evaluating MED Performance

Due to the once-through cooling of the vacuum pump that removes the vapour from the evaporation chamber, an accurate measurement of amount of water evaporated measurable will be challenging due to the addition of the cooling water inside the pump before entering a catchment tank. The method in which the amount of water evaporated will be calculated, will be by making use of Phreeq-C software to verify the volumetric calculations and level differences inside the MED. This software includes the PITZER database and calculation capabilities which include determining the amount of water evaporated based on the increase in the concentration of the minerals present.

III. METHODOLOGY

A. Assembly

Once the design was finalized and materials obtained, the assembly entailed milling the polycarbonate to the right sizes where after it was glued together. Stainless steel fittings and un-reactive reinforced plastic piping was used to assemble the closed water circuit running from the evaporation chamber to the recycling pump to the drip tray. The piping was further reinforced with stainless steel springs to ensure the vacuum will not influence the flow of the brine/water. The available

steam supply piping had to be adapted and positioned to the inlet of the MED with valves to control the supply and pressure with pressure and temperature gauges before, inside and after MED. A frame to house the different components was also designed and constructed. A silicon sheet lining was used as sealant beneath the lid of the MED to ensure an airtight seal. A continuous cooling liquid supply with buffer tank was incorporated to the design to ensure adequate vacuum pump operating temperatures.

B. Water Sampling and Analysis

Water/RO Retentate was sampled directly from Lethabo Power Plants RO-Retentate Stream using clean and dry 25l containers. Samples were sent for analysis to Midvaal Water Company, as their Scientific Services division and laboratory is SANAS (South African National Accreditation System) accredited. The results from this analysis were used for scale formation modelling.

C. Operation and Control of MED

The control of the MED comprises of the manipulation of various valves. The pressure valve on the steam supply line provides the means of altering the temperature of the steam entering the MED as the steam supply is placed under vacuum. A pressure regulating valve on the MED provides the means to manipulate the pressure in the MED. A valve regulating the flow from the recirculation pump provides the means of influencing the flow to the drip tray – ultimately the flow of water onto the heat exchange surface

IV. RESULTS

A. Performance of MED

1) Parameters

The targeted parameters were obtained. A steam supply temperature varying between 78°C and 80°C, paired with a vacuum varying between 0.40 and 0.44 bar inside the evaporation chamber of the MED ensured rapid evaporation. The temperature inside the MED stabilized at 60°C with the steam exit temperature stabilizing around 50°C.

2) Evaporation Rate

When evaluating the water level pre-and post-evaporation, an 8cm level difference translated into 24L of water being evaporated from the initial 70L over a 6-hour run time. Displayed in Figure 5 is the water flow onto the heat exchange surfaces.

B. Analysis of Water

The water prior to the evaporation and after evaporation were both analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to determine the elements present and to view the increase in concentration. These analyses were then used for scale prediction and modelling. Displayed in Table 2 is the increase in concentration of certain scale influencing and forming elements:



Fig 1: Drip tray's laminar water flow distribution on-to heat exchange surfaces

TABLE II: CONCENTRATION IN MG/L OF A) RO-RETENTATE BEFORE MED-EVAPORATION AND B) AFTER MED-EVAPORATION

Element:	a)	b)
K	10100	13400
Ca	2830	3310
Na	2000	1340
Mg	174,92	231,83

C. Prediction of Scale Formation and Modelling

Using the initial water analysis from Midvaal Water Company as input parameters paired with the operating conditions inside the MED the Figures 5,6 and 7 reveal temperature and pH at which Aragonite and Calcite are supersaturated and the Langelier Saturation Index.

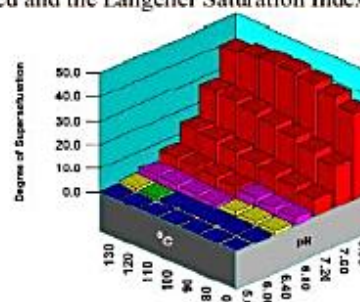


Fig 2: Aragonite Saturation Level vs Temperature vs pH

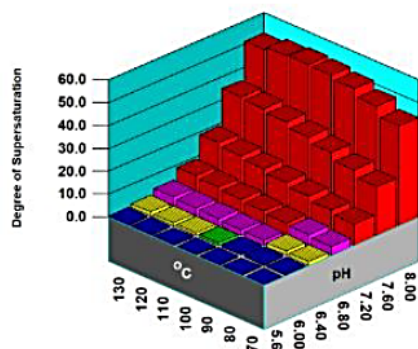


Fig 3: Calcite Saturation Level vs Temperature vs pH

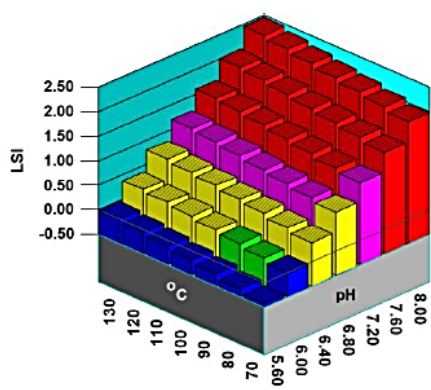


Fig 4: Langelier Saturation Index

These graphs were generated using French Creek Modelling Software.

