Pretreatment of Coal Power Plant RO Retentate using AR Floc 100

E. Fosso-Kankeu*, L. Van Schalkwyk, J. Van Der Linde, G. Gericke and F.B. Waanders

Abstract — The water purification process at Eskom includes a reverse osmosis (RO) treatment plant. There are several limitations to this process depending on the water characteristics. The most common problems limiting the success of water purification include scaling, biological fouling and corrosion. This study is mainly focused on reducing scale forming agents in the RO system. Scaling is the precipitation of calcium and magnesium salts onto the equipment, primarily the RO membrane. These salts start to precipitate once the salt concentration in the water is higher than the allowable solubility constant. These salts can be removed from the water by a process called coagulation-flocculation. The success of such a process is partly dependent on the type of flocculant and the dosage used. In this study the performances of one coagulant namely Rheofloc 5023 in combination with three flocculants including Rheofloc 5414, Genesys genefloc and AR floc 100 were tested at various dosages for the reduction of conductivity assimilated with ions in the RO retentate from coal power plant was investigated at 40 and 60°C. The AR floc 100 was determined to be the optimum flocculant required for the RO reject treatment. The optimum flocculant dosage resulted in 1 ppm along with a Rheofloc 5023 coagulant dosage of 0.7 ppm.

Keywords — AR floc 100, RO retentate, flocculation, conductivity.

I. INTRODUCTION

Eskom generates the majority of South Africa’s electricity and about half the electricity used in Africa.

Eskom is a large consumer of water from rivers and dams and account for approximately 1.5% of South Africa’s total water consumption [1-7]. The freshwater undergoes extensive purification and treatment before it can enter the production process. It might be challenging to recycle wastewater from the RO retentate stream, because of the increase in the concentration of minerals in the water due to water evaporation. When the concentration of dissolved metal ions is too high, the ions become concentrated and exceed the solution solubility in the cooling water. These concentrated ions result in scale formation (calcium carbonate) on the surfaces. Anion concentrate influences the amount of scaling taking place in the system. Dissolved metal ions include calcium, magnesium, iron, and anions include carbonate, phosphate, silica and sulphate. The portion of cooling tower process water being flushed down the drain is referred to as cooling reverse osmosis (RO) retentate water. The RO retentate is simultaneously replaced with fresh water.

Coagulation-flocculation involves the addition of a flocculant (polymer) to form flocs with small, destabilised particles in the water [9-14]. These flocs are larger aggregates that can be separated from the water more easily. Coagulation is a chemical process that neutralizes the solution whereas flocculation is a physical process that destabilises the small particles inside the solution. Crystallisation is based on the limited solubility of a compound in a solvent at certain conditions. Crystalline solids will form when the conditions change to a state where the solubility is lower than the concentration of the compound in the solvent.

For this project water samples were obtained from Grootvlei, one of Eskom’s power stations situated close to Balfour, Mpumalanga. The characteristics that influence the tendency of corrosion and scaling taking place include the pH, hardness (calcium), alkalinity, temperature and the total amount of dissolved solids in the water. The approach of this project is to treat water samples with different flocculants at difference dosages to determining the optimum treatment conditions for the RO retentate water at Eskom.

II. METHODOLOGY

A. Characterisation of water samples

The sampling trips to the power station plant were on the 23rd of July, 13th of August and 26th of August. The water samples obtained from Eskom were characterised before and after the experimental treatment. Parameters considered during the characterization of water samples included turbidity, pH, total hardness, conductivity and alkalinity.

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III. EXPERIMENTAL SETUP

The jar test equipment consisted of six small scale agitators which were connected to a speed motor with variable speed options.

Just before the rapid mixing started the coagulant and flocculant were added to the water sample in each beaker. There were six different coagulant dosages, each dosage in a different beaker, and only one flocculant dosage was used per run. The Rheofloc 5023 coagulant dosages included, 0.2 ppm, 0.5 ppm, 0.7 ppm, 2 ppm, 5 ppm and 7 ppm. The flocculant dosages included, 0.5 ppm and 1 ppm for Rheofloc 5414, also 0.5 ppm and 1 ppm for Genesys genefloc and lastly, 1 ppm and 7 ppm for AR floc 100.

