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Flocculant types and operating conditions influencing particles settling rates in feed water used at a coal power plant

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ABSTRACT

South Africa is a semi-arid country with an average rainfall less than half of the average rainfall worldwide. From the country limited water resource, 2%–3% of the water is used in energy generation. Thus the water intake from Eskom needs to be reduced to account for the depleting water resources in the country; effective treatment of the feed water among other can contribute to optimum operation and therefore possible saving during usage. The variation of the particles settling rate based on the type of coagulants and flocculants used during treatment of feed water was investigated in this research to determine the optimal conditions suitable to produce feed water of acceptable quality. Poly aluminium chloride (PAC), aluminium chlorohydrate and sodium aluminate were used as the inorganic polymeric coagulants and Alum was used as the inorganic monomeric coagulant. Two different types of inorganic polymeric flocculants were used as well as 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 and 0.8 ppm respectively. Ideal conditions for higher removal rate were flocculant addition during rapid mixing and approximately 60 s after the PAC addition.

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

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1. Introduction

South Africa is one of the countries with the lowest annual precipitation with an average of 497 mm/y. The South African population currently exceed 50 million and will continue to grow over the years while on the other hand water availability is continuously decreasing [1]. 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 [2]. It is estimated that 2%–3% of South Africa's water is used for energy generation [1], with most of the power stations located in more rural areas where people use surface water for their daily needs. Water used by power stations may then be discharged into the environment which can cause health risks for the local people [3].

According to the previous reports 1.15 L of water is used per kWh of electricity produced by coal power stations in China [4], whilst Eskom the power utility in South Africa is currently using 1.38 L/kWh. Eskom's target is to reduce this amount to 1.34 L/kWh by 2020. However, it must be mentioned that the water consumption of power plants in South Africa increased dramatically since 1950 as the need for energy increased with the rapid increase in population,

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industrialisation and economic growth [4]. The water usage on the other hand can be reduced by recovering, treating and re-use of the waste water 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, the organic matters having the potential to cause biological fouling [3]. This causes membrane fouling in downstream processes [5] where cooling towers for example have ideal conditions for algae to flourish. Accompanying the algae is the presence of calcium and magnesium salts which can cause scaling [3]. 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 [5].

There are mainly three coagulation mechanisms. These include charge neutralisation, sweep flocculation and destabilization by bridging. According to [6], 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 (Fig. 1.). These cationic species are absorbed by negatively charged particles and this in turn causes a charge reduction [7]. According to [8], charge neutralisation is the main mechanism that takes place when the adsorption area and the flocculants have opposite in charges. Most of the hydrophobic elements in water are negatively charged, therefore, in this instance cationic polymers will be suitable to neutralise 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 word, when the zeta potential is close to zero. Overdose of the flocculant can occur where charge reversal takes place and the van der Waals forces get weakened and the flocs disperse. Flocs formed through charge neutralisation are normally light, fragile and settles slowly, thus it is advised 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 [7]. An increase in concentration promotes an increase in the saturation of these metal salts which in turn promotes the precipitation of metal salts.

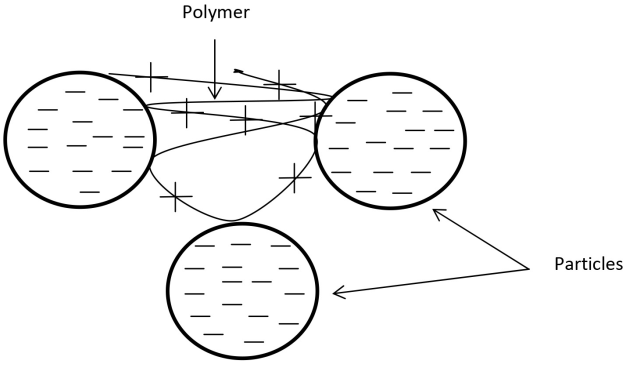

Fig. 1. A representation of charge neutralization.