French Creek software has thus confirmed that scale will form and that various elements will become over saturated at 80 °C, 0.48 bar pressure and a residence time of 6 hours. When using Phreeq-C modeling software, the amount of water that evaporated is slightly less than the volumetrically determined amount, depending on which element's balance used. When evaporating 24L of water with this modelling software differences from ICP-AES analyses occur as displayed in Table 6. The reason for this difference is because Phreeq-C did not take the scale formed on the heat exchange surface into account. According to the Phreeq-C modelling roughly 13L of water should be evaporated to obtain identical Calcium concentration to the ICP-AES analyses, but when taking the scale formation on the heat exchange surface into account and evaluating the increase of other non-scaling elements into account, 24L of water evaporated is deemed a realistic and accurate measurement. Furthermore, the speciation of elements before and after evaporation shows that more scale forming agents such as CaCO_3 and CaSO_4 are likely to occur after evaporation than in the feed water; implying that scale formation will probably takes place .

V. CONCLUSION

The designed bench-scale single effect vacuum evaporator exhibited a performance that complied with all the design requirements. The vacuum inside the vessel was maintained between 0.4 and 0.44 bar with the steam temperature varying between 78° and 80 °C. The evaporation rate of the RO-Retentate was volumetrically measured to be 4l/h (22.3L/m²/h) and this was verified by making use of PHREEQ-C modelling software. The improved structural integrity of the evaporator and vacuum pump cooling adaptations paired with the doubling of heat exchange surface area increased the evaporation tempo from 1.25l/h to 4l/h. This implies that roughly 34.5% of the feed water/RO-Retentate was evaporated that can then theoretically be recycled whilst absorbing some of the abundant heat present at the Power Station to in turn lower the amount of cooling water needed. The speciation using PHREEQ-C modelling software further shows that evaporation increases the concentration of scale forming agents, requiring the use of anti-scaling agents if the evaporator is to be operated for longer period of time.

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Determination of Suitable Anti-Scaling Agent to Inhibit Scale Formation of Water Processed in Coal Power Plant System

Elvis Fosso-Kankeu*, Christopher.E. Brider, Johannes Redelinghuys, Gerhard Gericke, Nico Lemmer and Frans Waanders

Abstract— Increasing pollution and scarcity of fresh water have prompted the need to develop and implement effective strategies to treat wastewater and reduce water usage. One such a strategy is to recirculate waste water in a power plant, but this strategy necessitates treatment. The considered water contains high levels of scale forming ions. Scale formation needs to be controlled, to practically increase the feasibility of recirculation processes. The selected test method to determine anti-scalant induction times is found to be inefficient and an improvement on the current method is proposed, and the possible causes for the inefficiency of the selected induction time test method highlighted. The main finding in this study was observed at 75°C as the anti-scalant PBTC performed better than ATMP; the former exhibiting longer induction time in reverse osmosis reject water.

Keywords—Anti-scalant, Scale, PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid), AMTP (Amino Trimethylene Phosphonic Acid), Cooling water.

I. INTRODUCTION

Water is the single most important resource to sustain biological life. Due to the importance of water, the conservation thereof is becoming more significant. “The 2015/16 drought was the most severe in 23 years, leading to all South Africa’s provinces, except Gauteng, being declared disaster areas” [1]. Coupled to that is the growing industrial pollution which put more pressure on the limited fresh water resource [2 - 17]. The high concentration of scale forming agents in such polluted water may pose significant problems when considering treatment through membrane or thermal technology. Scale build up in heat transfer units such as heat exchangers and membrane filters causes a decrease in the efficiency of heat transfer in a chemical or power plants cooling water system [18 - 20]. Maintenance to bring the

equipment back up to working efficiency, needs to continuously be implemented and during maintenance, production could decrease and economic factors are negatively influenced. If membranes and other equipment work less efficiently due to scale build up during operation, more water is wasted which could have being used as supply for drinking water or any other necessary use.

The determining factors of water shortages, will not only be determined by current main causes such as droughts but will also be determined by increased population growth. [21] “The Water Research Commission (WRC) emphasized the need for water resource managers and planners to think outside the box for unconventional water sources, since water shortages stretch far beyond a drought. The South African legislation and regulation forbids industries around the country from discharging waste water in the environment without prior treatment. South African power plants can use the produced waste water more efficiently by recirculation thereof back into the cooling system.

