Reduction of turbidity and hardness in coal power plant water: Investigation of the implication of flocculation and crystallisation mechanisms

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Dissertation submitted in fulfilment of the requirements for the degree Master of Engineering in Chemical Engineering at the North-West University

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ABSTRACT

Water is a scarce commodity in South Africa and one of the largest consumers of water is the industrial sector. Within the industrial sector, power generation uses a vast amount of water. This water is necessary for cooling equipment, as well as for steam generation for turbines. In this study chemical treatment processes adequate for the treatment of raw water as well as RO-reject water from the Grootvlei power station were developed through identification of suitable coagulants and flocculants as well as optimum operating conditions. Such initiative was carried out to assist Eskom in achieving its goal of zero liquid effluent discharge policy; thereby, to minimise its environmental footprint and reduce the amount of water abstracted from rivers. Two mechanisms of water treatment were considered, based on the nature of pollutants in the water, namely, the flocculation mechanism, which involves charge neutralisation and agglomeration of flocs, and the crystallisation mechanism, whereby super saturation occurs to promote crystal growth. The flocculation mechanism was applied to the treatment of raw water. Coagulants and flocculants were used to remove dissolved solids from the water; therefore, reducing turbidity of the water. Coagulants were used to neutralise the charge of the particles in the water, and flocculants were used to aid in the agglomeration of the particles. The optimal conditions were achieved using polyaluminium chloride (PAC) as a coagulant, at a dosage of 30 mg/L, and ARFLOC100 as a flocculant, at a dosage of 0.8 mg/L. This combination yielded turbidity as low as 2 NTU. Settling was relatively slow and a duration of 30 minutes was needed to achieve a 10 mL floc bed. With the treatment of RO-reject water, the crystallization mechanism was considered whereby lime and NaOH were used to reach super-saturation. With the super saturation, scaling agents, which are the main problem with the RO-reject water, would be insoluble, and crystals will form and precipitate. The optimal conditions when using lime were Rheofloc5023, 0.5 mg/L, ARFloc100, 0.2 mg/L and lime, 220 mg/L, at 60°C. This combination yielded a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54% and an alkalinity removal of 71%. When NaOH was used, the treatment was more efficient at 40°C. Rheofloc5414 was found to be the
best flocculant to use with a dosage of 220 mg/L NaOH. This yielded a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3% and an alkalinity removal of 50.6%. The settling velocity and stability of the crystals were, however, superior at higher temperatures with lime and NaOH, the Rheofloc5414 with the NaOH being more stable and quicker to settle and precipitate. The difference between these two mechanisms could be seen clearly in this study, as flocculation occurred more rapidly, and less slow mixing time was necessary to treat the raw water. It was clear that super-saturation was necessary for the crystallisation process to take place during the treatment of RO-reject water. The latter mostly contains ion pollutants, while raw water contains mostly organic pollutants. It can also be concluded that temperature is important in the crystallisation process initiated by lime, as the treatment was more efficient at higher temperatures. Lastly, it was seen that crystals are more stable and settle faster than the flocs that formed in the treatment of the raw water.

**Keywords:** Coal power plant water, crystallisation, flocculation, lime softening, raw water, RO-reject.
PRESENTATIONS AND PUBLICATIONS
Results from this dissertation was presented at conferences and submitted for publication in peer-reviewed journals.

Conference proceedings


Journal article
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<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACH</td>
<td>Aluminium chlorohydrate</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>NMRS</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric turbidity units</td>
</tr>
<tr>
<td>PAC</td>
<td>Polyaluminium chloride</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TCS</td>
<td>Timed complexation spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffractometer</td>
</tr>
<tr>
<td>ZLEDP</td>
<td>Zero liquid effluent discharge policy</td>
</tr>
</tbody>
</table>
CHAPTER 1: BACKGROUND AND MOTIVATION

1.1 Introduction
South Africa is classified as a water-scarce country – it has an average annual rainfall of 492 mm, while the average rainfall for the rest of the world is 985 mm. According to the Department of Water and Environmental Affairs, the demand for water in South Africa will exceed the water supply by 2025. It was determined in 2001 that the mining and industrial use of water was about 10.5% of the total water use in South Africa (RandWater, 2017).

Eskom is South Africa’s primary power supplier. It generates power mainly by using coal. Power generation requires water for several purposes. The Grootvlei Power Station is situated close to Balfour, Mpumalanga, South Africa, and it is the station from where water was obtained for this study. The power station belongs to Eskom and has a total station capacity of 1200 MW (Eskom, 2017). To generate this power – requires clean water. Raw water is obtained from the environment and it is treated using several techniques, including coagulation, flocculation, filtration, reverse osmosis and ion exchange.

Eskom has a zero effluent discharge policy, which indicates that minimal water is discharged back into the environment. First, the water is treated to reduce the natural organic matter (NOM) and metals in the raw water. This is done by coagulation and, currently, polyaluminium chloride (PAC) is used for this purpose. To remove undesired dissolved solids from the water, reverse osmosis (RO) is used. Another challenge with the use of such water is the presence of scale-forming agents in the water. Therefore, water hardness must be taken into consideration in the treatment of the water, as harder water will more likely precipitate and induce scaling on membranes of filtration units. Water hardness is relative to the concentration of magnesium and calcium salts in the water. Thus, these salts have to be removed from the water to reduce or eliminate scaling of membranes. This is done by using crystallisation, for which CaO is currently used. The objective of this project was to study mechanisms and reagents to determine which reagent will be most efficient in the treatment of the different types of water, and
at what concentration the reagent should be used, including influences attributed to temperature variation.

This study used mainly three chemical processes to treat water, namely, coagulation, flocculation and crystallisation. There are three common coagulation mechanisms. These are charge neutralisation, sweep flocculation and destabilisation by bridging. Charge neutralisation is the rapid hydrolysis of metal salts to form several cationic species. These cationic species are absorbed by negatively charged particles, which, in turn, cause a charge reduction. Sweep flocculation occurs when a high enough concentration of metal salts is added to the water samples, to induce precipitation of amorphous metal hydroxides. Destabilisation by bridging occurs when a polymer chain absorbs on more than one particle to form agglomerates (Li et al., 2006). This causes floc formation. Generally, monomeric and polymeric aluminium are effective coagulants (Koether, n.d). Several flocculants can be used including bentonite clay, hydrated lime, magnesium hydroxide and PAC. Flocculation and crystallisation work together closely with coagulation, though there are some differences between these processes. When crystallisation takes place, crystals are formed, and when flocculation/precipitation takes place, amorphous solids are produced. Crystallisation is a more intense process and it is less time effective than precipitation/flocculation (Astin, 1983).

The main substances that need to be removed from water are calcium and magnesium ions and sulphates. Other substances that require removal include barium, gypsum, calcium carbonate and ettringite. Calcium and magnesium can be removed from the water solution through two processes, namely ion-exchange and the lime soda process (Casicay & Frey, 1998). Normally, during ion-exchange, sodium is used to remove calcium and magnesium from water, and this softens the water. The lime soda process is a coagulation and flocculation process involving lime and/or hydrated lime being added to the water as a flocculant. In this, and in most other coagulation and flocculation processes, pH control plays an integral role in the precipitation of different metals. Thus, it is important that the pH of the treated water is optimal, to achieve the removal of the specific metals.
Other coagulants, which will be mentioned in Chapter 2, can be tested at various agitation speeds to observe the effects of impurity removal from the water. Conclusions on the efficiency of the impurity removal can be made through the following analyses: pH, conductivity, turbidity, total hardness, alkalinity, metal concentration (with inductively coupled plasma atomic emission spectroscopy (ICP-OES)) and the zeta potential. The chemical structure of flocculants and crystals can be determined using Fourier-transform infrared spectroscopy (FTIR), timed complexation spectroscopy (TCS), Nuclear Magnetic resonance spectroscopy (NMRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffractometer (XRD). The settling velocity can also be tested.

1.2 Aim of the study
The aim of this study was to investigate flocculation and crystallisation mechanisms and to determine optimal conditions for the removal of scale-forming agents from Eskom water.

1.3 Objectives of the study
Primary objective:
To develop an effective chemical process for the reduction of turbidity and hardness of water.

Secondary objectives:
- To increase the feasibility of wastewater recycling; and
- To develop a water treatment approach that will reduce the amount of feed water collected from the environment.

1.4 Problem statement
Eskom has to abide to a zero liquid effluent discharge policy it developed, which states that it cannot release wastewater back into the environment. Thus, water has to be recycled and re-used. By recycling and reusing water, less water needs to be extracted from the environment, which is another of Eskom’s goals. Water that needs to be
recycled and reused must, however, be treated, as it has high levels of total dissolved solids as well as a high scaling agent concentration. Scaling on equipment is one of the primary challenges experienced at power stations. Reducing the hardness of the water will decrease the rate at which scaling occurs, thus minimizing the cost of rescaling and the replacement of equipment. The quality of reverse RO-reject water is too low (it has very high total dissolved solids) to pre-empt further treatment using the RO system and, therefore, an effective pre-treatment process is required to lower the level of scale-forming agents considerably.

The necessity of pre-treatment is illustrated by Error! Reference source not found.. According to a French Creek simulation, upper limits of important parameters are breached, which means that scaling of equipment cannot be prevented by using anti-scaling agents alone.

Table 1: Treatment limit summary of MINEsat

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Current value</th>
<th>Lower limit</th>
<th>Upper limit</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (CaCO₃)</td>
<td>13.60</td>
<td>N/A</td>
<td>150.00</td>
<td>ACCEPTABLE</td>
</tr>
<tr>
<td>Gypsum (CaSO₄•2H₂O)</td>
<td>8.00</td>
<td>N/A</td>
<td>4.00</td>
<td>ABOVE LIMIT</td>
</tr>
<tr>
<td>Celestite (SrSO₄)</td>
<td>5.63</td>
<td>N/A</td>
<td>12.00</td>
<td>ACCEPTABLE</td>
</tr>
<tr>
<td>Barite (BaSO₄)</td>
<td>589.37</td>
<td>N/A</td>
<td>80.00</td>
<td>ABOVE LIMIT</td>
</tr>
<tr>
<td>Amorphous Silica (SiO₂)</td>
<td>0.00</td>
<td>N/A</td>
<td>1.20</td>
<td>ACCEPTABLE</td>
</tr>
<tr>
<td>Fluorite (CaF₂)</td>
<td>3.84</td>
<td>N/A</td>
<td>120.00</td>
<td>ACCEPTABLE</td>
</tr>
<tr>
<td>Langlier Index</td>
<td>1.59</td>
<td>N/A</td>
<td>2.50</td>
<td>ACCEPTABLE</td>
</tr>
<tr>
<td>Ryznar Index</td>
<td>4.15</td>
<td>N/A</td>
<td>2.80</td>
<td>ABOVE LIMIT</td>
</tr>
<tr>
<td>Anhydrate (CaSO₄)</td>
<td>4.90</td>
<td>N/A</td>
<td>4.00</td>
<td>ABOVE LIMIT</td>
</tr>
<tr>
<td>Aragonite (CaCO₃)</td>
<td>12.58</td>
<td>N/A</td>
<td>150.00</td>
<td>ACCEPTABLE</td>
</tr>
</tbody>
</table>

An abundance of gypsum, barite and anhydrate causes the induction of scaling. Thus scaling can occur more rapidly with the presence of these sulphate complexes. This indicates that the water should be treated through chemical flocculation and crystallization to reduce these abovementioned compounds. The high Ryznar index
predicts that the likelihood of calcium carbonate scaling to occur is high. Thus treatment is needed to remove these ions from the water.

1.5 Hypothesis
Identifying the mechanism and the correct chemicals with their dosage, will ensure that the treated RO-reject water can be recycled effectively into the system, and at lower cost. The treatment of raw water could be achieved through flocculation because of the dominance of organic pollutants in such water as well as a high turbidity, while the treatment of the RO-reject is likely to occur through crystallisation, as there is a high concentration of metal ions and a high concentration of scaling agents in the water.

References
CHAPTER 2: LITERATURE REVIEW

2.1 Water in South Africa
South Africa is an arid country with an annual rainfall of 492 mm; this is more or less half of the average rainfall for the rest of the world, which is 985 mm. According to the Department of Water and Sanitation, the water demand in South Africa will exceed the water supply by 2025. It was determined in 2001 that the mining and Industrial use of water was about 10.5% of the total water use in South Africa (see Figure 1) (RandWater, 2017).

Figure 1: Representation of water usage

2.2 Power generation
Eskom is South Africa’s main supplier of electricity. It has numerous power stations and types of power stations: 11 base load stations, three return-to-service stations, two hydroelectric peak demand stations, two pumped storage peak demand stations, four gas turbine peak demand stations and a wind energy facility (Eskom, 2017). Water is used in most of the stations’ cooling systems and boilers to produce steam to generate power. The water tested by this study was collected from a coal-fired wet cooled power station that uses RO for water recovery and re-use. To generate power, clean water is needed; hence, water is obtained from the environment - in the case of this study, the
lower Vaal River -and used in operations. Eskom has a zero effluent discharge policy which specifies that no water is to be discharged back into the environment (Eskom, 2017).

2.3.1 Nature of pollutants and their effect on the power plant system

2.3.1.1 Raw water
The raw water used in this study was obtained from the lower Vaal River, and it is characterised by several types of pollutants. NOM is present in the raw water from the river, and it consists of a wide variety of substances and chemicals that can foul the low-pressure membranes of a power station. If the molecular weight of the NOM is high, fouling will also occur more rapidly. According to Wang et al. (2014) there are several parameters for NOM, including colour, aromaticity, total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable organic carbon, assimilable organic carbon, bacterial regrowth, molecular weight distribution, hydrophobicity/hydrophilicity, trihalomethane formation potential and functional groups such as those that contain aliphatic, aromatic and nitrogen constituents. NOM can be influenced by several factors, including its origin, water temperature, ionic strength and the pH. DOC or TOC are the most commonly used parameters to quantify NOM. The analytical technique used to test DOC is by a DOC analyser at UV$_{254}$ nm. NOM can be removed from the water by dosing ultrafine PAC and ferric chloride, which increases the kinetics of adsorption. Other pollutants found in raw water are heavy metals, nitrates and phosphates. All of these pollutants decrease the efficiency of a cooling system, because scaling occurs on the walls of pipes and heat exchangers, which reduces the flow of water and the effectivity of heat exchange (Bernhardt et al., 2008). Membrane fouling can also occur which reduces the efficiency of the treatment system.