Destabilization by bridging is when a polymer chain absorbs on more than one particle to link them together, which causes strong flocs [7]. 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 interacts 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 amount of active sites will not be sufficient to adsorb enough particles. Flocs formed through bridging are stronger than those formed through other mechanisms [8] (Fig. 2.).

There are several flocculants that can be used which include Bentonite clay, hydrated lime, magnesium hydroxide and Polyaluminium chloride (PAC) (Fig. 3.). Flocculation and crystallisation work closely together with coagulation but 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

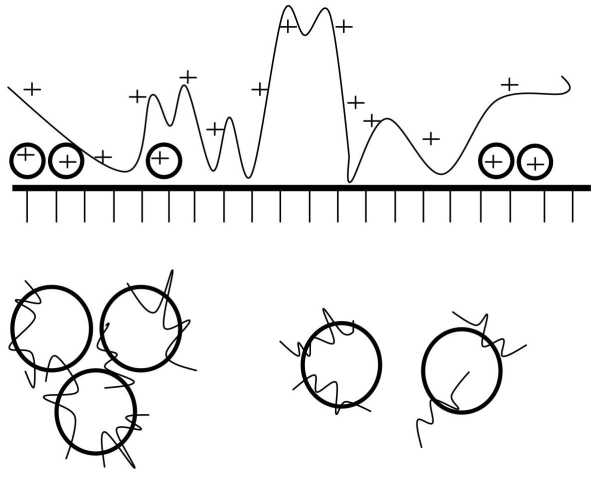

Fig. 2. A representation of destabilization of bridging.

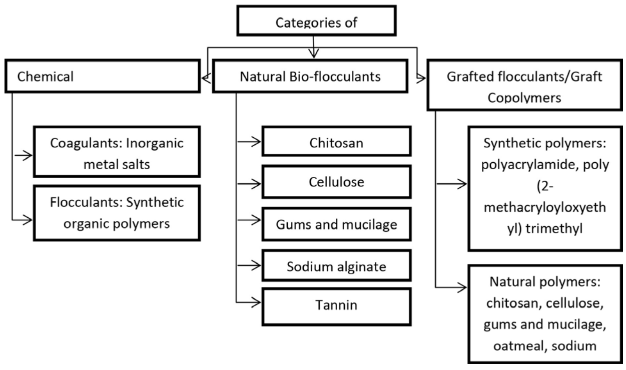

Fig. 3. Types of flocculants used in water treatment.

and it is less time effective than precipitation/flocculation [9]. The mechanism of particles removal from solution is also 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.

Aluminium and iron based coagulants are usually used for water treatment due to their cationic affinity [6]. These cationic particles bind to the anionic suspended solids, which in turn promotes settling. pH changes, dosage and temperature have an effect on the efficiency of this process [10]. 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 [11].

Due to the changes in the physico-chemical properties of water, the usage of polymeric coagulants is more widely 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. A reduction of colour is less efficient with the addition of PAC. PAC is less pH dependant 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 [12]. An example of a polymer is the polyquaternary amine, Genefloc, produced by Genesys International Limited [6], which is efficient over a large pH range and its cationic charge is located over the backbone of the long polymeric chain that can wrap around particles. Another advantage is that after the use of genefloc, no residue was found on membranes after five years of usage [6].

Organic coagulants are used to reduce secondary pollution and consist of different functional groups, which bind with impurities to form flocs with the addition to water [10]. Chitosan is an example of an organic coagulant besides the fact that it is also a cationic polymer. One disadvantage of the use of 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 [6].

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. [13,14].

An extremely important characteristic of solids when settling rates are calculated is the terminal settling velocity of the particles. It is calculated by doing experimental tests where the water with particles are added to a settling column and the supernatant is extracted from different points at different times [15]. 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 just measured over time.

This study is 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 aims to optimize operation processes at a coal power plant water treatment facility to address issues related to chemical over-dosage and equipment fouling.

2. Experimental procedure

2.1. Sample collection

Water samples were collected at the Grootvlei Power Station, Mpumalanga, South Africa in 25 L 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.