The possible use of process units; which could form part of a cooling water reuse system such as the use of multi-effect distillator to produce water with a sufficient quality from a Reverse-osmosis (RO) reject effluent, encounters the problem of scaling (mostly due to calcium carbonate and calcium sulphate in solutions) which can affect heat exchange capacity [18]. Furthermore, scale formation on reverse osmosis membranes can significantly reduce the water flux through the membrane, necessitating frequent and costly maintenance. Scale forms due to changes in the physical conditions of the water. Anti-scaling agents work to inhibit this formation by interfering with the scale forming mechanism; by interfering with clustering, nucleation, crystal growth, or flocculation. Scaling ions form clusters, thereafter these clusters can grow into crystal structures. Many anti-scaling agent mechanisms have been proposed. One of the more general proposed mechanisms is that anti-scaling agents act to inhibit the onset of nucleation of scaling ions or by inhibiting the crystal growth. [22] propose two kinetic models by which anti-scaling inhibition takes place. Generally anti-scalants do not eliminate the scaling constituents or its tendency; instead they delay the onset crystallization

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Figure B-2: Determination of suitable anti-scaling agent to inhibit scale formation of water processed in coal power plant system

(nucleation phase of crystallization) or retard the growth of mineral salt crystals (growth phase of crystallization) [22]. An example of an anti-scaling agent is polyaspartic acid, which is non-toxic, does not contain phosphorous and shows good biodegradability and the carboxylic, hydroxylic and acylamino functional groups in its chemical structure are what give this chemical its scale inhibiting properties, but does not show great inhibiting performance [23]. The functional groups having certain affinities to different scale forming substances.

By adding a suitable anti-scaling agent or a combination of more than one anti-scaling agent, the industry in turn could decrease maintenance costs on relevant equipment [26, 27]. A suitable method for determining anti-scalant induction time needs to be established and factors unaccounted for need to be taken into consideration while modifying the current method. Data from the current method of anti-scalant testing are analyzed and the possible cause of the failure of the method suggested.

II. EXPERIMENTAL

A. Materials and Methods

Sampling location was at Grootvlei coal fired power plant, where two water streams were sampled; cooling water blowdown/bleed off stream (CW-Blowdown), with a conductivity of 1.976 mS/cm and pH 7.4 and RO-reject stream, with a conductivity of 1.076 mS/cm and pH 7.8. The water was stored in a fridge under a dark cover, eliminating light and decrease the chances of pre-mature precipitation of CaCO_3 . Samples were placed at room temperature for a day before use thereof.

A synthetic water sample (control) was prepared by dissolving salts with a concentration of $0.005\text{mol/dm}^3 \text{CaCl}_2$ and $0.005\text{mol/dm}^3 \text{Ca(HCO}_3)_2$ in demineralized water. The pH of the control water was 7.5.

500 mL of the RO reject and cooling water blowdown samples were spiked with 0.105 g $\text{Ca(HCO}_3)_2$ and 0.138 g CaCl_2 ; amounting to the same content as the control solution. The synthetic control sample was used to investigate the difference between the sampled water (CW-blowdown and RO-reject), and the synthetic water sample and to note if the minerals in the sampled water interacts with the scale forming mechanism in any way.

B. ICP-OES Analysis

An ICP analysis using ICP Expert II, Agilent Technologies 720 ICP-OES (Agilent Technologies, USA) was performed to determine the concentration of calcium present in the two sampled waters.

C. EDTA Titration

Establishment of the amount of total hardness (sum of magnesium and calcium hardness as CaCO_3) and calcium hardness as CaCO_3 was achieved by an EDTA titration.

D. Static Induction Test

A static induction test was performed in order to determine the induction time of two anti-scalants. PBTC (2-Phosphonobutane-1,2,4-Tricarboxylic Acid) and AMTP (Amino Trimethylene Phosphonic Acid)

Anti-scalants were dosed into both samples, including the control solution. The anti-scalants were evaluated at temperatures of 25°C , 40°C and 75°C .

A dosage concentration of anti-scalant was selected by using a modelling program (French Creek Software®). After experimentation of the modeled dosage, final dosages of 0.2 ppm of PBTC and ATMP were chosen for the RO-reject sample and 0.1 ppm of PBTC and ATMP was chosen for the cooling water blowdown sample as well as a control solution, as these dosages showed a drop in conductivity within a reasonable time. RO-reject and CW-blowdown were spiked with $0.005\text{mol/dm}^3 \text{CaCl}_2$ and $0.005\text{mol/dm}^3 \text{Ca(HCO}_3)_2$

An Arduino Uno micro-controller was used to measure the resistivity of the samples over time by means of a voltage divider calculation:

$$R_{\text{water}} = \frac{V_{\text{out}} R_1}{V_s - V_{\text{out}}} \quad (1)$$

Where R_{water} is the resistivity of the water, V_{out} is the resistivity of the voltage read at the sensor and V_s is the output voltage of the source (Arduino). V_s is 5V, with R_1 a chosen voltage of $1740\ \Omega$. The resistance is chosen such that the sensor voltage can stay within the range of 0-5 V.