2.3.1.2 Reverse osmosis
RO is used to remove dissolved solids from the water. RO involves a semipermeable membrane with a negative pressure difference and ions that are not small enough to pass through the membrane and, thus remain in the retentate, which is called the RO-reject. The pressure is increased to overcome osmotic pressure to purify the water through this semipermeable membrane. In most cases, brine is formed. The brine
consists of several scaling agents, such as calcium carbonate and magnesium carbonate, gypsum and barite. These scaling agents should be removed from the water to reduce scaling in further processes (Greenlee et al., 2019). The aim of treating the RO reject is to remove the scaling agents; thereby, reducing the concentrations of the ions to a level low enough to prolong solubility, and to reuse this treated RO reject in the cooling system of the power plant.

2.4 Treatment mechanisms

2.4.1 Coagulation
There are three main coagulation mechanisms: charge neutralisation, sweep flocculation and destabilisation by bridging. Monomeric and polymeric aluminium are effective coagulants (Koether, n.d). According Chesters et al. (2009), coagulants are used to enlarge particles to enhance the filtration process.

2.4.1.1 Charge neutralisation
Charge neutralisation refers to the rapid hydrolysis of metal salts to form several cationic species, which are absorbed by negatively charged particles; this, in turn, causes charge reduction (Li et al., 2006). According to Lee et al. (2014), charge neutralisation is the primary mechanism that takes place when the adsorption area and the flocculants are opposite in charge. Most of the hydrophobic elements in water are negatively charged, thus, it is wise to use cationic polymers to neutralise the overall particle charge in the water. Because of Van der Waals force attractions between the positively and negatively charged molecules, the charge is neutralised, thus, reducing the zeta potential, which is the surface charge of the ions in the water. This is how the microflocs are formed. Optimum flocculation will occur when the particles are neutralised, in other words, when the zeta potential is minimised. When an overdose of the flocculant occurs, charge reversal takes place, and the Van der Waals forces are weakened, and the flocs disperse. Flocs formed through charge neutralisation are normally light and fragile, thus settle slowly.
2.4.1.2 Sweep flocculation
Sweep flocculation occurs when a high enough concentration of metal salts is added to the water to cause precipitation of amorphous metal hydroxides (Li et al., 2006). This precipitation is due to the increase in the saturation of the metal salts in the water, which causes precipitation of these salts.

2.4.1.3 Destabilisation by bridging
Destabilisation by bridging is the process that occurs when a polymer chain absorbs on more than one particle facilitate agglomeration, which causes strong floc formation (Li et al., 2006). Long polymers, for example Genefloc, which have high molecular weights and low charge densities, adsorb on particles through long loops and tails beyond the electrical double layer. This creates dangling polymers, which interact with molecules and create a ‘bridge” between the molecules. These polymers with longer chains work more efficiently, as they stretch between two particles to form a bridge. Sufficient space on the polymer is also needed, to entrap as many particles as possible. Excessive flocculants is inadvisable, as there will be minimal active sites to adsorb particles, thus, restricting the bridging effect. The quantity of polymers should also not be too low, as the amount of active sites will be insufficient to adsorb enough particles. Overall flocs formed through bridging are stronger than those formed through other mechanisms (Lee et al., 2014).

2.4.2 Flocculation and crystallisation
Several flocculants can be used to promote flocculation and crystallisation, among which bentonite clay, hydrated lime, magnesium hydroxide and PAC. Flocculation and crystallisation work together closely, though there are some differences between the two processes. When crystallisation takes place, crystal growth is promoted, and when flocculation takes place, flocs are formed by agglomeration and then precipitate. Crystallisation is a difficult process to manage and it is time consuming than precipitation/flocculation (Qasim et al., 2019).
2.5 Coagulants used for raw water treatment
Several types of coagulants can be used to remove the pollutants as described in Section 2.3.1.1. These coagulant types are monomeric coagulants, inorganic polymeric coagulants and organic polymeric coagulants. This is described in Section 2.5.

2.5.1 Monomeric coagulants
Examples of monomeric coagulants include aluminium sulphate and ferric chloride (Cheng, 2002). When these substances are added to water, several hydrolysis reactions occur which have a negative effect on the control of precipitation rates and causes metal hydroxides to precipitate (Cheng, 2002).

2.5.1.1 Aluminium sulphate
Aluminium sulphate is a trivalent substance commonly used as a coagulant to remove metals, fat, oil and grease (FOG) and is used for water clarification (Chesters et al., 2009). It is used to decrease turbidity and colour while removing of pathogens. The aluminium salts hydrolyse and form soluble monomeric species when the salts come in contact with water. The mechanism of the particle removal from water can be explained as a sequence of two events that occur sequentially. These two events are physicochemical events, i.e. double-layer compression, and enmeshment of precipitate particles. In double-layer compression, the particles overcome the repulsive forces, so that they can agglomerate and precipitate. In the precipitate enmeshment step, metal particles enmesh small particles when they form and settle (Mishra, 2016). In a comparison of aluminium sulphate and aluminium chlorohydrate (ACH), aluminium sulphate was superior to ACH in removing magnesium (16-7.5%), barium (87-20%), and strontium (66-15%), but inferior in removing calcium (44-65%). Mechanisms that occur when aluminium sulphate is added include charge neutralisation and sweep flocculation. By adding aluminium sulphate, carbonates in the water are converted to carbonic acid. The process is illustrated in Error! Reference source not found. to 4.

\[ \text{Al}_2(SO_4)_3 \cdot 18H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O \].........1
\[ \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 12H_2O \].........2
\[ CO_3^{2-}(aq) + H^+(aq) \leftrightarrow HCO_3^-(aq) \].........3
Adding aluminium sulphate also reduces the alkalinity in the water by reducing the bicarbonates in the water and it may also remove alkaline earth ions:

\[
\text{Al}_{2}(SO_4)_3 \cdot 14H_2O + 3\text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 6\text{CO}_2 + 14H_2O \]

Aluminium sulphate removes turbidity, with a high removal rate being reported in the experimental work by Lin et al. (2017), who achieved a removal rate of 64%. In a comparative study of aluminium sulphate and ferric sulphate done by Almojjly et al. (2018), they found that, for removing oil from water, aluminium sulphate had a 5% to 7% improved removal rate than the ferric sulphate.

One adverse effect of aluminium sulphate use is that it contaminates water with residual aluminium.

### 2.5.2 Inorganic polymeric coagulants

When polymeric coagulants, such as PAC and sodium aluminate, are added to water, fewer hydrolysis reactions take place, which, in turn, provides superior control of the reactions (Cheng, 2002). Using pre-polymerised inorganic coagulants, such as PAC, improves the coagulation, which, in turn, provides more stable flocs. Adding the polymers can reduce the speed of hydroxide precipitation, thus, the charged polymeric species can be contained for a longer time, which enhances charge neutralisation. The larger the species of coagulants, the stronger the absorption to the particle surface. Some common polymeric coagulants are polyaluminium ferric chloride, polyferrous sulphate and polyferric chloride (Mishra, 2016).

#### 2.5.2.1 Polyaluminium chloride

PAC is the most abundantly used aluminium-based inorganic polymer (Shen et al., 2017). It can be prepared by dissolving aluminium in HCl. PAC has been found to be an effective coagulant and that NOM can be sufficiently removed through neutralisation, adsorption and complexation (Mishra, 2016). PAC can also be used to remove metals, FOG and as an agent for water clarification (Chesters et al., 2009). One negative impact of using PAC is that an excessive amount of residual aluminium can be released in the treated water, which may be harmful to humans and other living organisms (Shen et al.,
2017). Keeley et al. (2016) found that PAC contributed to a 90% removal of DOC in water treatment. PAC also lowered the turbidity in that study to a value of 0.4 NTU, thus showing that PAC can be a useful coagulant for the removal process of turbidity in the raw water. A study conducted by Zhao and Li (2019), achieved 80.5% removal of chemical oxygen demand (COD) with PAC. A study by Liu et al. (2019) proved PAC could neutralise the charge in cells and reduce the interaction between these cells, which aided the agglomeration of the cells.

2.5.2.2 Sodium aluminate
Sodium aluminate is another compound that is used for treating water. It is usually used for colour removal, phosphorous removal, lime softening, pH control and silica reduction. It can also be used to reduce the turbidity of raw water (Chesters et al., 2009). A study by Pan et al. (2016) found that sodium aluminate aided in the removal of silica, which is a scale-forming agent. This study confirmed that sodium aluminate increased the tendency to crystallisation and aided in the formation of more stable crystals in the water, thus improving the efficiency of the treatment of water, as well as the removal of the precipitate that forms during the treatment.

According to Gao et al. (2002), sodium aluminate can be used as a coagulant in conjunction with aluminium sulphate. However, PAC is more efficient at higher pH values, which is the range of pH used in this study.

2.5.3 Organic polymeric coagulants
Organic coagulants are used to prevent secondary contaminants, which is a concern when conventional inorganic coagulants are used. Further benefits of using organic coagulants are that they are biodegradable and environmentally benign. Biofloculants include starches, chitosan, alginates and microbial materials that are produced by bacteria, fungi and yeast. Biofloculants have numerous functional groups that interact with a variety of contaminants, and ensures more stable flocs (Mishra, 2016). Biofloculants can be used when turbidity, COD, BOD, FOG and protein need to be reduced.
2.5.3.1 Polyamines
Polyamines are cationic coagulants with a medium molecular weight, mostly linear, which are soluble, have a long shelf-life, are odourless and can be used over a wide pH range. Due to the length of the molecule, these molecules wrap flocs together (Chesters et al., 2009). A study conducted by Wang et al. (2009) confirmed that polyamines can be used over a wide pH range. The study also confirmed a turbidity removal above 80%. Polyamines also had a great effect on the zeta potential of the water. In a study conducted by Lee et al. (2001) it was found that polyamines reduced the turbidity of raw water from 9.4 to 1 NTU and the TOC levels in the water from 3.3 to 1.97mg/L. According to a study conducted by Choi et al. (2001), polyamines in conjunction with aluminium sulphate could reduce the amount of aluminium sulphate used by 50%. Doing so makes the treatment more cost effective, minimises sludge production and increases dye removal in water (by 70%), with turbidity decreasing from 145 to 2 NTU. It was also found that the zeta potential decreased with increases in the concentration of polyamines. According to Yue et.al., (2008), polyamines is a sufficient compound to treat suspended solids and colouring matters in the water. These flocculants destabilize the particles due to compression of electrical double layers. Charge neutralisation occurs followed by adsorption to form particle-polymer-bridges. A small amount of these polyamines are needed and a low amount of sludge is formed through this process.

2.5.3.2 Chitosan
Chitosan is a cationic biopolymer that is one of the most promising coagulants being tested. It is a heteropolymer produced by the decay of chitin, and its features include the presence of amino groups, biocompatibility, biodegradability, hydrophobicity, antibacterial properties and an affinity for proteins. Characteristics of chitosan include large polymer chains, bridging of aggregates, high cationic charge density and precipitation, which makes it possible to apply it in coagulation-flocculation processes. It has been found to work effectively to reduce several contaminants in water, i.e. bentonite, kaolinite, bacteria, dyes and humic acid. A great deal of research has been conducted in relation to the removal of oil residue in water using chitosan. It was found that chitosan works 95% more effectively than PAC to reduce oil particles. Mechanisms that take place in the application of chitosan include charge neutralisation, adsorption,
precipitation coagulation, bridge formation and electrostatic patch. Chitosan should be pre-prepared by dissolving it in acetic acid (Mishra, 2016). According to a study conducted by Zeng et al. (2008), chitosan enhanced chemical oxygen demand removal by 1.8 to 23.7%, and reduced treatment costs by between 7% and 34%.

2.6 Coagulants used for reverse osmosis reject
The scaling agents in the RO reject need to be removed to prevent a negative impact on the downstream processes. Different coagulants (n=5) were considered in this study to determine which mechanism will work best: lime, ammonium hydroxide, sodium hydroxide, sodium carbonate and Genefloc, which is a polyquaternary amine.

2.6.1 Lime
Lime is used to increase the pH to reduce the solubility of metal ions in the water. Different grades of lime can be used to increase the pH. In this study, industrial-grade lime was used, which is more or less 50% lime. The calcium and magnesium ions react with carbonates and hydroxides respectively and precipitate at high enough pH values (usually above 9.3). Magnesium removal is possible only when the pH is high enough to precipitate Mg(OH)₂. Thus strontium, calcium and magnesium removal are pH dependent and lime is a relatively less expensive and highly effective substance to increase the pH (O'Donnell et al., 2016). According to Lim et al. (2002), when lime is added to water, it dissociates into calcium cations and hydroxyl anions. At high pH values, these ions bind with other ions in water to form crystals. An example of this is observed when calcium ions bind with sulphate ions, which form calcium sulphate and calcite, and hydroxyl ions bind with magnesium ions in the water to form magnesium hydroxide. This is represented in Equations 6, 7 and 8.

\[ Ca(OH)_2 \rightarrow Ca^{2+} + OH^- \] .................................................................6

\[ Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \] .................................................................7

\[ 2OH^- + Mg^{2+} \rightarrow Mg(OH)_2 \] .................................................................8

The precipitates that can form, as mentioned above, become insoluble at high pH values.
It was confirmed by Lim et al. (2002) that lime can also be used to treat sludge obtained through water treatment. The sludge crystallises using the same mechanism of ion substitution as illustrated in Equations 6, 7 and 8.