2.2. Water characterization

The temperature, pH and conductivity of the water were measured with the aid of a Lovibond SensoDirect 150 m. The turbidity was measured with a 2,100 Q meter from Hatch. 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 [16]. A 0.1 N H_2SO_4 solution was made and used as titrant. 20 mL of raw water and 80 mL of demineralized water were added into Erlenmeyer flask. Bromocresol green was added as indicator. 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. The alkalinity was calculated using the following equation:

$$\text{Alkalinity as mg}\frac{\text{CaCO}_3}{l}=\frac{A\times N\times 50000}{\text{Sample volume (mL)}} \tag{1}$$

where A is the volume of acid used (mL) and N is the normality of acid.

The total organic carbon (TOC) analysis was done at the Eskom Research Centre in Rosherville using the Sievers 900 TOC analyser. An Ultra Violet radiation was used in conjunction with ammonium persulphate to oxidize 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 Eq. (2):

$$\text{TOC} = \text{TC} - \text{TIC} \tag{2}$$

where TC is the total carbon and TIC is the total inorganic carbon.

The inductively coupled plasma atomic emission spectroscopy (ICP- OES) (Agilent Technologies, USA) was used to measure the metal concentration in the water samples. Ethylenediaminetetraacetic acid (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 NH_4Cl, 143 mL NH_4OH, 1.25 g Magnesium salt of EDTA and demineralized water. The samples to be titrated were prepared by adding

25 mL water sample and 25 mL demineralized 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:

$$\frac{\text{mgC}_\text{a}\text{CO}_3}{L} = \frac{A \times B \times 1000}{\text{Sample volume (mL)}} \tag{3}$$

where ***A*** is the titration volume for sample (mL) and *B* is the milligrams calcium carbonate corresponding to 1.00 mL EDTA titrant.

With regards 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 indicator and the sample was titrated with EDTA until the end point was reached. The calcium concentration was determined as follows:

$$\frac{\text{mgC}_\text{a}}{L} = \frac{A \times B \times 400.8}{\text{Sample volume (mL)}} \tag{4}$$

$$\text{Calcium hardness as mg}\frac{\text{CaCO}_3}{L} = \frac{A \times B \times 1000}{\text{Sample volume (mL)}} \tag{5}$$

where *A* is the titrant volume for sample (mL) and *B* is the 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 only consists of calcium and magnesium.

2.3. Coagulants

The inorganic polymeric coagulants used in this study were PAC, aluminium chlorohydrate (ACH) and sodium aluminate. Alum was used as an inorganic monomeric coagulant. RHEOFLOC 5414 and ARFLOC 100 which are polyamines and chitosan were used as coagulant aid. The first two mentioned are both polymeric and polyamine based foccuulants. The chitosan was prepared by adding it to a 0.1 M HCl solution, and then diluted to 1,000 mg/L.

2.4. Jar tests

Six 1 L beakers were used simultaneously in the jar test, then the paddles were immersed in the sample solutions added in these beakers and stirred to allow coagulation and flocculation processes to take place under rapid mixing and slow mixing respectively.

2.5. Coagulant optimization

Six water samples 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 s at 150 rpm. Thereafter slow mixing followed for 20 min at 50 rpm. A settling time of 30 min was allowed.

2.6. Coagulant aid optimization

After the optimum dosages of the different coagulants were determined, the coagulants were used in conjunction with the different coagulant aids, namely RHEOFLOC 5414, ARFLOC 100 and chitosan. The coagulant was added and rapid mixing was carried out at 150 rpm for 60 s, then the coagulant aid was added. Further rapid mixing was carried out for 30 s followed by slow mixing for 20 min at 50 rpm. The samples were left to settle for 30 min.

2.7. Optimization 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 s. After the addition of coagulant and coagulant aid, 30 s rapid mixing were conducted at 150 rpm and slow mixing for 20 min at 50 rpm. 30 min settling time were then allowed.