Two copper wires were placed in the water samples. Stirring was achieved by using a jar test stirrer, which stirs the solution at 60 rpm. Six jars, containing 500 mL each of the water samples were tested simultaneously, consisting of two blank samples, two ATMP dosed samples and two PBTC dosed samples. The samples were heated up by means of circulating hot water on a tray containing the six jars.

The measured resistivity was converted to conductivity, where data was then treated with a Savitzky-Golay smoothing algorithm, to eliminate noise from the data.

III. RESULTS AND DISCUSSION

A. Sample Pre-Analysis

The calcium content of the samples determined using ICP-OES was 83.61ppm in the CW-Blowdown sample and 170.4 ppm in the RO-reject sample.

An EDTA titration resulted in a total hardness as CaCO_3 of 275.08 mg CaCO_3/L , of which the Calcium hardness was determined as 160.46 mg CaCO_3/L , for the CW-Blowdown sample, whereas the RO-reject sample contained 558 mg CaCO_3/L , of which the Calcium hardness was 348 mg CaCO_3/L

B. Static Induction Test at 25°C

Note: Conductivities are not accurate due to noise,

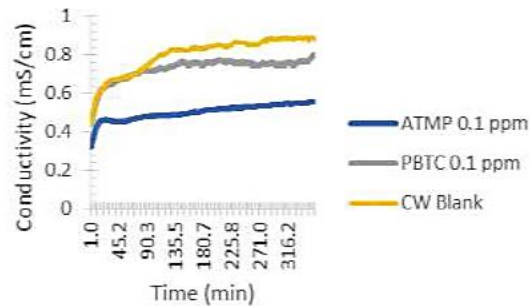


Fig 7: Conductivity over time (CW sample 40°C)

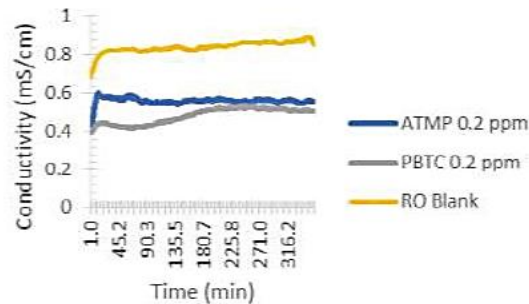


Fig 8: Conductivity over time (RO sample 40°C)

In Fig 7 and Fig 8 it seems that the rate of change in conductivity decreases during the initial increase in temperature of the water, which could be indicative of the occurrence of precipitation, which could be the case for Fig 7 as this behavior occurs on the Blank sample, but for Fig 8 the behavior occurs in the PBTC dosed sample and not in the blank sample, which is inconsistent and counter intuitive to the idea that anti-scalants increase induction time.

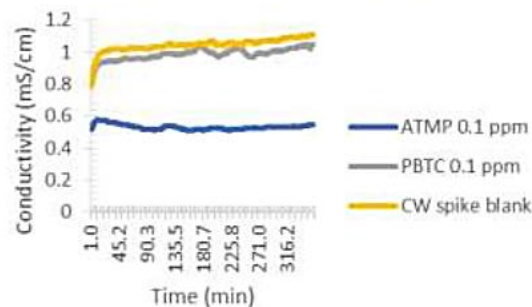


Fig 9: Conductivity over time (CW spike sample 40°C)

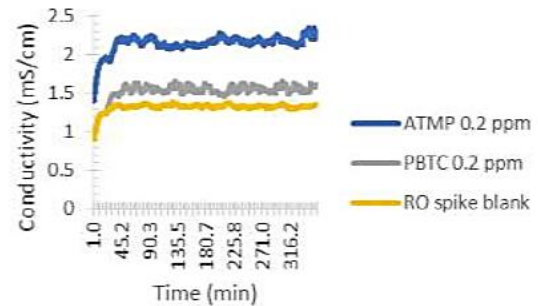


Fig 10: Conductivity over time (RO spike sample 40°C)

At 40°C, there is no observable change in conductivity, and giving rise to the same situation as for 25°C, the control solution and samples are both below super saturation at 40°C to undergo precipitation of CaCO_3 .

A graph obtained from the French Creek Modelling application, MineSat™, reveals that the degree of supersaturation for the CW-blowdown and RO-reject stream is relatively low at a temperature of 40°C and a pH 7.4 for CW-Blowdown and pH of 7.8 for RO-reject (Note: the color coding is from Blue which is good to red which is bad and the color can be noted in Fig 11 and Fig 12)

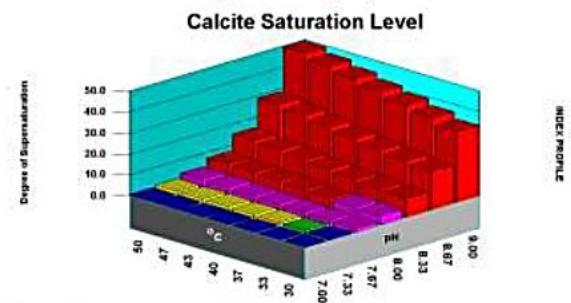


Fig 11: French creek modelling for CW-blowdown sample. Adapted from: French Creek software's MineSat™ [24]