2.6.2 Ammonium hydroxide
Ammonium hydroxide is used for the same purpose as lime, as discussed in Section 2.6.1. CaCO$_3$ precipitates predominantly in the presence of ammonium hydroxide, thus, it can be used as an alkaline reagent for softening water. When this alkaline reagent is added, the following reaction occurs.

\[ OH^- + HCO_3^- \leftrightarrow CO_3^{2-} + H_2O \] .........................................................9

Therefore, the CaCO$_3$ precipitates due to the following reaction:

\[ Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \] ........................................................................10

The mechanism when ammonium hydroxide is added to water is illustrated by the reaction that can be seen in Equation 11.

\[ Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3 + (NH_4)_2CO_3 + 2H_2O \] ......11

The ammonia carbonate that forms as a by-product is unstable and can decompose into carbon dioxide and ammonia.

\[ (NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O \] .........................................................12

These gases change the phase structure of the calcium carbonate crystals, which ensures an irregular shaped growth (Malanova et al., 2014).

2.6.3 Sodium hydroxide
Sodium hydroxide can also be used as an alkaline reagent for water softening. Particularly precipitate calcium carbonate, by the following reaction (Equation 13):

\[ Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O \] .............13

The calcium carbonate will precipitate and sodium carbonate will form as a by-product, which is more stable than the ammonia carbonate that will form with the addition ammonium hydroxide (Malanova et al., 2014). According to the study done by Malanova et al. (2014), sodium hydroxide is a good reagent to use for water softening as CaCO$_3$.
precipitates (Equation 13). Sodium hydroxide is, however, expensive than lime and is less freely available than lime.

2.6.4 Sodium carbonate
Sodium carbonate can be used to remove Fe(II) and Fe(III) from water; although, further research should be done to test its effects on the calcium and magnesium concentration, as it increases the pH of the water, which can make CaCO₃ insoluble (Akinwekomi et al., 2017). When there is an excessive quantity of carbonates in water, it reacts with hydrogen and forms bicarbonates. This reduces the carbonates that can bind with the problematic ions, for example, calcium ions. The pH will not be as high as is necessary, as bicarbonates will form and thereafter fewer hydroxide ions will be available (Zhang et al., 2015). According to a study conducted by Silva et al. (2012), manganese precipitation in the form of manganese carbonate can occur in mine water when sodium carbonate is added. At a pH of 8.5, 99.9% of manganese can be removed from water through the precipitation of manganese carbonate.

2.6.5 Genefloc (Polyquaternary amine)
Genefloc is a polyquaternary amine that can function over a large pH range, and which is produced by Genesys International Limited, Cheshire, UK. The positive charge of these molecules can be found in the backbone of the polymer chain, thus, if there is excess flocculant in the water, it will adhere across the length of the membrane surface and not by its sub-branches. The Genefloc should be dosed early in a pre-treatment system and not at the filtration system. Further advantages of Genefloc are: 1) it is safe to use and 2) minimal Genefloc residue can be found on membranes after five years of use (Chesters et al., 2009).

2.7 Using lime with a coagulant aid
Lime was used in the present investigation as it is the most cost-effective chemical that can be used to increase the pH. However, a coagulant aid may be necessary to neutralise the surface charge. Polymeric flocculants, discussed in Sections 2.5 and 2.6, are used to neutralise the surface charge and aid in the agglomeration of particles through charge patching or bridging, which will ensure that the particles precipitate or float depending on the density of the agglomerated particles (Chesters et al., 2009). The
density of CaCO$_3$, the product that will probably form, is high relative to the density of water, thus, it will sink. The agglomeration of the particles will then aid in the treatment of water.

2.8 Parameters considered in this study
Several parameters were considered to ensure that the correct coagulants and flocculants were used as well as their optimal dosages. These parameters will be explained in the following subsections.

2.8.1 Total hardness and alkalinity with titrations
By definition, titrations involve the slow addition of a solution with a known concentration to a known volume with an unknown concentration, until the reaction reaches a stage where it is neutralised. The unknown concentration can then be determined (Chao, D., et.al, 2000).

2.8.1.1 Total hardness
Total hardness is the concentration of the hardening agents in the water and the possible scaling agents that need to be removed, with CaCO$_3$ and MgCO$_3$ being the primary compounds of interest. A reduction in total hardness leads to less scaling on equipment and membranes for RO systems.

2.8.1.2 Alkalinity
Alkalinity can provide information about the carbonate, bicarbonate and hydroxide content of a water sample. Carbonates react with calcium forming calcium carbonate, which causes scaling in heat exchangers and membranes. Thus, a reduction in the alkalinity yields less carbonates and hydroxides, which decreases scaling. A chosen amount of sample can be used for this test, and 0.1 N sulphuric acid is used as a titrant (Rice et al., 2012).

Two methods can be used to determine the alkalinity, one with a pH meter and one with indicators. In the first method (pH meter), the starting pH is measured. If the pH is above 8.3, the titrant is added until the pH is 8.3 and a measurement is taken; then a titrant is subsequently added until a pH of 4.5 is reached. In the second method, phenolphthalein is used as an indicator for a pH of 8.3, when the colour of the sample
changes from pink to transparent. Thereafter, bromosol green is added for a 4.3 pH, whereby the sample colour changes from blue to green (Rice et al., 2012).

The alkalinity can then be calculated using Equations 14-15.

\[
\text{Alkalinity} \left( \frac{\text{mgCaCO}_3}{L} \right) = \frac{A \times N \times 50000}{\text{mL sample}} \] ..................................14

Where:
A = mL standard acid used, and
N = Normality of standard acid

\[
\text{Total alkalinity} \left( \frac{\text{mgCaCO}_3}{L} \right) = \frac{(2B - C) \times N \times 50000}{\text{mL sample}} \] ........15

With:
B = mL titrant to first recorded pH,
C = total mL titrant, and
N = Normality of acid.

The different types of alkalinity can be calculated using Equations 16 and 17.

\[
\text{CO}_3^{2-} = 2P - 2[\text{OH}^-] \] .........................................................16

\[
\text{HCO}_3^- = T - 2P + [\text{OH}^-] \] .........................................................17

Where:
P = phenolphthalein alkalinity, and
T = Total alkalinity.

The relationship between the different alkalinitities is illustrated in Table 2.
### Table 2: Relationship between different alkalinities

<table>
<thead>
<tr>
<th>Result of titration</th>
<th>Hydroxide alkalinity as CaCO₃</th>
<th>Carbonate alkalinity as CaCO₃</th>
<th>Bicarbonate alkalinity as CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P&lt;1/2T</td>
<td>0</td>
<td>2P</td>
<td>T-2P</td>
</tr>
<tr>
<td>P=1/2T</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P&gt;1/2T</td>
<td>2P-T</td>
<td>2(T-P)</td>
<td>0</td>
</tr>
<tr>
<td>P=T</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Source: Rice et al. (2012)

#### 2.8.2 pH

The pH was calculated by measuring the hydrogen ion concentration in an aqueous solution measured by a probe connected to a pH meter. The pH provided data about the acidity of the solution, and is usually measured using a probe that is connected to a pH meter (Covington, A.K., 1985).

#### 2.8.3 Conductivity

Conductivity is the potential for a substance to conduct or transmit electricity and sound. Metal ions increase the conductivity of a solution. Thus, a lower conductivity will prove that metal ions have been removed from the water. Conductivity is normally measured with a probe connected to a conductivity meter, and the units for conductivity are Siemens/meter (S/m) (Lenntech, 2017). For water that is to be used in the cooling system, the conductivity should be less than 4 mS/cm.

#### 2.8.4 Turbidity

The turbidity of water can be described as the haziness or cloudiness of the water. Dissolved solids can increase the turbidity of water. Turbidity is measured in Nephelometric Turbidity Units, (NTU,) and it is normally measured with a spectrometer as shown Figure 2 (Lamotte, 2017):
Light is omitted through the lens, into the sample. The light that is not transmitted through the sample is measured with the detector, and the measurement is taken. The turbidity should be less than 100 NTU for use in the cooling system.

2.8.5 Settling velocity
Settling velocity, also called the terminal velocity, plays an important role in the flocculation process, as it describes the velocity of the particles precipitating (Zhiyao et al., 2008). The treated water is added to a settling column or cone, whereby the amount of crystals settled and the time taken for that amount of crystals to settle is recorded. Calculations, first order derivatives, are then made to determine the settling or terminal velocity of the crystals/flocs.

References


CHAPTER 3:
CHAPTER 3: FLOCCULANT TYPES AND OPERATING CONDITIONS INFLUENCING PARTICLE SETTLING RATES IN FEED WATER USED AT A COAL POWER PLANT

3.1 Abstract
South Africa is a semi-arid country with an average rainfall of less than half of the average rainfall of the rest of the world. Of the country’s limited water resources, 2-3% of the water is used for energy generation. Thus, the water intake by Eskom needs to be reduced, to avoid depleting the country’s water resources. Treating feed water effectively is one of the ways Eskom can contribute to optimise operations and, therefore possibly save water. This research study investigated the variation of particle settling rate based on the type of coagulant and flocculant used to treat feed water. The aim was to determine optimal conditions for producing feed water of acceptable quality. PAC, ACH and sodium aluminate were used as inorganic polymeric coagulants, and alum was used as the inorganic monomeric coagulant. Two different types of inorganic polymeric flocculants were used, as was chitosan, as the organic polymeric coagulant. It was found that using PAC in conjunction with a polyamine resulted in better removal of hardness and turbidity at 30 ppm and 0.8 ppm respectively. Ideal conditions for higher removal rates were flocculant addition during rapid mixing, and approximately 60 seconds after the PAC was added.

Keywords: Feed water, Flocculation, Hardness, Power plant, Turbidity

3.2 Introduction
South Africa is one of the countries with the lowest annual precipitation in the world, with an average of 497 mm/year. The South African population currently exceeds 50 million, and it will continue to increase, while water availability is continuously decreasing (Thopil and Pouris, 2016). Climate change, pollution and the wastage of water are the main factors that decrease the availability of water. It was predicted that, in about seven years, the water demand in South Africa will exceed the water supply (Nkhotokwa, 2017). It is estimated that 2-3% of South Africa’s water is used for energy generation (Thopil and Pouris, 2016). Most of the country’s power stations are located
in rural areas, where people use surface water for their daily needs. Should water used by power stations be discharged into the environment, it can cause health risks for local people (Aboubaraka et al., 2017).

According to reports, coal-fired power stations in China use 1.15 L of water to generate 1 kWh of electricity (Zhang et al., 2017), whilst Eskom, the power utility in South Africa currently uses 1.38 L/kWh. Eskom’s target is to reduce this amount to 1.34 L/kWh by 2020. It must be mentioned that the water consumption of power plants in South Africa increased dramatically after 1950, as the need for energy increased with the rapid increase in population, industrialisation and economic growth (Zhang et al., 2017). Water usage by power stations can be reduced by recovering, treating and reusing wastewater and, thus, reducing the raw water intake that is required for power generation.

Raw water is extracted from rivers in South Africa, which can contain various substances that cause high turbidity in the water. These substances can be of organic or inorganic origin, and the organic matter has the potential to cause biological fouling (Aboubaraka et al., 2017), which causes membrane fouling in downstream processes (Yu et al., 2016) where cooling towers, for example, have ideal conditions for algae to flourish. In addition to algae, calcium and magnesium salts are present, which can cause scaling (Aboubaraka et al., 2017). Coagulation and flocculation have the potential to remove large amounts of impurities, for example, bacteria, minerals and organic substances, in conjunction with disinfection processes to produce potable water (Yu et al., 2016).

There are mainly three coagulation mechanisms, namely, charge neutralisation, sweep flocculation and destabilisation by bridging. According to Chesters et al. (2009), coagulants are used to enlarge particles to enhance the filtration process. Charge neutralisation is the rapid hydrolysis of metal salts to form several cationic species (see Figure 3). These cationic species are absorbed by negatively charged particles, which, in turn, causes a charge reduction (Li et al., 2006). According to Lee et al. (2014), charge neutralisation is the main mechanism that takes place when the adsorption area and the flocculants have opposite charges. Most of the hydrophobic elements in water
are negatively charged; therefore, in this instance, cationic polymers will be suitable for neutralising the overall charge in the water. This is due to the Van der Waals force attractions between the positively and negatively charged particles, thus, reducing the zeta potential. Optimum flocculation will occur when the particles are neutralised, in other words, when the zeta potential is close to zero. An overdose of the flocculant can occur where charge reversal takes place, the Van der Waals forces are weakened and the flocs disperse. Flocs formed through charge neutralisation are normally light and fragile and settle slowly, thus, it is advisable to use heavier polymers with a bridging effect for these mechanisms.

On the other hand, sweep flocculation occurs when high concentrations of metal ions are added to the solution to promote precipitation of metal hydroxides (Li et al., 2006). An increase in concentration promotes an increase in the saturation of these metal salts, which, in turn, promotes the precipitation of metal salts.

Destabilisation by bridging occurs when a polymer chain absorbs on more than one particle, to link them together, which causes strong flocs (Li et al., 2006). Long polymers with high molecular weight and low charge densities adsorb on particles through long loops and tails beyond the electrical double layer. This creates dangling polymers, which interact with particles and create a “bridge” between the particles. Polymers with
longer chains will work more effectively, as the polymers should stretch between two particles to form the bridge. Sufficient space on the polymer is also needed to entrap as many particles as possible. Excessive particles obtained from raw water should not be used, as there will be no active sites to adsorb particles, thus, restricting the bridging effect. The quantity of polymers should not be too low, as the number of active sites will not be sufficient to adsorb enough particles. Flocs formed through bridging are stronger than those formed through other mechanisms (Lee et al., 2014) (Error! Reference source not found.).

There are several flocculants that can be used, including bentonite clay, hydrated lime, magnesium hydroxide and PAC (Figure 5). Flocculation and crystallisation work closely together with coagulation, though there are some differences between these two processes. When crystallisation takes place, crystals are formed and when flocculation/precipitation takes place, amorphous solids are produced. Crystallisation is
a harder process to produce, as crystal growth is required from a crystal that forms; it is also less time effective than precipitation/flocculation (Qasim, M., et.al., 2019). The mechanism of particle removal from the solution is vastly influenced by the type of flocculant used; furthermore, the evaluation of the overall performance of a treatment process takes into consideration flocculant dosage and particle settling rate.