During rapid mixing, the interaction between the chemicals and the particles in solution was enhanced while during the slow mixing period the flocs were able to agglomerate and form precipitate Error! Reference source not found.

![Jar test mixing equipment](image)

IV. EXPERIMENTAL PROCEDURE

A. pH, conductivity and turbidity

The pH of each sample was determined by using a HANNA HI 8424 pH meter. The conductivity meter used was the Lovibond SensoDirect 150 water quality meter and the turbidity was measured using a HACH 2100Q portable turbidity meter.

B. Alkalinity

The endpoint titration method was used to determine the alkalinity of the water. This method is explained in a book called the Standard Methods for the Examination of Water and Wastewater Error! Reference source not found.

- Standard solution was prepared by dissolving 1.0075 g of 98% H₂SO₄ in 1 L demineralized water
- 50 mL of the treated water was used for these titrations
- A few drops of Phenolphthalein were added to the sample to obtain a pink colour.
- H₂SO₄ was added with a burette until the solution colour turned from pink to colourless.
- Another indicator namely Bromocresol green was added at this stage to determine the volume needed to obtain a pH of 4.5 at which the indicator changes the colour from blue to light green.

C. ICP-OES analysis

The concentration of each metal in the treated RO retentate water was obtained by using an Inductively coupled plasma - optical emission spectrometry (Agilent Technologies 700 Series ICP-OES. Since the total hardness of these samples are relatively high, the samples were diluted (x100). The total hardness was calculated with Eq. 1: Error! Reference source not found.

\[
CaCO_3 \ (mg/L) = 2.497(Ca, \ mg/L) + 4.118(Mg, \ mg/L)
\] (1)

D. Chemical composition

The dried flocs were obtained using a Hettich Zentrifugen ROTOFIX 32 A centrifuge. This was done by decanting the purified RO retentate water, pouring the remaining flocs into a centrifuge tube and using the centrifuge to separate the liquid from the flocs completely. The flocs were dried for 24 hours at 50°C in an incubator. The dried flocs were sent for SEM-EDS analysis to determine the morphology and the elemental composition of the flocs.

E. Settling velocity

A cone was used to evaluate the settling velocity of the flocs that were formed during the jar test. The settling rate was determined by observing the changes of volume taking place in the cone over time. The cone was marked from 1 to 10 mL and the time was recorded when the flocs reached each volume mark. The volume over time curve was obtained which allowed to determine the settling rate. The settling test was done by following the same procedure as the optimization jar tests and performing the cone test directly after slow mixing.

F. Stability test

The floc stability was determined by observing the change in the treated water directly after a jar test has been done. A jar test was done with the best coagulant and flocculant dosage but this time at 60°C at the same speed and time intervals. After the 30 minutes settling period, the flocs were disturbed through further rapid mixing for 30 seconds and then the turbidity was determined with the turbidimeter every 50 seconds to obtain a graph of turbidity versus time. This was use to determine the stability of the flocs.

V. RESULTS AND DISCUSSION

A. Optimization

1) pH, conductivity and turbidity

a) Rheofloc 5414 – Flocculant 1

Firstly, the Rheofloc 5414 flocculant was used to do the jar tests. The conductivity removal results are shown in the graph below, Fig 2. The conductivity was not successfully removed with Rheofloc 5414. For the 1 ppm flocculant dosage, the conductivity removal was less than zero percent meaning the conductivity increased with an average of 2%. For the 0.5 ppm flocculant dosage, the conductivity was removed successfully for the coagulant dosages; 0.2 ppm, 0.5 ppm, 0.7 ppm and 2 ppm. For both the coagulant and flocculant dosage of 0.5 ppm,
the best results for the removal of conductivity was obtained reducing the conductivity of the water by 10%.

The turbidity of these water samples was initially very low and therefore the experiments did not have a significant effect on the turbidity removal. The turbidity removal for the dosage 7 ppm coagulant and 0.5 ppm flocculant gave the optimum result.

b) Genesys Genefloc – Flocculant 2

The conductivity results for Genesys Genefloc are shown below in Fig 3. The conductivity removal results of the Genefloc dosage 0.5 ppm was more stable than that of the Rheofloc 5414 but also not sufficient in the removal of conductivity. The 1 ppm flocculant dosage shows two peaks in the graph at 0.5 ppm and 7 ppm. The optimum conductivity removal with Genefloc was 35% and 36%.