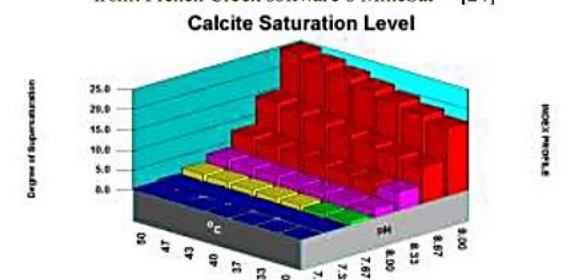


Fig 12: French creek modelling for RO-reject sample. Adapted from: French Creek software's MineSat™ [24]

D. Static induction test at 75°C

Experimental induction tests on the samples and solutions at 75°C produced a diversity of results.

IV. IMPROVEMENTS

A. Improvement of Testing Method

An improved method of testing the anti-scalants is proposed whereby, a closed jar cylinder is used in place of an open jar. A closed jar can better aid in controlling the temperature and pressure while keeping the contents constant, by overcoming excessive evaporation of water. An accurate and reliable measuring device should be used and more variables should be taken into consideration, such as pH, which can allow to monitor the behaviour of critical elements or compounds in solution such as bicarbonate, carbonate and carbon dioxide content.

V. CONCLUSION

At 25°C there is hardly any change in conditions when temperature of the sample is changed from ambient temperature to 25°C. Conductivity remains constant for all samples, which indicates that the samples are below supersaturated conditions.

After temperatures are reached at 40°C, conductivities remain fairly constant for all samples.

Increasing the temperature to 75°C shows a diversity of trends. In some cases conductivity drops during the initial temperature increase phase, while in others a drop in conductivity was observed only when the targeted temperature was reached. However, in general the anti-scalant PBTC performed better than ATMP both for RO reject water and CW. Overall, it is important to note that in the context of laboratory study aiming to compare the performance of anti-scalants, one must ensure that the solutions considered are supersaturated if results are to be obtained in a short time.

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Prof Elvis Fosso-Kankeu has been the recipient of several merit awards.

Determination of Water Evaporation Rate in an Assembled Bench Scale MED and Impact of Anti-Scaling Agents on the Morphology of Scale

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Abstract— A bench scale horizontal tube falling film evaporator was assembled in order to investigate the feasibility of implementing multi effect distillation (MED) technology in the treatment of retentate from the reverse osmosis water purification process in order to decrease water intake/usage. The main challenge regarding this application of technology is the scaling that will occur as the water becomes more concentrated, and an investigation of the effects of different anti-scaling agents and temperature on the morphology of the formed scale is paired with the primary investigation. The bench scale evaporator exhibited satisfactory performance and evaporation (1.25 L/h); while in the batch study, the acrylic copolymer anti-scaling agent yielded the most scale inhibiting performance at a temperature beneath 70°C.

Index Terms—MED, anti-scaling agents, horizontal tube falling evaporator, scale inhibition.

I. INTRODUCTION

South Africa is one of many water-scarce countries. It is therefore imperative to utilize water sparingly to prevent a water restriction/scarcie threat. Water scarcity is an indefinite problem which is also exacerbated by climate change (global warming). Despite the water shortage the country is facing, there is a high demand of water usage in the industries as well as for human consumption. It is therefore essential to treat and re-use industrial wastewater effluent to alleviate the problem. Another advantage regarding water re-use is to avoid on-going discharge of effluent of poor quality back to the water-course, a condition which is detrimental to the ecosystem.

Scale and corrosion is one of the main common problems that the industries encounter due to concentrated cooling water [1]. Eskom, the national Power Utility, is aware of this problem and has thus initiated investigation towards aggressive management and proper use of fresh and waste waters. The poor quality of cooling water is attributed to evaporation which occurs in the cooling towers, when natural water vapor escapes

at the top of the towers causing high concentration of salts/minerals. Concentrated cooling water with such a quality is prone to scaling and corrosion of the heat exchangers and the inner surface of the pipe-system [2]. On the other hand, the salt content of the cooling water crystallizes and accumulates in the ponds of the cooling tower, which also requires cleaning, thus adding to the operating costs [2].