Figure 4: Types of flocculants used in water treatment

Aluminium and iron-based coagulants are usually used for water treatment, due to their cationic affinity (Chesters et al., 2009). These cationic particles bind to the anionic suspended solids, which, in turn, promote settling. pH changes, dosage and temperature have an effect on the efficiency of this process (Fosso-Kankeu et al., 2016). Alum is an effective monomeric coagulant in most types of water, if the pH is between 5 and 7.5. Aluminium hydroxide is formed with the addition of alum to water, which precipitates and causes a decrease in the turbidity of the water (Manda et al., 2016).
Due to the changes in the physico-chemical properties of water, polymeric coagulants are commonly used, of which most are aluminium and iron-based. PAC is an example of a polymeric aluminium-based coagulant. It is an improvement over alum, as it removes turbidity more efficiently, there are no insoluble residues, and it does not have a negative impact on the clarifier. Reducing of colour is less efficient with the addition of PAC. PAC is less pH dependent than alum.

Coagulant aids, such as polyamines, chitosan and bentonite, are used to increase floc size, which, in turn, improve the settling velocity, as well as the stability of the flocs (Bu et al., 2016). An example of a polymer is the polyquaternary amine, Genefloc, which is produced by Genesys International Limited in Cheshire, UK (Chesters et al., 2009), and which is efficient over a large pH range. Its cationic charge is located over the backbone of the long polymeric chain that can wrap around particles. Another advantage is that, after using Genefloc, no residue is found on filtration membranes after for years of use (Chesters et al., 2017).

Organic coagulants are used to reduce secondary pollution. They consist of different functional groups, which bind with impurities to form flocs when added to water (Fosso-Kankeu et al., 2016). Chitosan is an example of an organic coagulant; it is also a cationic polymer. One disadvantage of using organic coagulants is that they are pH-sensitive, as they consist of amino groups. Normally, at a pH above 6, the coagulant loses its charge (Chesters et al., 2009).

One parameter used to test the efficiency of coagulants and flocculants is the settling velocity. The concentration of the suspended solids, floc size, strength, structure and density influence the settling velocity and settling regime (Burger et al., 2017).

An extremely important characteristic of solids in relation to calculating settling rates is the terminal settling velocity of the particles. It is calculated by doing experimental tests that involve the water with particles being added to a settling column, and the supernatant being extracted from different points at different times (Piro et al., 2011). Another method of determining the settling velocity is using an Imhoff cone. The same procedure is followed as when a settling column is used, the floc bed is measured over time.
This study was conducted to determine the optimal coagulant, coagulant aid and dosage for effective treatment of feed water for steam generation at a coal power plant. To assess the performance of the coagulant and coagulant aid, parameters such as turbidity, hardness and settling velocity were considered. This study aimed to optimise operation processes at a coal power plant water treatment facility, to address issues related to chemical over-dosage and equipment fouling.

3.3 Experimental procedure

3.3.1 Sample collection
Water samples were collected at the Grootvlei Power Station, Mpumalanga, South Africa, in 25 L plastic, rinsed, containers. The samples were taken up-stream from the coagulant dosing point. Sample containers were covered by black plastic sheets to protect from light penetration, and transported back to the university, where the water was tested.

3.3.2 Water characterisation
The temperature, pH and conductivity of the water were measured with the aid of a Lovibond SensoDirect 150 meter, from Lovibond in Amesbury, UK. The turbidity was measured with a Hatch 2 100 Q meter. The sample was added to a cell then it inserted into the meter and the turbidity was measured. The alkalinity of the water was measured by using titration and the end-point method (Rice et al., 2012). A 0.1 N H$_2$SO$_4$ solution was made and used as a titrant. A volume (20 mL) of raw water and demineralised water (80 mL) were added to Erlenmeyer flask. Bromocresol green was added as an indicator to all flasks tested. The starting pH was measured and the titrant was added until the sample colour changed from blue to a light green. This is the point at which the pH reaches the 4.5 end-point (Rice et al., 2012). The alkalinity was calculated using Equation 14:

$$\text{Alkalinity as } mg \text{ CaCO}_3/l = \frac{A \times N \times 50,000}{\text{sample volume (mL)}}$$

Where:

A = volume of acid used (mL), and
N = Normality of acid.

The TOC analysis was done at the Eskom Research Centre in Rosherville, using the Sievers 900 TOC analyser. Ultraviolet radiation was used in conjunction with ammonium persulphate to oxidise the organic composites in the sample to carbon dioxide, which was then measured. The inorganic compounds along with the total amount of carbon were measured separately to calculate the TOC, as seen in Equation 15, where TC is the total carbon and TIC is the total inorganic carbon.

\[ TOC = TC - TIC \]  

The ICP-OES (Agilent Technologies, USA) was used to measure the metal concentration in the water samples. A plasma is a conducting gaseous mixture of cations and electrons of which the net charge is zero. Argon is frequently used in this plasma, as it can absorb enough power from an external source to maintain temperatures, as high as 1000 K, where it sustains further ionization. The samples were not diluted, as the concentration of the metal ions were not exceeding the limits that could be read.

EDTA titrations were used for the quantification of the total hardness as well as the calcium and magnesium concentrations. For both total hardness and the calcium titrations, a standard EDTA solution was prepared. In the determination of the total hardness, an ammonium-based buffer was prepared using 16.9 g NH₄Cl, 143 mL NH₄OH, 1.25 g magnesium salt of EDTA and demineralised water. The samples to be titrated were prepared by adding 25 mL water sample and 25 mL demineralised water together. Calmagite was added as indicator. The sample was titrated with EDTA until the sample colour changed from blue to purple. The total hardness was then calculated using the following equation:

\[ mg \text{ CaCO}_3/L = \frac{A \times B \times 1000}{\text{sample volume (mL)}} \]
A = titration volume for sample (mL), and

B = milligrams calcium carbonate corresponding to 1.00 mL EDTA titrant.

With regard to the calcium titration, a 1 N NaOH buffer was prepared. This buffer was added to a 50 mL water sample. Murexide was added as an indicator and the sample was titrated with EDTA until the end point was reached. The calcium concentration was determined as follows (Equations 21 and 22):

\[
mg \ Ca/L = \left( \frac{A \times B \times 403.8}{sample \ volume \ (mL)} \right) \quad \text{……………….21}
\]

\[
\text{Calcium hardness as } mg \ CaCO_3/L = \left( \frac{A \times B \times 1000}{sample \ volume \ (mL)} \right) \quad \text{……22}
\]

Where:

A = titrant volume for sample (mL), and

B = milligrams calcium carbonate corresponding to 1.00 mL EDTA titrant.

The magnesium concentration could then be calculated by subtracting the calcium concentration from the total hardness concentration, with the assumption that the total hardness consists of only calcium and magnesium.

### 3.3.3 Coagulants

The inorganic polymeric coagulants used in this study were PAC, aluminium ACH and sodium aluminate. Alum was used as an inorganic monomeric coagulant. Rheofloc5414 and ARFloc100, which are polyamines, and chitosan, were used as coagulant aids. The first two mentioned are both polymeric and polyamine-based flocculants. The chitosan was prepared by adding it to a 0.1 M HCl solution, and then diluting to 1 000 mg/L.

### 3.3.4 Jar tests

Beakers (n=6, 1L) were used simultaneously for the jar test, then the paddles were immersed in the sample solutions added to these beakers and stirred to allow coagulation and flocculation processes to take place under rapid mixing and slow mixing respectively.
3.3.5 Coagulant optimisation
Water samples (n=6) were used for a coagulant at different dosages. These coagulants were PAC, ACH, sodium aluminate and alum. The coagulant was added and rapid mixing was carried out for 60 seconds at 150 rpm. Thereafter, slow mixing followed for 20 minutes at 50 rpm. A settling time of 30 minutes was allowed.

3.3.6 Coagulant aid optimisation
After the optimum dosages of the different coagulants were determined, the coagulants were used in conjunction with the different coagulant aids, namely Rheofloc5414, ARFLOC100 and chitosan. The coagulant was added and rapid mixing was carried out at 150 rpm for 60 seconds, then the coagulant aid was added. Further rapid mixing was carried out for 30 seconds followed by slow mixing for 20 minutes at 50 rpm. The samples were left to settle for 30 minutes.

3.3.7 Optimisation of time between addition of coagulant and coagulant aid
The optimal dosages of coagulant and coagulant aid were used while varying the time between the addition of these two substances between 0 and 90 seconds. After the addition of coagulant and coagulant aid, 30 seconds rapid mixing was conducted at 150 rpm and slow mixing for 20 minutes at 50 rpm; thereafter 30 minutes settling time was then allowed.

3.3.8 Optimisation of mixing regime after coagulant aid addition
The optimal dosages were used and the same method as mentioned in Section 3.3.7 were considered; however, the coagulant aid was added at the start of the slow mixing period.

3.3.8 Settling rate tests
A cone was used for the settling rate tests and to determine the rate of sludge build-up and turbidity removal. First, the cone was calibrated from 1 to 10 mL; directly after the jar test, the sample was added to the cone and the time was recorded as the solids settled, to reach the bottom, with 1 mL intervals.
3.3.10 Morphology analysis
Wattman® filter paper with a 0.45 µm pore size was used to filter the treated water. The filter paper was dried at room temperature for 24 h. The flocs were analysed with a QEMSCAN automated mineralogy apparatus at Eskom’s Research Centre at Rosherville.

3.4 Results and discussion
3.4.1 Water characterisation

Table 3 shows water characterisation parameters and the values obtained at different days of sampling. This represents the control samples. The significant difference in the turbidity is due to fluctuation in the river water quality.

Table 3: Water characterisation results

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>16 May</th>
<th>5 July</th>
<th>11 August</th>
<th>28 August</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.55</td>
<td>7.98</td>
<td>8.01</td>
<td>7.65</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>16.8</td>
<td>13.9</td>
<td>16.4</td>
<td>15.5</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>21.07</td>
<td>30.69</td>
<td>15.58</td>
<td>22.46</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>165.57</td>
<td>164.78</td>
<td>159.53</td>
<td>162.67</td>
</tr>
</tbody>
</table>

3.4.2 Jar tests
3.4.2.1 Coagulant screening
The different coagulants were tested to determine the best coagulant to use with this specific raw water. The coagulants tested were PAC, ACH, aluminium sulphate and sodium aluminate. The dosage of each coagulant was varied from 5 to 30 mg/L and the results are shown in Figure 5.
It can be seen clearly that sodium aluminate has the lowest turbidity removal (15%) of the three coagulants assessed. Alum and ACH had better turbidity removal efficiencies than the sodium aluminate. It was found that a 30 mg/L dose of PAC yielded 94% reduction in the turbidity. This coincides with a study conducted by Keeley et. al., (2016) which found that PAC lowered the turbidity of water to 0.4 NTU. Thus confirming that PAC is an adequate compound to remove the turbidity from the water.

### 3.4.2.2 Coagulant aid screening

Optimisation processes carried-out in the lab showed that coagulant or coagulant aid, used separately, could not achieve sufficient removal of turbidity, thus, coagulant and coagulant aid (flocculant) pairing was considered, to ensure that the coagulation and flocculation processes work efficiently.

Thus, PAC and ACH were used as coagulants in conjunction with Rheofloc5414, chitosan and ARFloc100 as coagulant aids. Firstly, the PAC was used with the different
coagulant aids at a dosage of 30 ppm and the coagulant aids were dosed between 0.2 and 1.2 mg/L. The results are shown in Figure 7.

As can be seen in Figure 6, chitosan is not an effective coagulant aid, as it achieved the lowest turbidity removal. Both ARfloc100 and Rheofloc 5414 reduced the turbidity to less than 5 NTU at a dosage of 0.8 mg/L in conjunction with the 30 mg/L PAC. The plant can only handle a maximum dose of 0.8 mg/L flocculant, thus in conjunction with the 30 mg/L PAC, the 0.8 mg/L RHEOFLOC 5414 replicates the best conditions for the removal of turbidity; the final turbidity achieved was averaged at 2.13 NTU. This is confirmed by Keeley et al., (2016), which states that PAC is a coagulant that can be used to remove turbidity from the water.

The same flocculant dosages were used in conjunction with 25 mg/L of ACH coagulant dosage. See Figure 8.
Figure 7: Turbidity of ACH with various coagulant aids

As seen in Figure 7, chitosan is the least effective flocculant used in conjunction with the ACH. ARfloc 100 with a dosage of 0.8 mg/L reduced the turbidity to close to 4 NTU in conjunction with the 25 mg/L ACH dosage. The lowest turbidity was recorded with a Rheofloc 5414 dosage of 0.8 mg/L, reaching a value of 3.02 NTU. A study conducted by Wu et.al, (2011) confirmed that using a coagulant aid with PAC is advantageous as less PAC is necessary and the efficiency of the water treatment is increased.

The optimal dosage was found to be 30 mg/L of PAC with a 0.8 mg/L dosage of Rheofloc 5414, which yielded a turbidity of 2.13 NTU.

3.4.2.3 Time lapse differentiation between of coagulant and flocculant supplementation

The optimum dosages mentioned were used to determine the optimum time required to lapse between coagulant and flocculant dosing stages. The time was varied between 0 and 90 seconds and the results can be seen in Figure 8.
Figure 8: Turbidity difference due to the time between the addition of coagulant and flocculants

The optimum time between the addition of the coagulant and flocculant was determined to be 60 seconds, resulting in a final turbidity of 2.46 NTU. Thus after 60 seconds, the flocs were broken and settled slower.

3.4.2.4 Mixing regime for flocculant addition

The jar test was repeated to determine if the flocculant should be added during slow mixing (50 rpm) or rapid mixing (150 rpm). First, the flocculant was added during slow mixing, the final turbidity recorded was 9.07 NTU. Thereafter, the flocculant was added during rapid mixing, which yielded a turbidity of 2.1 NTU. Thus the flocculant is more effective when the addition takes place during rapid mixing.