For Genesys Genefloc, the turbidity was successfully removed with the 1 ppm flocculant dosage at coagulant dosages greater than 0.2 ppm. The optimum turbidity removal was 26% resulting from a coagulant dosage of 5 ppm and 1 ppm flocculant dosage.

c) AR floc 100 – Flocculant 3

The conductivity removal results are shown in Fig 4 with AR floc 100 as flocculant. The conductivity removal results average at a value of 17% for 1 ppm AR floc 100 and 24.5% for 7 ppm AR floc 100. The optimum conductivity removal at 7 ppm flocculant is 25% at a coagulant dosage of 2 ppm. Since 7 ppm is much higher than 1 ppm flocculant, it might be considered to use the 1 ppm flocculant dosage for economic reason. This aspect will also be taken into consideration later in this study.

The turbidity removal with AR floc 100 was unsuccessful. The turbidity increased for both flocculant dosages.

2) Alkalinity

The alkalinity removal overall was very successful with an average of 53% for all three flocculants. This shows that each flocculant is sufficient, in fact, the optimum conditions were determined prior to this study. These experiments were carried out at 40 °C and after the optimum dosage were determined the temperature was changed to 60 °C to assess the effect of higher temperature on the performance of the coagulant and flocculants. The alkalinity removal results showed the same trend for the three flocculants. A spike in the alkalinity removal was observed around the coagulant dosages 0.5 ppm and 0.7 ppm. A significant reduction in the alkalinity removal was observed at a coagulant dosage greater than 0.7 ppm and afterwards a gradual increase was observed. This section consists of three figures displaying the trend of the results and the optimum conditions thereof are discussed.

The alkalinity removal with Rheofloc 5414 as flocculant averaged at 55% at 0.5 ppm flocculant and 54% at 1 ppm flocculant. In Fig 5 it is shown that the best Rheofloc 5414 dosage is 0.5 ppm with a coagulant dosage of 0.7 ppm. This dosage resulted in an alkalinity removal of 59%.

The results obtained with Genesys genefloc is shown in Fig 6. The best flocculant dosage was 1 ppm at an optimum coagulant dosage of 7 ppm. This resulted in an alkalinity removal of 57%. The 5 ppm coagulant dosage reduced the alkalinity by 53% which is only 4% lower, while using less coagulant, making it cost effective.

The alkalinity removal with AR floc 100 as flocculant is shown in Fig 7. The best alkalinity removal result obtained was 62% at 7 ppm AR floc 100 and 0.5 ppm coagulant dosage. The alkalinity removal with AR floc 100 was 4% better than with Rheofloc 5414 and Genesys genefloc as flocculants. Since the cost of the chemicals are considered it is better to choose the dosage of 1 ppm AR floc 100 and 0.7 ppm coagulant with a
removal of 57%. The alkalinity removal is thus only 5% less and the flocculant expenses will be much cheaper than that of 7 ppm. AR floc 100 could therefore be considered as the optimum flocculant to remove the alkalinity of RO retentate water at Eskom.

The optimum flocculant and coagulant dosage resulted in AR floc 100 with a dosage of 1 ppm and a coagulant dosage of 0.7 ppm. This was the best result considering the expenses and the efficiency. The best flocculant was also tested with the optimum dosage at 60°C. At a pH of 9.03 the conductivity removal was successful reducing the conductivity with 25%, although the turbidity of the water increased by 34% at these conditions. The alkalinity removal resulted in 51% which was 7% less than the removal at 40°C.

B. Settling velocity

The settling velocity of the flocs at 40 °C and 60°C is summarized in Error! Reference source not found.. The settling velocity decrease with time due to the density difference of the flocs. Initially the flocs have a high density which leads to a high settling rate. As time progresses the settling velocity reduces due to the lower density of the remaining flocs. These flocs that remain in solution, will take more time to settle. The 10 mL floc bed was obtained within 109 seconds at 40°C and in 114 seconds at 60°C.