The present study focuses on the investigation of utilizing reverse osmosis (RO) retentate generated at the power plant's water treatment plant as feed water (back-up) to replenish water which evaporates in the cooling towers. However, the quality of the RO reject water is not suitable for cooling purposes, and therefore requires pre-treatment prior to be supplied to the cooling towers. Reject from the primary RO module is high in salinity (above 11000 ppm) and the recirculation through the RO system is not economically viable. Elsewhere, sea water of higher salt concentration has been effectively treated using multi effect distillation (MED) systems [3]. However, the main limitation of such system has been the scale formation on the tubing system responsible for heat exchange, therefore affecting the efficiency of the MED. This implies that the MED paired with the anti-scaling agents could be hybridized to the existing water treatment system at ESKOM for the treatment of relatively high salinity solutions. Traditional methods employed in wastewater treatment for industrial purposes include filtration, coagulation, decarbonization, degassing, and ion exchange, which are expensive and labor intensive as well as ineffective at times [4]. This investigation is therefore relevant as it can offer a cost-effective alternative in which wastewater can be stabilized in terms of scaling and corrosion, which is also applicable to brine solution.

If the prevention of scale formation and corrosion can be achieved by using stabilizing agents, more water can then be recycled. This stabilization will ensure the elimination of scale formation as well as corrosion [3], especially in heat exchangers. Furthermore, this will lead to reduction of water abstraction from the water-course [4].

This study is the primary investigation of the performance of a bench-top single effect evaporator for the concentration of brine in RO water reject from a coal power plant.

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II. METHODOLOGY/EXPERIMENTAL

2.1) Design and construction of single effect evaporator

2.1.1) Materials

When designing this evaporator, the three major components that the evaporator consists of were considered. The heat exchange surface, the vessel in which evaporation will take place and the drip-tray inside the vessel that dispenses the water onto the heat exchange surface.

The corroding and scale forming properties of all materials that forms part of the evaporator were evaluated. It has been established that polymers and certain polyvinyl chlorides are the appropriate materials to use when constructing the vessel of the evaporator as these polymers will not influence the concentrated water (RO retentate) that will be used in the evaporator, as these materials are corrosion as well as scaling resistant [5].

The drip tray consists polymers and poly vinyl chlorides paired with stainless steel components, as stainless steel is stable enough to resist scaling and corrosion within the water it is exposed to [6].

The heat exchange surface inside the evaporator is a metallic material, as the heat conductivity of the surface is key. Copper as well as Cu-Ni alloys have been established as successful heat exchanging surfaces especially in seawater cooled heat exchangers [7], with a mild corrosion resistance [8]. This seawater is comparable to the RO brine that the evaporator will concentrate, thus making a copper heat exchange surface applicable. The above materials are easily available and from an economic view point favorable.

Scaling can however form on this copper heat exchanger surface, and steps must be taken to prevent this from happening in order to maintain the efficiency of the heat exchange surface. This can be achieved by the addition of anti-scaling agents and controlled by the manipulation of the conditions inside the evaporator, as scaling is more prone to form at higher temperatures.

The pump that is integral to the recycle of brine from the vessel to the drip-tray is exposed to the reverse osmosis (RO) brine, and must also be composed of the appropriate materials. This pump, in order to comply with this requirement, is a magnetic drive, single stage, centrifugal pump that is constructed with thermoplastics in order to maintain chemical resistance and eliminate influence on the RO brine's concentration. Figure 1 visualizes these three major components:

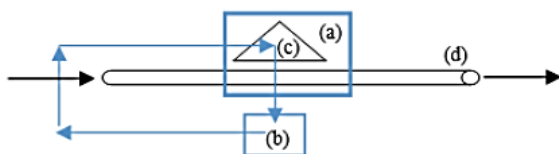


Fig. 1. Major components in design; (a), evaporating vessel; (b), recycle pump; (c), drip-tray; (d), heat source/exchange surface.

2.1.2) Design

The most intricate part of the design of the evaporator is the drip tray that evenly and with laminar flow distributes the RO brine onto the heat exchange surface. The size of the aperture, the distance between the apertures and the distance above the heat exchange surface being the factors carrying the most weight when designing the evaporator. Other weight bearing factors include the flow rate of the water moving through the drip tray, the type of flow inside the drip tray, the conductivity of the heat exchange surface as well as the length of the heat exchange surface.

The evaporator's heat source is a steam kettle/boiler that will supply steam through the heat exchange surface. This does however have a negative consequence as the temperature of the steam will be above the critical temperature where scaling is prone, as it has been reported that at a temperature above 80°C, significantly increases the rate of scale formation [3]. In order to lower the temperature whilst keeping the steam in a vapor phase to ensure efficient heat exchange, the pressure needs to be lowered. This is accomplished by the introduction of a vacuum pump.

The lowering of temperature of the heat exchange surface in order to minimize scaling in essence also lowers the evaporation tempo of the clean water from the RO brine. The pressure of the entire chamber thus also needs to undergo a pressure reduction for the water to evaporate at an adequate rate.

2.1.3) Configuration

The configuration of the evaporator consists of:

- A chamber containing the heat exchange surface and a drip tray
 - The chamber is placed under vacuum via the vapor outlet of the chamber.
 - The heat exchange surface is placed under vacuum via it's outlet from the chamber.
- A water catching tank beneath the drip tray that gets recycled to the drip tray.