2.8. Optimization of mixing regime after coagulant aid addition

The optimal dosages were used and the same methods as mentioned earlier were considered, but the coagulant aid was added at the start of the slow mixing period.

2.9. Settling rate tests

A cone was used for the settling rate tests and the rate of sludge build-up and turbidity removal was determined. 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 mL intervals.

2.10. 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 analyzed with a QEMSCAN automated mineralogy apparatus at the Eskom's Research Centre in Rosherville.

3. Results and discussion

3.1. Water characterization

Table 1 shows water characterization parameters and the values obtained at different days of sampling. This represents the control samples. The significant difference in the turbidity is due to the fluctuation in the river water.

Table 1
Water characterisation results

	16 May	5 July	11 August	28 August
pH	7.55	7.98	8.01	7.65
Temperature (°C)	16.8	13.9	16.4	15.5
Turbidity (NTU)	21.07	30.69	15.58	22.46
Conductivity (µS/cm)	165.57	164.78	159.53	162.67

4. Jar tests

4.1. 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 and aluminium sulphate and sodium aluminate. The dosage for each coagulant was varied from 5 to 30 mg/L and the results are shown in Fig. 4.

It can clearly be seen that sodium aluminate has the lowest turbidity removal (15%) of these three coagulants. Alum and ACH had better turbidity removal efficiencies than the sodium aluminate, but it was found that 30 mg/L dosage of PAC yielded 94% reduction in the turbidity.

4.2. Coagulant aid screening

Optimization processes carried out in our lab showed that coagulant or coagulant aid used separately could not achieve considerable removal of turbidity, thus it was considered to combine both coagulant and coagulant aid (flocculant) to ensure that the coagulation and flocculation processes work efficiently.

Thus PAC and ACH were used as coagulants in conjunction with RHEOFLOC 5414, chitosan and ARFLOC 100 as coagulant aids. First, 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 Fig. 5.

As can be seen in Fig. 5, chitosan is not an effective coagulant aid as it had the least turbidity removal. ARfloc 100 reduced the turbidity less than 5 NTU at a dosage of 0.8 mg/L in conjunction with the 30 mg/L PAC. The plant can handle a maximum 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 and the final turbidity was 2.13 NTU.

The same flocculant dosages were used in conjunction with 25 mg/L ACH coagulant dosage.

As seen in Fig. 6, chitosan is the least effective flocculant used in conjunction with the ACH. ARfloc 100 reduced the turbidity to close to 4 NTU in conjunction with the 25 mg/L ACH dosage with a dosage of 0.8 mg/L. The lowest turbidity was recorded with a RHEFLOC 5414 dosage of 0.8 mg/L reaching a value of 3.02 NTU.

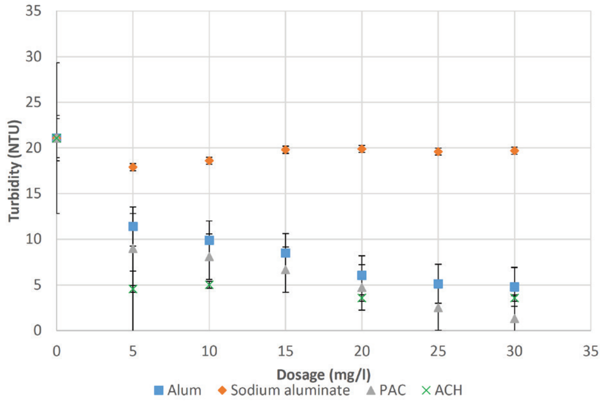

Fig. 4. Turbidity measurement obtained with various coagulant dosage additions.

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

4.3. Time between addition of coagulant and flocculant

The optimum dosages mentioned were used to determine the optimum time between the coagulant and flocculant dosage. The time was varied between 0 and 90 s and the results can be seen in Fig. 7.