3.4.3 Total hardness

The total hardness of the untreated water calculated using Equation (14) was 27.4 mg CaCO₃/L. After treatment of the raw water, the total hardness decreased to 26.3 mg CaCO₃/L. This shows a reduction of only 4% in the total hardness. Thus, this treatment is not effective for total hardness reduction. However, the real issue with the raw water
treatment is not the hardness, but the turbidity, which makes this treatment option viable and effective.

3.4.4 Calcium content
Using the end-point method, the calcium content of the treated water was 10.18 mg Ca CO$_3$/L and the calcium hardness was 25 mg CaCO$_3$/L. This was more or less similar to the untreated water, as a pH increase was necessary to remove calcium and magnesium ions from the water.

3.4.5 Major metals in raw water
The ICP-OES results of the untreated as well as the treated raw water can be seen in Table 4.

Table 4: ICP-OES results

<table>
<thead>
<tr>
<th>Component</th>
<th>Untreated raw water (mg/L)</th>
<th>Treated raw water (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>3.14</td>
<td>0.33</td>
</tr>
<tr>
<td>Calcium</td>
<td>12.17</td>
<td>11.86</td>
</tr>
<tr>
<td>Iron</td>
<td>1.90</td>
<td>0.02</td>
</tr>
<tr>
<td>Potassium</td>
<td>4.32</td>
<td>3.87</td>
</tr>
<tr>
<td>Magnesium</td>
<td>6.53</td>
<td>6.12</td>
</tr>
<tr>
<td>Sodium</td>
<td>8.06</td>
<td>7.71</td>
</tr>
</tbody>
</table>

It can be concluded that the treatment mechanism removed mainly aluminium and iron, and that the main metals responsible of the hardness such as magnesium and calcium were not removed from the water.

3.4.6 Alkalinity
The alkalinity was determined using the end-point method. Before treatment, the alkalinity was 20 mg CaCO$_3$/L. After treatment the alkalinity had remained almost unchanged, at a value of 21 mg CaCO$_3$/L, implying that the treatment had no effect on the alkalinity changes in the water.
3.4.7 Total organic carbon
The TOC was 5.53 mg/L before treatment and 2.9 mg/L after treatment. Thus, the treatment yielded a 52% reduction of TOC.

3.4.8 Sludge build-up over time
The sludge build-up was determined by adding the optimum coagulant and flocculant dosage during rapid mixing. Three tests were conducted and the results are shown in Figure 9.

![Figure 9: Sludge build-up (floc bed formation) with addition of coagulant and flocculant during rapid mixing](image)

The data for Test 3 shown in Figure 9, are the average of the numerous tests (n=3), thus, \( y = -0.0058x^2 + 0.6921x -10.362 \), with \( x \) being time, will be used for the computations in this section. To determine the settling velocity rate, this equation is differentiated and the result is given by: \( y' = -0.0116x + 0.6921 \). The settling velocity follows the same trend as discovered by Many et.al., (2019). Thus, the rate of sludge build-up was determined as shown in Table 5.
Table 5: Sludge build-up rate regarding rapid mixing regime

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Rate of sludge build-up (mL/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.518</td>
</tr>
<tr>
<td>20</td>
<td>0.460</td>
</tr>
<tr>
<td>30</td>
<td>0.344</td>
</tr>
<tr>
<td>40</td>
<td>0.228</td>
</tr>
<tr>
<td>50</td>
<td>0.112</td>
</tr>
</tbody>
</table>

Initially, the flocs rapidly settle, as all the heavier particles with a higher density accumulate and settle. Thereafter, the settling rate decreases, as all the remaining particles are lighter and have lower densities. The settling rate was relatively low when the time approaches 60 minutes, thus indicating that settling ceased. It took 52 minutes for a 10 mL floc bed to form.

Thereafter, supplementary tests (n=3) were conducted using the optimum jar test conditions determined as well as the optimum coagulant and flocculant dosages. These results can be seen in Figure 10.
Figure 10: Sludge build-up rate with optimal dosage conditions

Again the average of the tests (n=3), generated, \( y = -0.033x^2 + 1.6914x - 11.885 \) which can be used throughout this section. Differentiating this equation gives \( y' = -0.066x + 1.6914 \), which represents the rate of sludge build-up. The results of the sludge build-up are given in Table 6.

**Table 6: Sludge build-up rate with optimal dosage conditions**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Rate of sludge build-up (mL/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.361</td>
</tr>
<tr>
<td>10</td>
<td>1.031</td>
</tr>
<tr>
<td>15</td>
<td>0.701</td>
</tr>
<tr>
<td>20</td>
<td>0.371</td>
</tr>
<tr>
<td>25</td>
<td>0.0414</td>
</tr>
</tbody>
</table>

As can be seen from Table 5 and Table 6, the optimum jar test conditions ensured an initial sludge build-up rate of 100% than when the coagulant and flocculant were both supplemented simultaneously during rapid mixing. This is due to denser flocs forming
when the jar test was done at optimum conditions. The flocs also rapidly settled within 30 minutes, a time at which the floc bed-volume did not increase. A 10 mL floc bed formed after 25 minutes, which is 27 minutes faster than when the coagulant and flocculant were both supplemented simultaneously during rapid mixing.

### 3.4.9 Turbidity removal rate

The data from the graphs obtained for the turbidity corresponded with the sludge build-up rate data, illustrating that the turbidity was removed faster initially and then slowed towards the end of the settling time. It can also be seen in Figure 11 and Figure 12 that the turbidity removal rate was better in the rapid mixing regime. This finding also correlates with the sludge removal rate data.

![Figure 11: Turbidity removal rate during the slow mixing regime](image)
Figure 12: Turbidity removal rate during rapid mixing regime

3.4.10 Morphology
The morphology of the flocs were analysed using QUEMSCAN, and yielded the results shown in Table 7.

Table 7: Morphology results

<table>
<thead>
<tr>
<th>QUEMSCAN parameters</th>
<th>Vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale: Calcium silicate</td>
<td>19.6</td>
</tr>
<tr>
<td>Scale: Calcite/lime (Si)</td>
<td>17.3</td>
</tr>
<tr>
<td>Scale: Calcium magnesium silicate (Mn)</td>
<td>18.1</td>
</tr>
<tr>
<td>Scale: (Ca, Mg, Al) silicate (Si)</td>
<td>15.6</td>
</tr>
<tr>
<td>Scale: Magnesium silicate</td>
<td>0.2</td>
</tr>
<tr>
<td>Dolomite</td>
<td>3.4</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>7.1</td>
</tr>
<tr>
<td>Sand/FA: Kaolinite/mica</td>
<td>8.3</td>
</tr>
<tr>
<td>Sand: Quartz/feldspar</td>
<td>9.1</td>
</tr>
<tr>
<td>Component</td>
<td>Quantity</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Iron oxide/brass</td>
<td>0.1</td>
</tr>
<tr>
<td>Iron sulphide/sulphate</td>
<td>0.2</td>
</tr>
<tr>
<td>Clay: Iron (Al) silicate</td>
<td>0.4</td>
</tr>
<tr>
<td>Paint: Titanium oxide</td>
<td>0.2</td>
</tr>
<tr>
<td>Other</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The main components in the flocs were calcium, silicate, calcite, calcium magnesium silicate, calcium magnesium aluminium silicate and magnesium silicate. Traces of gypsum, sand and fly ash were also found in the flocs. These compounds may cause scaling, which can be removed through further treatment using crystallisation. Figure 13 presents a QEMSCAN photomicrograph indicating all the substances found in the flocs.

![Figure 13: QEMSCAN photomicrograph of flocs](image)

Most of the kaolinite in the flocs are fly ash cenospheres. Iron oxide and brass present can be found as small particles, as well in the filtered flocs. It can be seen from Figure 14 that calcium silicate and calcite are the substances with the highest quantity in the flocs. Figure 15 represents the aluminosilicate cenospheres present in the filtrated flocs.
3.5 Conclusion
PAC was found to be the best coagulant at a dosage of 30 mg/L. In conjunction with the PAC, the best flocculant was a polyamine, at a dosage of 0.8 mg/L. At the Grootvlei power station, the same dosages and chemicals are used to treat raw water, thus, confirming that this power station uses optimum amounts of chemicals during raw water treatment. However, the plant can improve the treatment process further by adding the flocculant during the rapid mixing period, 60 seconds post PAC addition. The turbidity achieved was as low as 2 NTU. The mechanism was confirmed with settling velocity tests. This finding confirms that the flocculant should be added during rapid mixing. It was found that it takes 30 minutes to form a 10 mL floc bed. The method developed did not reduce the hardness of the water, a challenge which must be addressed in further studies.

References


CHAPTER 4:
CHAPTER 4: INVESTIGATION OF SETTLING VELOCITY OF PARTICLES IN THE PROCESS OF CRYSTALLISATION AND CHEMICAL FLOCCULATION OF REVERSE OSMOSIS REJECT WATER

4.1 Abstract

Power generation processes generate wastewater that is rich in scale-forming agents and which, requires suitable pre-treatment prior to further treatment with an RO system. In this study, Rheofloc5023 was used as a coagulant, while Rheofloc5414, ARFloc100 and Genefloc were the selected flocculants applied after the pH adjustment with lime and NaOH to alter the solubility of the ions in the water. The tests were conducted at 40°C and 60°C to observe the effect that temperature has on the treatment process. Four parameters were considered during the optimisation process, namely, the conductivity, turbidity, total hardness and alkalinity. When lime was used, it was found that the treatment was superior at 60°C with ARfloc100 as flocculant. A coagulant dosage of 0.5 mg/L, a flocculant dosage of 0.2 mg/L, and a lime dosage of 220 mg/L were found to be optimal for a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54% and an alkalinity removal of 71%. When NaOH was used, Rheofloc5414 at 40°C was found to be optimal with coagulant and flocculant dosages of 5 mg/L and 0.5 mg/L. This yielded a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3% and an alkalinity removal of 50.6%. Thus, lime treatment was more efficient for the removal of scaling agents from the water. However, it was found that settling occurred faster at 60°C with both lime and NaOH, and that the latter had a better settling velocity characterised by formation of more stable crystals. This finding was confirmed with a scanning electron microscope, as the treatment with NaOH and Rheofloc5414 at 60°C had larger and more densely packed crystals. From the above findings, it is suggested that lime should be used for treatment, as it removed more scaling agents and it is less expensive and more readily available than NaOH.
4.2 Introduction
Coal power plants use large volumes of water to lower high temperatures, and to power turbines with steam to generate electricity. The power sector is the largest industrial water user around the world; however, there is limited information in relation to water management by some power plants. In South Africa, the main power utility Eskom is reported to use 1.38 L of water per kWh of electricity. This is relatively high compared to China, where power stations use 1.15 L of water to generate a kWh of electricity (Zhang et al., 2017). Such data, coupled the strict national water regulations, have motivated Eskom to embark on a campaign to reduce its water usage to 1.34 L/kWh by 2020, hence, the adoption of a Zero Liquid Effluent Discharge policy (ESKOM, 2017), which aims to recycle wastewater in order to reduce the volume of water extracted from rivers and to minimise Eskom’s footprint.

Currently, Eskom has a well fuelled water treatment system, which includes RO; however, after a number of cycles of RO treatment, the concentration of total dissolved solids in the retentate is relatively high, making the RO no longer suitable for the treatment of such salted water (RO-reject), which will normally be discharged in a sump (Eskom, 2017). However, the policy recently adopted by Eskom has resulted in consideration of pre-treatment processes, to significantly reduce the total dissolved solids level in RO-reject prior to further treatment with the RO system. The RO-reject water considered by this study was collected from the Grootvlei power station, which is situated near Balfour, Mpumalanga, South Africa. This water brine consists of calcium and magnesium salts, which can scale downstream equipment and cause a reduction of equipment efficiency. These scaling agents need to be removed from the water. Such scaling agents can be removed through a crystallisation process.

Crystallisation is the process of super-saturation where the scaling agents in the water become insoluble due to a high concentration of these scaling agents. Flocculation is then used to ensure that these crystals that form agglomerate, and the mass of the crystals increases, which in turn aids in the settling of the crystals (Qasim et al., 2019).

Polyamines are cationic coagulants with a medium molecular weight, mostly linear, which are soluble, and have been, and can be used over a wide pH range, as
demonstrated by Koether (2017), who achieved a turbidity removal above 80% under optimum conditions. Due to the length of the molecule, these molecules wrap flocs together (Astin, 1983). In a study conducted by Lee et al. (2001), it was found that polyamines reduced the turbidity of raw water from 9.4 NTU to 1 NTU and the TOC levels in the water from 3.3 mg/L to 1.97 mg/L. According to a study conducted by Choi et al. (2001), polyamines, in conjunction with aluminium sulphate, could reduce the amount of aluminium sulphate used by 50%. This makes the treatment more cost effective and minimises sludge production. The turbidity also decreases from 145 NTU to 2 NTU. The polyamines used were Rheofloc and ARfloc 100.

Genefloc is a polyquaternary amine that can function over a large pH range and which is produced by Genesys International Limited, manufactured in Cheshire, UK. The positive charge of these molecules can be found in the backbone of the polymer chain. Thus, if there is an excess of flocculants in the water, it will adhere across the length of the membrane surface and not by its sub branches (Astin, 1983).

Lime is used to increase the pH and reduce the solubility of metal ions in the water. Different grades of lime can be used to increase the pH. In this study, industrial-grade lime was used, which consists of more or less 50% lime. The calcium and magnesium ions react with carbonates and hydroxides respectively and precipitate at high pH values. Strontium, calcium and magnesium removal is pH dependant, and lime is a relatively less expensive and highly effective substance to increase the pH (O'Donnell et al., 2016). According to Lim et al. (2002), when lime is added to water, it dissociates into calcium cations and hydroxyl anions. At high pH values, these ions bind with other ions in water to form crystals. For example, calcium ions can either bind with sulphate ions or carbonate ions, which form insoluble calcium sulphate or calcite respectively, and the hydroxyl ions can bind with magnesium ions in the water to form magnesium hydroxide.