2.2) Simulation of scale formation and effect of anti-scaling agent

In order to compare the morphology of the scale and effect of three different anti-scaling agents, small copper pipes were submerged inside beakers containing the RO retentate/brine obtained from ESKOM's Komati Power Station with the anti-scaling agents. These beakers were placed inside an agitated incubator and evaporated in order to let scale form. The three selected anti-scaling agents used in this experiment was:

- Poly (sodium 4-styrene) sulfonate - (Anti-scaling agent no 1)
- Acrylic copolymer - (Anti-scaling agent no 2),
- Maleic polymer - (Anti-scaling agent no 3)

These anti-scaling agents were selected as they have different qualities and applications. Anti-scaling agent no 1 has the highest molecular weight and its main application is to

function as a scale inhibitor and dispersant for metal salts and oxides as well as being an anionic polyelectrolyte. Anti-scaling agent no 3 has a molecular weight considerably less than that of no 1 and shares certain qualities. This anti-scaling agent's main application is to function as a scale inhibitor and dispersant for metal salts and oxides paired with being dopant for conducting polymers, thus also making it an anionic polyelectrolyte. Anti-scaling agent no 2's molecular weight is the smallest and has slightly different qualities than that of the first two. This anti-scaling agent has the benefit of being water soluble, can sequester metal ions and is hydrolytically and thermally stable. Its main application includes being a scale inhibitor, builder in detergents, aid in soap and detergent processing and control of water hardening. These anti-scaling agents all are manufactured by Sigma-Aldrich, a company owned by the Merck Group.

These anti-scaling agents were dosed at two different concentrations, namely 10 and 15 ppm and the simulation was completed at 95°C and 70°C where after the scale was examined by means of SEM-EDS analysis, in order to characterize the scale.

III. RESULTS

3.1) Evaporation rate of constructed bench scale MED

The bench scale evaporator was operated for 36 hours, and 45 litres of water was evaporated at a rate of 1.25 litre/hr.

3.2) Conditions of operation

The evaporator can be viewed as two processes operating simultaneously. The first is that of the heat source (system A) and secondly that of the vessel (system B).

System A comprises of a single horizontal copper pipe that functions as a heat exchanger and is connected to a boiler that continuously supplies steam, as well as a vacuum pump at the outlet of the copper pipe.

The heat exchange conditions are manipulated by the vacuum pump connected to the outlet of the exchanger. Under steady operation, the temperature of the steam is lowered from 100°C to 67°C as desired, paired with a vacuum pressure reduction of 36 kPa, before entering the vessel. The outlet temperature of the steam is lowered to 40°C, with the vacuum pressure reduction of 61 kPa, by the heat exchange that takes place in the vessel.

System B comprises of a vessel that houses the drip-tray as well as copper pipe heat exchanger through it. Ideally the vacuum on the vessel must be similar to that system A's, but due to the structural integrity of the vessel paired with the design of the brine outlet/catchment tank that is insufficient to operate under that amount of stress, the vacuum on the vessel has been decreased.

The temperature inside the vessel under steady operation is 36 degrees, with a vacuum pressure reduction of 9kPa.

The overall process schematic can be viewed in the figure below:



Fig. 2. Combined illustration of system A and B to showcase operating conditions

3.3) Effects of anti-scaling agents on morphology of scale

The SEM analysis images below depict the differences in the performance of the anti-scaling on the deposits formed by the RO retentate exposed to copper piping in a batch system at a temperature of 95°C:

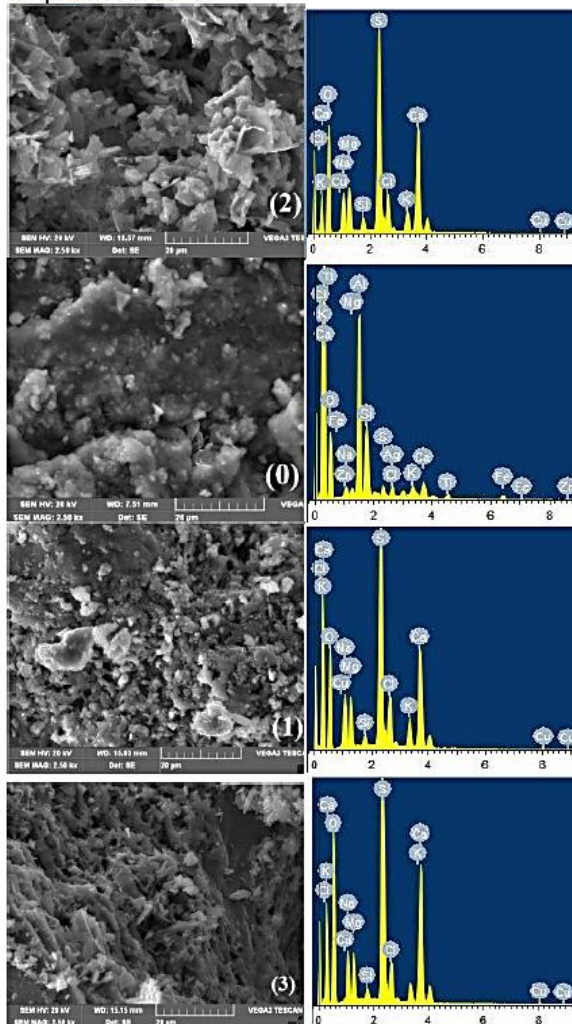


Fig. 3 SEM images and EDS-graphs showing deposit structures and compositions following usage or not of different anti-scaling agents after an evaporation period of 12 h, at temperature of 95°C; (0), No anti-scaling agent; (1), 15ppm anti-scaling agent no 1; (2), 15ppm anti-scaling agent no 2; (3), 15ppm anti-scaling agent no 3.

The SEM images paired with the EDS analysis graphs display an abundance of calcium carbonate as well as calcium sulphate present in the deposited minerals [9]. It has been reported that at temperatures above 40°C, pure amorphous

calcium carbonate transforms to aragonite via vaterite formation [10]. The morphology with no anti-scaling agent shows mixed crystals containing Mg/Ca formed over a mainly magnesium hydroxide layer (brucite) of crystals covering the metallic substrate [3]. The reduction in scale formation, nucleation sites and adhesion of deposited minerals onto the formed scale is evident with the introduction of the anti-scaling agents as there is a clear variation of the scale morphology. Although it is apparent that scaling has formed, the anti-scaling agent has prevented the formation of pure complete aragonite crystals. The results indicate that the effectiveness of the agents aren't precisely identical. Anti-scaling agent no 2 shows the biggest reduction in nucleation sites as well as reduction of scale formation, followed by anti-scaling agent no 3, and anti-scaling agent no 1.

3.4) Effects of temperature on morphology of scale

The images below display the variation in the scale morphology as influenced by the temperature at which the water gets evaporated and how this influences the amount of nucleation sites. It further shows the degree of adhesion of scale and size distribution of the scale as a function of time and temperature of the water inside the agitated incubator.

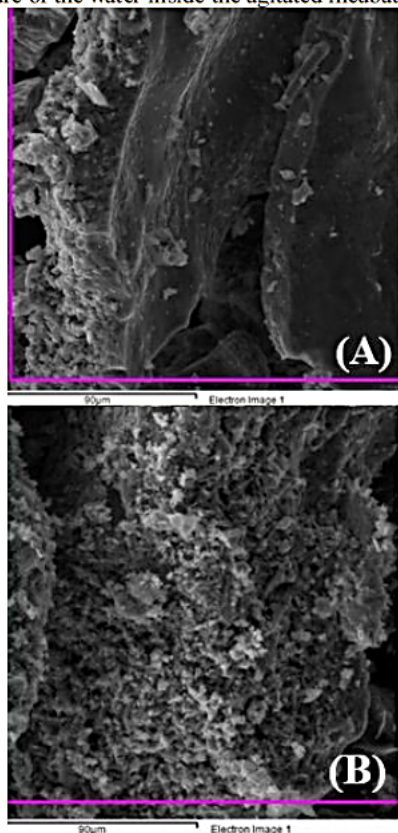


Fig. 4 SEM images showing deposit structures of a different nature with respect to morphology, nucleation present, and scale adhesion to crystal after a test period of 12 h, 15ppm of Anti-scaling agent 1; (A), $t = 70^{\circ}\text{C}$; (B), $t = 95^{\circ}\text{C}$

The SEM images show aragonite crystals that was initially amorphous calcium carbonate that transformed via vaterite to aragonite, as well as calcium sulphate as seen in Figure 2 [9]. The results indicate that much more nucleation sites were activated at 95°C with the morphology of the scale displaying the adhesion and scale formation on crystals than at 70°C . Mixed crystals containing calcium and magnesium grew on top of the aragonite crystals.

IV. CONCLUSION

The morphology of the scale formed by the RO brine that was obtained and tested showed clearly that conditions below 80°C are favorable to maximize scale inhibition [3]. The anti-scaling agents all displayed a reduction in scale formation potential, with acrylic copolymer (Anti-scaling agent 2) as an active ingredient displaying the largest degree of inhibition.

With regards to the bench scale evaporator, system A is more than satisfactory and needs no modification to increase evaporation rate. It fulfils all requirements and is suitable for a further investigation. System B's structural integrity and brine outlet/catchment tank design is the evaporation's limiting effect and a further investigation into improving the vessel's structural integrity needs to be initiated. Furthermore, the brine outlets of the vessel paired with the brine catchment tank designs needs to be re-evaluated and adapted to optimize the evaporator. System B has been operated at a lower pressure for short periods of time, and displayed immense evaporation in these short periods of time, displaying the feasibility of this investigation as well as the advantages of this type of water treatment.

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