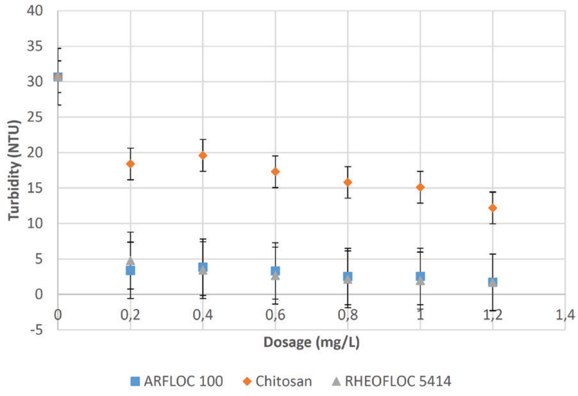

Fig. 5. Turbidity with addition of PAC and various coagulant aids.

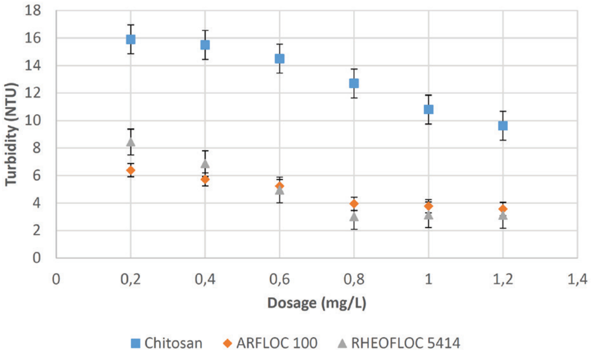

Fig. 6. Turbidity of ACH with various coagulant aids.

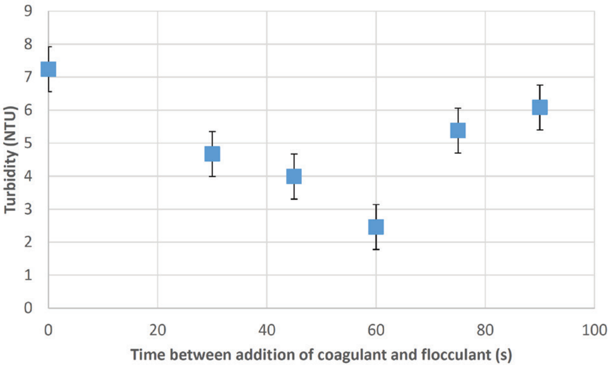

Fig. 7. Turbidity difference due to the time between the addition of coagulant and flocculants.

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

5. 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 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.

5.1. Total hardness

The total hardness of the untreated water calculated using Eq. (3) was 27.4 mg $CaCO_3$/L. After the treatment of the raw water, the total hardness decreased to 26.3 mg $CaCO_3$/L. This shows only a reduction of 4% of 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.

5.2. Calcium content

Using the end point method, the calcium content of the treated water was 10.18 mg Ca/L and the calcium hardness was 25 mg $CaCO_3$/L. This was more or less the same than the untreated water, as a pH increase is necessary to remove calcium and magnesium.

5.3. Major metals in raw water

The ICP-OES results of the untreated as well as the treated raw water can be seen in Table 2.

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

5.4. Alkalinity

The alkalinity was determined using the end point method. Before treatment, the alkalinity was 20 mg $CaCO_3$/L. After treatment the alkalinity remain almost constant at a value of 21 mg $CaCO_3$/L, implying that the treatment has no effect on the alkalinity of the water.

Table 2
ICP-OES results

Component	Untreated raw water (mg/L)	Treated raw water (mg/L)
Aluminium	3.14	0.33
Calcium	12.17	11.86
Iron	1.90	0.02
Potassium	4.32	3.87
Magnesium	6.53	6.12
Sodium	8.06	7.71

5.5. 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.

5.6. Sludge build up over time

The sludge build-up was determined when the optimum coagulant and flocculant dosage was added during rapid mixing. Three tests were conducted and the results are shown in Fig. 8.