Sodium hydroxide can also be used as an alkaline reagent for water softening. The calcium carbonate will precipitate and sodium carbonate will form as a by-product, which is stable (Malanova et al., 2014). According to the study done by Malanova et al. (2014) sodium hydroxide is a good reagent to use in water softening, as CaCO₃
precipitates. Sodium hydroxide is, however, more expensive than lime and is less freely available than lime.

This study assessed the performance of the coagulants in Section 4.2, flocculants and lime and sodium hydroxide in the removal of hardness, alkalinity and conductivity from RO- reject water, and investigated the effect of temperature on their performance.

4.3 Experimental procedure

4.3.1 Sample collection
Samples were collected in 25 L, plastic, rinsed drums from the RO system at the Grootvlei Power Station. The water was collected at the taps that release wastewater that could no longer be treated through the RO system, and which was then discharged to the sumps. Samples were transported to the Water Laboratory at the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom); the water containers were covered with black plastic and stored in a refrigerator prior to use.

4.3.2 Water analysis
During the analysis of water, different parameters were considered, measured and calculated. This included pH, measured with a Hannah pH meter, and conductivity, measured with a Lovibond100 meter; turbidity was measured using a HACH 2100Q portable turbidity meter. Total hardness and alkalinity were measured through titrations.

4.3.3 Coagulants
Rheofloc5023 was used as a coagulant and dosages ranging from 0.2 mg/L to 7 mg/L were used in the optimisation tests. The dosages used were 0.2, 0.5, 0.7, 2, 5 and 7 mg/L, and the effect of dosage was carried out in duplicate during the optimisation procedure. This coagulant is used for wastewater treatment at the power plant and was kindly offered by personnel.

The flocculants used in the optimisation process have been discussed in Section 4.2 and included Rheofloc5414, obtained from the plant, ARfloc100, obtained from the labs at the university, and Genefloc, obtained from Genesys international. The dosages considered for each of these flocculants were 0.2, 0.7, 1 and 7 mg/L.
The pH needs to be increased to improve crystallisation; this was done with the addition of calcium hydroxide, lime (CaOH). A dosage of 220 mg/L was used to increase the pH to 10.1, where magnesium and calcium ions are no longer soluble in the water, and, thus, likely to precipitate. At the optimal coagulant and flocculant dosages, the lime was replaced with the same concentration of sodium hydroxide (NaOH), to observe the difference in efficiency of treating the RO-reject water.

4.3.4 Jar test
A six-paddle jar test apparatus with a water bath connected to it was used, to ensure that the temperature of the samples remained constant. During the jar test run, rapid mixing occurred at 240 rpm for five minutes, at which point the coagulant and flocculant were added to the samples. Thereafter, slow mixing occurred for 90 minutes at 80 rpm. At the start of the slow mixing period, the lime or NaOH was added to the sample. After the slow mixing period, settling occurred for 30 minutes, before the tests were conducted.

4.3.4.1 Optimisation
The optimum dosage of the coagulant was determined by keeping constant the dosage of flocculant in the six beakers while altering the coagulant dosage in each beaker, as discussed in Section 4.3.3. Mixing and settling occurred as discussed in Section 4.3.4. Thereafter, the following tests were conducted to observe the optimal conditions for each flocculant: conductivity, turbidity, total hardness and alkalinity. The percentage removal of each of these parameters was calculated by taking into account their initial values before treatment of the water. The optimal conditions determined using lime were considered during treatment with NaOH.

4.3.5 Settling velocity tests
The optimal dosages were used to determine the settling velocity of the particles that formed. This was done by using the same mixing method as for the optimisation process. Instead of 30-minutes settling time, the sample was added into a calibrated Imhoff cone directly after the mixing occurred. The Imhoff cone was calibrated by adding 1 mL of water at a time and marking the volume of the water up until a 10 mL
mark is reached. Thus, the volume of the sludge could be observed until it reached 10 mL.

4.3.6 Stability tests
Similar optimal dosages were used to determine the stability of the sludge that was formed. The mixing regime was followed and, after mixing, a 30 minute settling time was allowed. Thereafter, the samples were mixed for 30 seconds at a speed of 100 rpm. Then, the sample’s turbidity was measured at three-minute intervals to determine how rapidly the sludge settled after disturbance. Subsequently, a similar method was followed; albeit at a higher mixing speed of 200 rpm to determine the difference between the two disturbance speeds.

4.3.7 Morphology analysis
After the settling tests had been conducted, the water was decanted and the crystals were obtained and dried in an oven for 24 hours at 50°C. The morphology of the crystals was determined using a scanning electron microscope (TECSAN, model VEGA 3 XMU from Czech Republic, with 10 micron lens). This model is equipped with a tungsten filament that is used as an electron source. This source operates in Nano space while an energy-dispersive X-ray (EDX) spectroscopy, incorporated to the SEM, carried out a compositional analysis. The sample was carbon coated to improve the conductivity of the sample. Backscatter and secondary detectors were used to determine the surface morphology of the sample. A high voltage of 20 kV was used at different magnifications using Vega software. The compositional analysis was determined using INCA software from Oxford on a selected area. The size of the particles, as well as the compounds in the particles, were visible through this apparatus. The dried crystal samples were also characterised using a Philips X’Pert pro MPD X-ray diffractometer, at 40 kV and 30 mA, with scan speed of 2 °/min and a scan range of 3-90° and a step width of 0.01°, to determine the crystallinity of the compounds. A higher crystallinity refers to more stable crystals that formed.
4.3.8 Model prediction
Tests on the above-mentioned parameters were conducted and the information that was gathered was used to build a geochemical model on French Creek software. It was found that, when using lime, that calcite, anhydrite and gypsum were the leading scaling agents, with a saturation level vs pH curve for the calcite illustrated in the Figure 15.

![Figure 15: Saturation level of calcite with addition of lime](image)

Figure 15 shows clearly that the calcite will precipitate at a pH of 10.1, which was used in this study. The concentration of lime that should be used was also calculated with French Creek - this is indicated in Figure 16.
As 100% lime was used in the simulation, it can be calculated that 200 mg/L lime should be used. The same prediction was done using NaOH (200 mg/L) inducing calcite saturation and the results are given in Figures 18 and 19.

Figure 16: Lime dosage profile
Figure 17: Saturation level of calcite with addition of NaOH
4.4 Results and discussion

4.4.1 Water characterisation
Prior to any investigation, water was characterised by considering physico-chemical parameters, such as conductivity, turbidity, total hardness and alkalinity. The results obtained are presented in Table 8.

Table 8: Results of water samples characterisation

<table>
<thead>
<tr>
<th>Conductivity (mS/cm)</th>
<th>Turbidity (NTU)</th>
<th>Total hardness (mgCaCO₃/L)</th>
<th>Alkalinity (mgCaCO₃/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.92-7.38</td>
<td>0.85-4.44</td>
<td>783.6-2084</td>
<td>58-60</td>
</tr>
</tbody>
</table>

Table 8 indicates that the conductivity and total hardness of the RO-reject water samples were very high, with the potential to form scale, and could not, therefore, be considered for further cycles using the RO system without pre-treatment.
4.4.2 Geochemical simulation with French Creek
Using the French Creek model to simulate the scale potential of RO-reject water with the cations and anions concentration shown in Table 9, the data in Table 10 was generated. According to Rahardianto et al. (2007), higher concentrations of scale precursor ions, such as Ca$^{2+}$, Ba$^{2+}$, SO$_4^{2-}$ and CO$_3^{2-}$ in the membrane retentate beyond solubility limits, are likely to cause mineral salt scaling as mineral scalants, i.e. barite, calcite and gypsum.

**Table 9: Cations and anions from French Creek**

<table>
<thead>
<tr>
<th>Cations (mg/L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (as Ca)</td>
<td>826</td>
</tr>
<tr>
<td>Magnesium (as Mg)</td>
<td>357</td>
</tr>
<tr>
<td>Barium (as Ba)</td>
<td>0.444</td>
</tr>
<tr>
<td>Strontium (as Sr)</td>
<td>5.71</td>
</tr>
<tr>
<td>Sodium (as Na)</td>
<td>882.9</td>
</tr>
<tr>
<td>Potassium (as K)</td>
<td>192</td>
</tr>
<tr>
<td>Lithium (as Li)</td>
<td>4.79</td>
</tr>
<tr>
<td>Iron (as Fe)</td>
<td>0.125</td>
</tr>
<tr>
<td>Ammonia (as NH$_3$)</td>
<td>0</td>
</tr>
<tr>
<td>Aluminum (as Al)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anions (mg/L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride (as Cl)</td>
<td>551</td>
</tr>
<tr>
<td>Sulfate (as SO$_4$)</td>
<td>4611</td>
</tr>
<tr>
<td>Dissolved CO$_2$ (as CO$_2$)</td>
<td>3.34</td>
</tr>
<tr>
<td>Bicarbonate (as HCO$_3$)</td>
<td>172.9</td>
</tr>
<tr>
<td>Carbonate (as CO$_3$)</td>
<td>7.56</td>
</tr>
<tr>
<td>Silica (as SiO$_2$)</td>
<td>0.00</td>
</tr>
<tr>
<td>Phosphate ($^0$Fr)</td>
<td>0.300</td>
</tr>
<tr>
<td>H$_2$S (as H$_2$S)</td>
<td>0.00</td>
</tr>
<tr>
<td>Fluoride (as F)</td>
<td>6.90</td>
</tr>
<tr>
<td>Boron (as B)</td>
<td>2.07</td>
</tr>
</tbody>
</table>
The various minerals with the potential to cause scale on the RO membrane were obtained as shown in Table 10.

**Table 10: Scaling potential generated with French Creek**

<table>
<thead>
<tr>
<th>Scaling potential</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (CaCO₃)</td>
<td>9.03</td>
</tr>
<tr>
<td>Aragonite (CaCO₃)</td>
<td>8.36</td>
</tr>
<tr>
<td>Magnesite (MgCO₃)</td>
<td>3.23</td>
</tr>
<tr>
<td>Anhydrite (CaSO₄)</td>
<td>1.02</td>
</tr>
<tr>
<td>Gypsum (CaSO₄·2H₂O)</td>
<td>1.68</td>
</tr>
<tr>
<td>Barite (BaSO₄)</td>
<td>111.37</td>
</tr>
<tr>
<td>Celestite (SrSO₄)</td>
<td>1.05</td>
</tr>
<tr>
<td>Ferric Hydroxide (Fe(OH)₂)</td>
<td>147.77</td>
</tr>
<tr>
<td>Siderite (FeCO₃)</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Ferric hydroxide and barite are most likely to form scaling according to the French Creek model simulation. These compounds can be removed from water by stimulating crystallisation at superstation level, which with can be achieved with the aid of coagulants and flocculants. In a study carried out by Tomaszewksa and Bodzek (2013), which aimed to desalinate geothermal water in an integrated system, including ultrafiltration and two independent reverse osmosis systems, a theoretically selected phosphate scaling inhibitor failed to protect the membrane against scaling, as minerals, including barite, crystallised on the membrane. A separate study conducted by Sun et al. (2017) showed the potential of ferric hydroxide to scale in pipes; thereby, affecting effective treatment of water. According to Martinez-Ruiz et al. (2018), barite crystals form when barium reacts to an abundance of sulphates in the water, thus, the potential of barite forming is an indication that the crystallisation mechanism is taking place during the tests. According to Yan et al. (2017) inhibiting and reducing barite is important, as barite has a negative impact on laminar and turbulent flow.
4.4.3 Optimisation of dosages and conditions
During the optimisation of the dosages of coagulants and flocculants, Rheofloc 5023 was used as a coagulant with the following dosages (mg/L): 0.2, 0.5, 0.7, 2, 5 and 7. This was used in conjunction with 220 mg/L lime, as well as the different flocculants. These flocculants were Rheofloc 5414, ARfloc100 and Genefloc. The parameters that were used to determine the optimal conditions included conductivity, turbidity, total hardness and alkalinity. Two different temperatures were also used to determine the optimal conditions for operation, namely 40°C and 60°C.

4.4.3.1 Rheofloc5414 as flocculant
The first flocculant used with Rheofloc5023 was Rheofloc5414, which was used in conjunction with a lime dosage of 220 mg/L.

4.4.3.1.1 Conductivity removal
The reduction of conductivity at 40°C can be seen in Figure 19.

![Figure 19: Conductivity removal with Rheofloc5414 as flocculant at 40°C](image)

As can be seen in Figure 19, conductivity removal was the highest at 9.2% at a coagulant dosage of 2 mg/L and a Rheofloc5414 dosage of 1 mg/L at 40°C. Thus, at
that dosage, 9.2% of the dissolved ions were removed from the solution. However, the optimal dosage was found to be a coagulant dosage of 0.2 mg/L with a flocculant dosage of 0.2 mg/L, as there was insignificant difference observed compared to the maximum removal of conductivity.

The results obtained using the same coagulant and flocculant dosages at 60°C can be seen in Figure 20.

![Figure 20: Conductivity removal with Rheofloc5414 as flocculant at 60°C](image)

As can be seen in Figure 20, the optimal conditions at 60°C were a coagulant dosage of 0.2 mg/L with a flocculant dosage of 0.2 mg/L. The extent of reduction of the conductivity at these dosages was 46%. Thus, there was a reduction of 46% in the dissolved ions in the treated water. It can also be observed that the removal of conductivity at 60°C was relatively consistent compared to that at 40°C.

It can, therefore, be suggested that conductivity removal at 60°C is superior to conductivity removal at 40°C. This was due to super-saturation that improves at higher temperatures; with more scaling agents formed at these temperatures, partly due to evaporation. In a study conducted by Zhang et al. (2017), scaling occurred frequently at
higher temperatures, thus, super-saturation occurred and fewer particles were soluble in the water. Elevated temperatures are likely to induce an increase in precipitation.

4.4.3.1.2 Turbidity removal

The turbidity removal of the coagulant and flocculant dosages at 40°C can be observed in Figure 21.