It is recommended to proceed with 40°C since it would be less costly to run the system at a lower temperature.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Setting velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>0.321</td>
</tr>
<tr>
<td>50</td>
<td>0.257</td>
</tr>
<tr>
<td>60</td>
<td>0.214</td>
</tr>
<tr>
<td>70</td>
<td>0.184</td>
</tr>
<tr>
<td>80</td>
<td>0.161</td>
</tr>
<tr>
<td>90</td>
<td>0.143</td>
</tr>
<tr>
<td>100</td>
<td>0.128</td>
</tr>
<tr>
<td>60°C</td>
<td>0.265</td>
</tr>
<tr>
<td>40</td>
<td>0.199</td>
</tr>
<tr>
<td>50</td>
<td>0.159</td>
</tr>
<tr>
<td>60</td>
<td>0.133</td>
</tr>
<tr>
<td>70</td>
<td>0.114</td>
</tr>
<tr>
<td>80</td>
<td>0.100</td>
</tr>
<tr>
<td>90</td>
<td>0.088</td>
</tr>
</tbody>
</table>

C. Flocculation

1) Slow mixing regime

In the slow mixing regime, the flocs were mixed at 100 rpm before the stability test was done. The average slope for the stability test at 40°C was -5.37. The same calculation was performed with the stability test trendline at 60°C and a slope of -13.13 was obtained. The rapid decrease in turbidity indicate that the floc stability is much higher at 60°C than at 40°C.

2) Rapid mixing regime

A stability test was also done at 200 rpm for both 40°C and 60°C. For the stability test at 40°C, the slope of the average trendline was -5.02. For the stability test at 60°C, a slope of -18.40 was determined. Since the turbidity decrease faster at 60°C, it is shown that the flocs are more stable than at 40°C.
Finally, it can be concluded the best floc stability will be obtained at 60°C.

D. ICP-OES analysis

The main objective of this project was to reduce the alkalinity and total hardness of the RO retentate water at Eskom power station. The results of the ICP-OES analysis are summarized in Table III and IV. This indicates the total hardness removal efficiency of the treatment with AR floc 100. The best calcium and magnesium removal efficiency according to the ICP-OES analysis is 46% for a flocculant dosage of 1ppm at 60°C. The results between 1 and 7 ppm did not differ significantly as seen in the tables below.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Total hardness (CaCO₃) (mg/l)</th>
<th>Content reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated RO</td>
<td>224.25</td>
<td>-</td>
</tr>
<tr>
<td>1 ppm</td>
<td>160.57</td>
<td>42%</td>
</tr>
<tr>
<td>7 ppm</td>
<td>181.42</td>
<td>45%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Total hardness (CaCO₃) (mg/l)</th>
<th>Content reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated RO</td>
<td>224.25</td>
<td>-</td>
</tr>
<tr>
<td>1 ppm</td>
<td>187.43</td>
<td>46%</td>
</tr>
<tr>
<td>7 ppm</td>
<td>182.23</td>
<td>45%</td>
</tr>
</tbody>
</table>

E. SEM EDS analysis

The chemical composition analysis was performed for the RO retentate treated at 40°C and 60°C. It can be observed that the flocs formed at 60°C are smaller in size compared to the flocs formed at 40°C; this is due to increased dehydration taking place at a higher temperature resulting in more rigid or stable but less heavier flocs. The crystallization was advanced at 60°C and resulted in the formation of crystals and nanorods as observed in Fig 8 and Fig 9. The energy dispersive spectra of the respective images show the entrapment of elements such as Ca, Mg, Yb, Na, Si, K, Al, Co, Br and Cu in the flocs which can contribute in the reduction of scale formation.

VI. CONCLUSION AND RECOMMENDATIONS

In conclusion, the coagulation-flocculation treatment method was successful in removing total hardness and alkalinity from the RO retentate water at Eskom. The characteristics of the untreated RO retentate showed a pH ranging between 7.8 and 8.7, an average turbidity of 4.48 NTU and a conductivity of 4.48 mS.

The AR floc 100 was identified as the best flocculant suitable for the RO reject treatment. The optimum flocculant dosage was 1 ppm combined with a Rheofloc 5023 coagulant dosage of 0.7 ppm. The settling velocity of the flocs formed during coagulation-flocculation was determined along with the stability thereof. The settling velocity results at 40°C and 60°C were found to be very similar. A floc bed of 10 mL was obtained within 109 seconds at 40°C and 114 seconds at 60°C. The stability of the flocs was higher at 60°C compared to 40°C.

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