The data for test 3 shown in Fig. 8 are the average of the three tests, thus $y = -0.0058x^2 + 0.6921x - 10.362$, with x being time, will be used for the calculations in this section. To determine the settling velocity rate, this equation is differentiated and the result is given by:

$$y' = -0.0116x + 0.6921 \tag{6}$$

Thus the rate of sludge build-up was determined as shown in Table 3.

At first the flocs settle faster, as all the heavier particles with higher density accumulate and settle. Thereafter the rate decreases as all the remaining particles are lighter and have lower densities. The settling rate is negative when the time approaches 60 min, thus indicating that no settling occurs. It took 52 min for a 10 mL floc bed to form.

Thereafter, three tests were conducted using the optimum jar test conditions determined as well as the optimum coagulant and flocculant dosages. These results can be seen in Fig. 9.

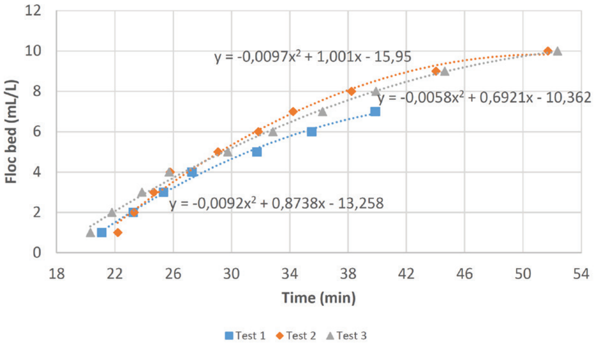

Fig. 8. Sludge build-up (floc bed formation) with addition of coagulant and flocculant during rapid mixing.

Table 3
Sludge build-up rate regarding rapid mixing regime

Time (min)	Rate of sludge build-up (mL/s)
10	0.518
20	0.460
30	0.344
40	0.228
50	0.112

Test 3 is again the average of the three tests, thus $y = -0.033x^2 + 1.6914x - 11.885$ 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 can be seen in Table 4.

As can be seen from Table 3 and 4 the optimum jar test conditions ensure an initial sludge build-up rate two times faster than when the coagulant and flocculant were both added at the same time during rapid mixing. This is due to denser flocs that form when the jar test was done at optimum conditions. The flocs also settled faster as the settling was completed after 30 min, time at which the floc bed volume did not increase. 10 mL of floc bed formed after 25 min which is 27 min faster than when the coagulant and flocculant were both added at the same time during rapid mixing.

5.7. Turbidity removal rate

The data from the graphs obtained for the turbidity correspond with the sludge build-up rate data, illustrating that the turbidity is removed faster initially and then slower nearing the end of the settling time. It can also be seen in Figs. 10 and 11 that the turbidity removal rate is better in the rapid mixing regime. This also correlates with the sludge removal rate data.

5.8. Morphology

The morphology of the flocs was analyzed using QUEMSCAN and yielded the results shown in Table 5.

The main components in the flocs are 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.

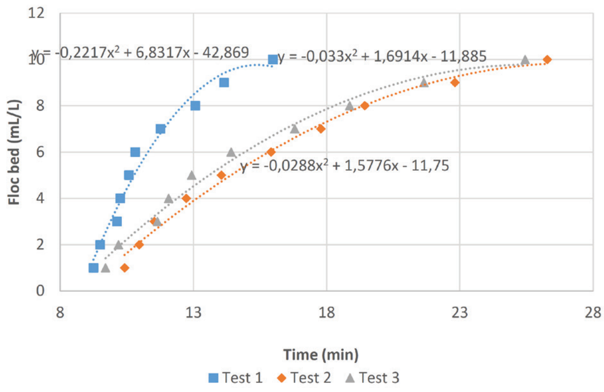

Fig. 9. Sludge build-up rate with optimal dosage conditions.

Table 4
Sludge build-up rate with optimal dosage conditions

Time (min)	Rate of sludge build-up (mL/s)
5	1.361
10	1.031
15	0.701
20	0.371
25	0.0414

Fig. 12 is a QEMSCAN photomicrograph indicating all the substances in the flocs.