![Graph showing turbidity removal at different dosages](image)

**Figure 21: Turbidity removal with Rheofloc5414 as flocculant at 40°C**

As shown in Figure 21, there was an increase in the turbidity with all the dosages used, because of the relatively low initial values of the turbidity before treatment. At 40°C, the optimum regarding turbidity was a coagulant dosage of 0.5 mg/L and a flocculant dosage of 7 mg/L, for which there was an increase of only 13% in turbidity.

The turbidity removal at 60°C is given in Figure 22.
As can be seen in Figure 22, a decrease in the turbidity of water was achieved with only two flocculant dosages, 0.2 mg/L and 7 mg/L. The optimal dosage was, however, a coagulant dosage of 0.5 mg/L and flocculant dosage of 7 mg/L, which yielded a turbidity removal of 26%. Thus, at higher temperatures, turbidity removal was superior, due to the same reasons given for conductivity removal in Section 4.4.3.1.2.

4.4.3.1.3 Total hardness removal
The total hardness reduction with the same coagulant and flocculant dosages at 40°C is given in Figure 23.
Figure 23: Total hardness removal with Rheofloc5414 as flocculant at 40°C

This is an important parameter, as it relates directly to the amount of scaling agents in the water. It can be seen in Figure 23 that the highest removal at 40°C was achieved with a coagulant dosage of 7 mg/L and a flocculant dosage of 1 mg/L. These dosages yielded a total hardness reduction of 17.1%. The optimal dosages, however, were a coagulant and flocculant dosage of 0.2mg/L, as fewer reagents were needed to obtain a total hardness removal of 12%. This relates to a 12% reduction of the scaling agents in the water.

The total hardness removal at 60°C is given in Figure 24, using the same coagulant and flocculant dosages.
As can be seen in Figure 24, the optimal dosage at 60°C is a coagulant and flocculant dosage of 0.2 mg/L, which yielded a total hardness removal of 53%, implying that there are 53% less scaling agents in the water under these conditions. It can also be stated that any of these dosages can be used, but the 0.2 mg/L dosages are optimal, as it will be the most cost effective dosage to use.

The higher efficiency at higher temperatures is due to increased super-saturation and a decrease in the solubility of the scaling agents in the water, as stated by Zhang et al. (2017). Thus, crystallisation was more effective and with an increase in the precipitation of insolubles; higher temperatures are likely to provide more energy which can then facilitate rapid reaction to form crystals (Muryanto et al., 2014).

**4.4.3.1.4 Alkalinity removal**
Removal of alkalinity with the same coagulant and flocculant dosages at 40°C are illustrated in Figure 25.
Figure 25: Alkalinity removal with Rheofloc5414 as flocculant at 40°C

As can be seen from Figure 25, the optimal conditions for alkalinity removal at 40°C are a coagulant dosage of 5 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded a 72% reduction in the alkalinity in the water, which relates to a 72% reduction in the carbonates in the water.

The alkalinity removal of the same dosages at 60°C can is illustrated in Figure 26.
As can be seen in Figure 26, optimal alkalinity removal of 77%, was achieved with a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L at 60°C. This achievement relates to 77% less carbonates in the treated water at these conditions.

The efficiency of alkalinity removal was higher at increased temperatures because of the decrease in solubility accompanying an increase in super-saturation. This was also found in a study by Zhang et al. (2017).

4.4.3.2 ARFloc100 as flocculant
The next flocculant used was ARFloc100 in conjunction with 220 mg/L lime. The dosages used for the ARFloc were 0.2 mg/L, 0.5 mg/L, 1 mg/L and 7 mg/L.

4.4.3.2.1 Conductivity removal
The results of conductivity removal obtained using ARFloc100 at 40°C in conjunction with the coagulant, Rheofoc5023, and lime can be seen in Figure 27.
Figure 27: Conductivity removal with ARFloc100 as flocculant at 40°C

It is clear from Figure 27 that a higher flocculant dosage yielded a better conductivity removal. The highest conductivity removal at 40°C, 22%, was measured when a coagulant dosage of 5 mg/L was used in conjunction with a 7 mg/L flocculant dose. The optimal dosage was, however, a coagulant dose of 0.2 mg/L and a flocculant dose of 7 mg/L, which yielded a conductivity removal of 20%. This indicated a 20% reduction of dissolved solids from the water after treatment.

With the same dosages, the conductivity removal at 60°C can be observed in Figure 28.
It can be seen from Figure 28 that less coagulant and flocculant was needed to reach an improved conductivity removal at 60°C. The coagulant and flocculant dosages that yielded the highest conductivity removal at this temperature were 0.5 mg/L and 1 mg/L respectively, which yielded a 39.4% reduction in conductivity. The optimal dosages were, however, a coagulant dosage of 0.2 mg/L and a flocculant dosage of 1 mg/L. This yielded a conductivity removal of 39.2%.

The conductivity removal was, once again, higher at 60°C. This finding was due to the increase in the super-saturation levels and the decrease in the solubility of the dissolved solids, which then precipitated, thus, reducing the conductivity of the water after treatment.

4.4.3.2.2 Turbidity removal
The turbidity removal results obtained from the same coagulant and flocculant dosages at 40°C can be seen in Figure 29.
In general, there was an increase in turbidity when the coagulant and flocculant were added into the water sample, except at coagulant and flocculant dosages of 5 mg/L and 0.2 mg/L, as well as 7 mg/L and 0.5 mg/L, respectively. The optimal dosages regarding turbidity removal were 5 mg/L coagulant and 0.2 mg/L flocculant dosage, which yielded a 14% reduction in turbidity.

With the same dosages, the turbidity removal at 60°C can be seen in Figure 30.

Figure 29: Turbidity removal with ARFloc100 as flocculant at 40°C
Figure 30: Turbidity removal with ARFloc100 as floculant at 60°C

The turbidity increased with almost every dosage used, except at coagulant and floculant dosages of 5 mg/L and 0.2 mg/L respectively at 60°C. Therefore, these were the optimal dosages at these conditions, and yielded only a turbidity removal of 8%.

Thus, in this case, turbidity removal at 40°C was more efficient than at 60°C; however, further investigation could be required to ascertain the reasons behind such an unexpected trend.

4.4.3.2.3 Total hardness removal

The same floculant, coagulant and dosages were used to test the reduction in the total hardness of the water and the results at 40°C as illustrated in Figure 31.
As can be seen in Figure 31, optimal total hardness removal at 40°C was obtained using a coagulant dosage of 0.7 mg/L and a flocculant dosage of 7 mg/L, yielding a removal of 25.8%, at which the level achieved was 25.8% less scaling agents in the water after treatment.

The total hardness removal with the same dosages at 60°C can be seen in Figure 32.
Figure 32: Total hardness removal with ARFloc100 as flocculant at 60°C

Total hardness removal at 60°C was significantly higher than at 40°C and required less reagents. The optimal dosages at these conditions was 0.5 mg/L coagulant dosage and 0.2 mg/L flocculant dosage, yielding a 54.3% reduction in scaling agents in the water after treatment. A trend can also be seen in Figure 32, that the coagulant dosage of 0.5 mg/L was at a peak, and as the coagulant dosage increased after this peak, the total hardness removal decreased; therefore, an excess of coagulant or flocculant was likely to have destabilised the crystallisation process.

Generally, higher temperatures increase the total hardness removal of water as precipitation increases. This was also seen in a study by Zhang et al. (2017).

4.4.3.2.4 Alkalinity removal
Using the same dosages of flocculant and coagulant, the alkalinity removal at 40°C can be seen in Figure 33.
The optimal dosages regarding alkalinity removal at 40°C were 2 mg/L coagulant and a 7 mg/L flocculant, which yielded an alkalinity removal of 72%, indicating 72% less carbonates in the treated water.

The alkalinity removal with the same dosages at 60°C can be seen in Figure 34.
According to Figure 34, the highest alkalinity removal at 60°C occurred with a coagulant dosage of 0.5 mg/L and a flocculant dosage of 1 mg/L. These dosages yielded a 73% reduction in the alkalinity after treatment. However, the optimal dosages for alkalinity removal at 60°C are a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 71%.

At 60°C, lower dosages were needed to achieve almost similar alkalinity removal rates as at 40°C. It can also be said that, when ARFloc100 was used, the coagulant dosage should not exceed 0.5 mg/L, as the efficiency of the treatment decreases with an increase in its dosage.

### 4.4.3.3 Genefloc as a flocculant

The next flocculant used was Genefloc at dosages of 0.2 mg/L, 0.5 mg/l, 1 mg/L and 7 mg/L, used with the coagulant dosages discussed previously, and 220 mg/L lime.
4.4.3.3.1 Conductivity removal

The results obtained at 40°C with regards to conductivity removal with this flocculant, Genefloc, in conjunction with the coagulant, Rheofoc5023, and lime can be seen in Figure 35.

As can be seen from Figure 35, low Genefloc dosages yielded better conductivity removal, with an optimal dosage of 0.5 mg/L coagulant and a flocculant dosage of 0.2 mg/L. These dosages yielded a 22% reduction in conductivity. Higher flocculant dosages did not react well with regard to conductivity removal from the water.

The same dosages were used to determine the conductivity removal at 60°C, and the results can be seen in Figure 36.
It can be seen in Figure 36 that lower dosages yielded a better result at 60°C. The optimal dosage at 60°C for conductivity removal is a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.2 mg/L, which yielded a 38% reduction in the conductivity of the treated water, which was significantly higher than the 22% removal achieved at 40°C. At a flocculant dosage above 0.2 mg/L, the efficiency of treatment decreased significantly with regard to conductivity removal.

An increase in the temperature increased the efficiency of the conductivity removal from the water. This trend was due to an increase in precipitation because of higher supersaturation, as well as an increase in the evaporation of the water.

4.4.3.3.2 Turbidity removal
The same dosages were used to determine the turbidity removal and the results at 40°C can be seen in Figure 37.
As can be seen from Figure 37, the optimal conditions for turbidity removal at 40°C were a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded 28% removal of the turbidity after treatment. With Genefloc dosages ranging from 0.5 mg/L to 7 mg/L, the turbidity increased, due to an overdose in flocculant.

The same dosages were used to determine the turbidity removal at 60°C and the results can be seen in Figure 38.
The optimal turbidity removal at 60°C yielded a 6.4% removal at a coagulant dosage of 2 mg/L and flocculant dosage of 1 mg/L. There was an increase in the turbidity with the other dosages, due to the initial low turbidity of the water sample prior to the treatment. The treatment at lower temperatures induced a higher turbidity removal.

**4.4.3.3 Total hardness removal**

The same dosages were used to determine the total hardness removal of the treated water at 40°C, and the results can be seen in Figure 39.
Figure 39: Total hardness removal with Genefloc as flocculant at 40°C

As can be seen from Figure 39, the highest total hardness removal at 40°C was achieved at a coagulant dosage and flocculant dosage of 7mg/L, which yielded a 21% removal. The optimal dosages were, however, a coagulant dosage of 0.2 mg/L and a flocculant dosage of 0.5 mg/L, which yielded a total hardness removal of 19%. Thus, there were 19% less scaling agents present in the treated water.

The same dosages were used to determine the total hardness removal at 60°C, and the results are illustrated in Figure 40.
As can be seen from Figure 40, the optimal dosages for total hardness removal at 60°C were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L. These dosages yielded a total hardness removal of 54%.

At higher temperatures, the total hardness removal was elevated, because of the precipitation of the crystals that formed due to super saturation.

### 4.4.3.3.4 Alkalinity removal

The same dosages were used to determine the alkalinity removal at 40°C and the results can be seen in Figure 41.
As can be seen from Figure 41, the highest alkalinity removal was achieved with a coagulant dosage of 7 mg/L in conjunction with a flocculant dosage of 0.2 mg/L, which yielded alkalinity removal of 67%. The optimal dosages were, however, a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 64%, which represents a 64% reduction of the carbonates in the treated water.

The same dosages were used to determine the alkalinity removal at 60°C and the results can be seen in Figure 42.
Figure 42: Alkalinity removal with Genefloc as flocculant at 60°C

As can be seen from Figure 42, the optimal dosages for alkalinity removal at 60°C were a coagulant dosage of 0.5 mg/L and a flocculant dosage of 0.2 mg/L, which yielded an alkalinity removal of 73%.

Higher temperatures induced higher alkalinity removal as the carbonates precipitate as crystals due to an increased super-saturation at these higher temperatures.

4.4.3.4 Optimal dosages using lime

The optimal dosage for each flocculant and temperature can be seen in Table 11.

Table 11: Summary of optimal dosages

<table>
<thead>
<tr>
<th>Flocculant and temperature</th>
<th>Coagulant dosage (mg/L)</th>
<th>Flocculant dosage (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheofloc5414 @ 40°C</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Rheofloc5414 @ 60°C</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>ARfloc100 @ 40°C</td>
<td>0.7</td>
<td>7</td>
</tr>
<tr>
<td>ARfloc100 @ 60°C</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Genefloc @ 40°C</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Genefloc @ 60°C</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The parameters measured at these optimal conditions can be seen in Table 12.

**Table 12: Parameters at optimal dosages using lime**

<table>
<thead>
<tr>
<th>Flocculant and temperature</th>
<th>Conductivity removal (%)</th>
<th>Turbidity removal (%)</th>
<th>Total hardness removal (%)</th>
<th>Alkalinity removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheofloc5414 @ 40°C</td>
<td>8</td>
<td>-99</td>
<td>12</td>
<td>62</td>
</tr>
<tr>
<td>Rheofloc5414 @ 60°C</td>
<td>46</td>
<td>-20</td>
<td>53</td>
<td>77</td>
</tr>
<tr>
<td>ARfloc100 @ 40°C</td>
<td>4</td>
<td>-58</td>
<td>19</td>
<td>54</td>
</tr>
<tr>
<td>ARfloc100 @ 60°C</td>
<td>36</td>
<td>-61</td>
<td>51</td>
<td>71</td>
</tr>
<tr>
<td>Genefloc @ 40°C</td>
<td>-13</td>
<td>-19</td>
<td>17</td>
<td>54</td>
</tr>
<tr>
<td>Genefloc @ 60°C</td>
<td>38</td>
<td>-170</td>
<td>54</td>
<td>73</td>
</tr>
</tbody>
</table>

From Table 12, it can be seen clearly that treatment with lime, the effective temperature was 60°C than 40°C. This finding was due to the increase in super saturation when the temperature increases. The increased effectiveness at higher temperatures is partially due to the evaporation and an increase in ion energy at high temperatures, which promoted crystal formation and settling. According to (SUEZ Water Technologies & Solutions, 2012), hot lime softening is effective than cold lime softening. The data in Table 12 illustrates the fact that the treatment was effective at a higher temperature, thus hot lime softening was proven to be more effective. It can be seen that the turbidity increased, as the turbidity before the treatment was already low. There was also a conductivity increase when Genefloc was used at 40°C.

If all the parameters are taken into account, Genefloc was the least efficient flocculant used in conjunction with lime, thus, it should be disregarded for the settling velocity and stability tests.
4.4.3.5 Using NaOH instead of lime

The optimal conditions for the coagulants and flocculants were used to determine the effect of lime replacement by NaOH on the treatment of the water sample. The results for the conductivity removal, turbidity removal, total hardness removal and alkalinity removal are given in Table 13.

Table 13: Parameters at optimal dosages using NaOH

<table>
<thead>
<tr>
<th>Flocculant and temperature</th>
<th>Conductivity removal (%)</th>
<th>Turbidity removal (%)</th>
<th>Total hardness removal (%)</th>
<th>Alkalinity removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheofloc5414 @ 40°C</td>
<td>1.26</td>
<td>58.75</td>
<td>20.31</td>
<td>50.57</td>
</tr>
<tr>
<td>Rheofloc5414 @ 60°C</td>
<td>-4.66</td>
<td>5</td>
<td>21.87</td>
<td>64.37</td>
</tr>
<tr>
<td>ARfloc100 @ 40°C</td>
<td>0.63</td>
<td>29.17</td>
<td>20.17</td>
<td>54.02</td>
</tr>
<tr>
<td>ARfloc100 @ 60°C</td>
<td>-4.28</td>
<td>16.81</td>
<td>21.51</td>
<td>63.22</td>
</tr>
<tr>
<td>Genefloc @ 40°C</td>
<td>0.19</td>
<td>73.33</td>
<td>20.74</td>
<td>58.62</td>
</tr>
<tr>
<td>Genefloc @ 60°C</td>
<td>-5.23</td>
<td>16.39</td>
<td>20.38</td>
<td>63.22</td>
</tr>
</tbody>
</table>

From Table 13, it can be concluded that NaOH will be more efficient only if turbidity was the main parameter investigated. This conclusion was reached mainly as a result of the colour of the reagents. Lime has a white milky colour when it was added to the samples, thus, increasing the turbidity of the samples. NaOH is transparent, with little to no effect on the turbidity when added to the samples, only influencing the presence of particles in suspension.

It was also found that NaOH is efficient at lower temperatures as at these lower temperatures an increase in conductivity was observed, thus, reducing the running costs of the treatment process. However, NaOH is expensive than lime and is not as freely available as lime. Lime is also more efficient in removing dissolved solids and scaling agents, thus, lime will be a better option for removing these substances.
Settling velocity tests, stability tests and the morphology tests can be used to assess the potential of flocculants and the effect of temperature on the water treatment process further.

4.4.4 Settling velocity tests
Using the optimal conditions obtained from testing the conductivity, turbidity, total hardness and alkalinity, settling velocities were tested with all the best flocculants, namely, Rheofloc5414 and ARFloc100. The tests were conducted at 40°C and 60°C with lime as well as NaOH. The results can be seen in Figure 43 and Table 14.

![Figure 43: The results of the settling velocity tests](image)
<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Settling velocity (mL/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rheofloc5414 at 40°C with lime</td>
</tr>
<tr>
<td>0</td>
<td>0.0294</td>
</tr>
<tr>
<td>5</td>
<td>0.0291</td>
</tr>
<tr>
<td>10</td>
<td>0.0288</td>
</tr>
<tr>
<td>15</td>
<td>0.0285</td>
</tr>
<tr>
<td>20</td>
<td>0.0282</td>
</tr>
<tr>
<td>25</td>
<td>0.0279</td>
</tr>
<tr>
<td>30</td>
<td>0.0276</td>
</tr>
</tbody>
</table>
When using lime, the fastest settling rate was observed when ARfloc100 was used at 60°C. According to the settling prediction model in Figure 43, the settling will be concluded in 874 seconds. It is also clear that, when using lime, settling will occur faster at higher temperatures.

When NaOH is used, the settling occurs faster at higher temperatures with Rheofloc5414. Using the prediction model in Figure 43, it was estimated that complete settling will occur within 11 seconds.

It can be concluded that treatment with NaOH promotes faster settling than when the water is treated with lime.

4.4.5 Stability tests
Stability tests were conducted with Rheofloc5414 and ARfloc100 in conjunction with lime and NaOH at 40°C and 60°C. The coagulant and flocculant were added and rapid mixing occurred for five minutes, then slow mixing occurred for 90 minutes, at which point the lime or NaOH was added. A 30-minute settling time was allowed and the turbidity was measured. Thereafter disturbances of 100 rpm and 200 rpm were applied. After the disturbance, the turbidity was measured at three-minute intervals, until the original turbidity was reached. These results can be seen in Table 15.

Table 15: Stability test results

<table>
<thead>
<tr>
<th>Reagents used</th>
<th>Time (min)</th>
<th>100 rpm disturbance</th>
<th>200 rpm disturbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheofloc5414 at 40°C with lime</td>
<td>21</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>ARFloc100 at 40°C With lime</td>
<td>20</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Rheofloc5414 at 60°C with lime</td>
<td>22</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ARfloc100 at 60°C with lime</td>
<td>13</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Rheofloc5414 at 40°C with NaOH</td>
<td>21</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>ARFloc100 at 40°C with NaOH</td>
<td>28</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Rheofloc5414 at 60°C with NaOH</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>ARFloc100 at 60°C with NaOH</td>
<td>7</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

When lime was used, the ARFloc100 at 60°C was the most stable crystals that formed, because it took the least amount of time for the turbidity to reach the same value as before the disturbance occurred. This was attributed to better bonds that formed with the addition of this polyamine. This finding coincides with the results of the settling velocity tests, thus, using lime with ARfloc100 will give the heaviest, most stable flocs and remove a large quantity of the impurities from the water.
When NaOH was used, the most stable crystals were formed when Rheofloc5414 was used at 60°C even more stable than the crystals formed using lime. Smaller amounts of impurities were removed from the water than when using lime, thus, lime will still be the best option.

4.4.6 Morphology analysis

4.4.6.1 Scanning electron microscope
The morphologies of the flocs were determined using a scanning electron microscope. The flocs formed when using lime in conjunction with the optimal conditions of ARfloc100 at 60°C can be seen in Figure 44.

![Electron image of crystals formed using lime with ARFloc100 at 60°C](image)

Figure 44: Electron image of crystals formed using lime with ARFloc100 at 60°C
In Figure 44 it can be seen that small, dense flocs formed, that are smaller than 10 µm. It was also determined that CaO is the most predominant compound in the flocs, with a weight percentage of 33.37%; this is illustrated in Figure 45.
The morphologies of the flocs were determined using a scanning electron microscope. The flocs formed when using NaOH in conjunction with the optimal conditions of Rheofloc5414 at 60°C can be seen in Figure 46.

In Figure 46 it can be seen that larger flocs formed than the flocs that formed when lime was used, and they are densely packed. This explains why the crystals formed when NaOH was used, which were determined to be more stable, and have a better settling velocity. Here, too, CaO was the dominant compound in the flocs, with a weight percentage of 60.1%. This was confirmed as shown in Figure 47.
4.4.6.2 X-ray diffractometer results

X-ray diffractometer quantitative analytical results, showing crystallinity are represented in Figure 48.

From Figure 48, it can be observed that the best crystallisation took place when ARFloc100 was used in conjunction with lime at 60°C. This finding reiterates that when lime softening is done, the crystallisation mechanism takes place; however, improved crystallinity will also take place at higher temperatures due to super-saturation of the ions that form mineral scalants that are likely to precipitate in the treated water.
4.5 Conclusion and recommendations

RO-reject water was tested and it was found that the levels of total dissolved solids were abnormally high, which meant the water cannot be considered directly for further cycles in the RO system. Pre-treatment was done to reduce the solubility of scale-forming agents, to stimulate the formation and growth of crystals that would lead to rapid settling. This aim was achieved using lime and NaOH to adjust the pH while flocculants, namely Rheofloc5414, ARFloc100 and Genefloc were used for the agglomeration of crystals. The removal of scaling agents was assessed by monitoring the variation of conductivity, hardness, turbidity and alkalinity. It was found that a dosage of 220 mg/L lime or NaOH was sufficient to increase the pH to a value of 10.1, which was suitable for reducing the solubility of calcium and magnesium in the water. On the other hand, an increase of temperature to 60°C resulted in improved performance of flocculants. Optimal dosages of flocculants varied with the neutralising agent used. A coagulant dosage of 0.5 mg/L, a flocculant dosage of 0.2 mg/L and a lime dosage of 220 mg/L were found to be optimal for a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54% and an alkalinity removal of 71%. When NaOH was used, Rheofloc5414 at a dosage of 0.5 mg/L and a coagulant dosage of 5 mg/L at 40°C was found to be optimal for a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3% and an alkalinity removal of 50.6%. The crystals resulting from the use of NaOH were found to settle faster and were found to be more stable. The diversified advantages in using either NaOH or lime suggests the need of further perform a cost analysis to determine the combination of chemicals that will be of superior benefit to the industry.

References


CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

Eskom extract water from the Vaal River for cooling and steam generation; however, the raw water is highly contaminated with NOM and microorganisms, which are likely to form biofilm and affect the performance of membrane and heat exchanger systems downstream. The primary aim of this study was to develop a chemical treatment approach suitable for effective removal of suspended particles from the feed water. This aim was achieved by identifying suitable coagulants and flocculants that are effective at lower dosages. The main principles used involved using coagulants to improve the stabilisation. Suspended solids in suspension, while using coagulant aids or flocculants to agglomerate the colloids, which increased in density and settled under the influence of gravitational force. The main parameters considered to assess the treatment of feed water were its turbidity and conductivity. PAC, ACH, aluminium sulphate and sodium aluminate were used as coagulants, and their dosages were varied from 5 to 30 mg/L. Three coagulant aids were used, namely, Rheofloc5414, chitosan and ARFloc100. These coagulant aids were used at dosages ranging from 0.2 to 1.2 mg/L. PAC in conjunction with ARFloc100 was found to perform well at dosages of 30 mg/L and 0.8 mg/L respectively. The turbidity that was achieved with these dosages was as low as 2 NTU. Settling velocity tests confirmed that the flocculant or coagulant aids should be added during rapid mixing, and that it would take 30 minutes to achieve a floc bed of 10 mL. It could clearly be seen that both coagulant and flocculant were necessary to, firstly, neutralise the charge, and then, to agglomerate the particles to encourage settling. Thus, according to the results, the flocculation mechanism occurred.

With the amount of wastewater streams generated at Eskom, RO-reject water is of significant concern, because of the high level of total dissolved solids, which is related to the high concentrations of scale-forming agents in the water. In this case, it was imperative to pre-treat the water before any further membrane treatment, due to the high potential for scale formation, which is likely to reduce the efficiency of downstream processes. The second major aim of this study was therefore, to develop optimum conditions using suitable chemicals for the removal of scale-forming agents from RO-reject water collected from an Eskom power plant. The approach taken in this section was to reduce the solubility of scale-forming ions in solution, using either lime or NaOH. Subsequently, the agglomeration of crystals formed was stimulated using flocculants such as Rheofloc5414, ARFloc100 and Genefloc. When using lime in the proportion of 220 mg/L, ARFloc100 at
60°C was found to be the optimal flocculant at a dosage of 0.2 mg/L, combined with a Rheofloc5023 (coagulant) dosage of 0.5 mg/L. This combination yielded a conductivity removal of 36%, a turbidity increase of 59%, a total hardness removal of 54% and an alkalinity removal of 71%. When NaOH was used, the optimal removal of the pollutants was achieved with Rheofloc 5414 (0.5 mg/L) and Rheofloc 5023 (5 mg/L) at 40°C. These conditions yielded a conductivity removal of 1.26%, a turbidity removal of 58.75%, a total hardness removal of 20.3% and an alkalinity removal of 50.6%. During the settling tests, it was found that settling occurred faster at 60°C than at 40°C, and that the crystals initiated by NaOH settled faster. The crystals formed with NaOH were also more stable, which was confirmed with scanning electron microscope images. However, more scaling agents were removed using lime, as it promotes attainment of super-saturation of scale-forming ions, including calcium and magnesium. It is, therefore suggested that lime, which is also less expensive, be used.

The difference between the flocculation mechanism and crystallisation mechanism was clearly observed when treating feed water and RO-reject water, respectively. When treating the feed or raw water, less time was necessary to achieve maximum agglomeration of colloids for floc formation during slow mixing, which was confirmed by the mechanism of flocculation as stipulated in the literature review. However, for the treatment of RO-reject there was a need to increase the pH sufficiently and reach a super-saturation level for the scale-forming ions to become insoluble in water and form crystals, an approach that was not necessary with raw water dominated with organic pollutants. Temperature also played a huge role in the crystallisation, especially when lime was used in the RO-reject treatment. A significant improvement could be seen in the removal of the scaling agents at high temperatures. Temperature control was not necessary with the flocculation mechanism, as high efficiencies could be reached at room temperature. It could also be seen that, when crystallisation occurred, the stability and the settling velocity was superior to that achieved with flocculation.

A limited range of coagulants and flocculants were investigated in this study. It is recommended that other chemicals, with the ability to promote either flocculation or crystallisation depending of the water treated, be considered too.