Most of the kaolinite in the flocs is fly ash cenospheres. Iron oxide and brass present can be found as small particles as well in the filtered flocs (see Fig. 13).

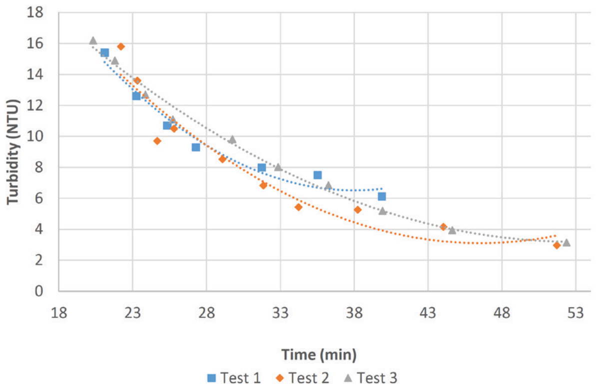

Fig. 10. Turbidity removal rate during the slow mixing regime.

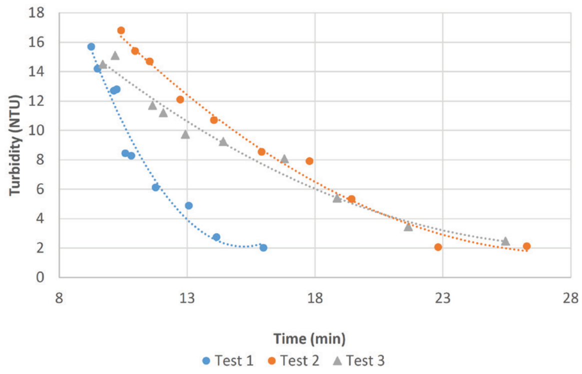

Fig. 11. Turbidity removal rate during rapid mixing regime.

Table 5
Morphology results

	Vol. %
Scale: Calcium silicate	19.6
Scale: Calcite/lime (Si)	17.3
Scale: Calcium magnesium silicate (Mn)	18.1
Scale: (Ca, Mg, Al) silicate (Si)	15.6
Scale: Magnesium silicate	0.2
Dolomite	3.4
Anhydrite	7.1
Sand/FA: Kaolinite/mica	8.3
Sand: Quartz/feldspar	9.1
Iron oxide/brass	0.1
Iron sulphide/sulphate	0.2
Clay: Iron (Al) silicate	0.4
Paint: Titanium oxide	0.2
Other	0.3

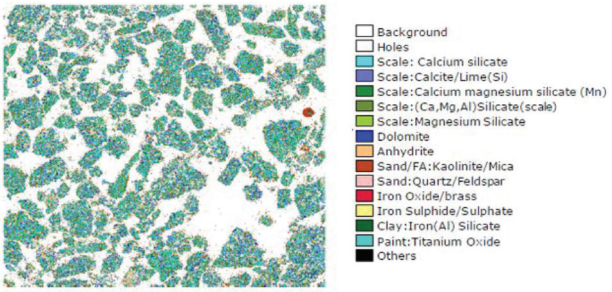

Fig. 12. QEMSCAN photomicrograph of flocs.

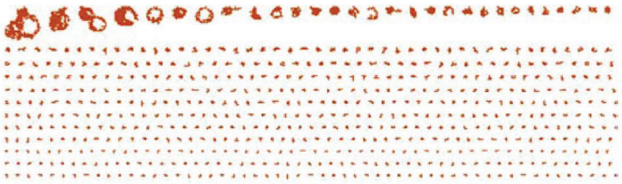

Fig. 13. Aluminosilicate cenospheres present in filtrated flocs.

6. Conclusion

PAC was found to be the best coagulant with 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 the raw water, thus confirming that this power station used optimum amounts of chemicals during raw water treatment. However, the plant can further improve the treatment process if the flocculant is added during the rapid mixing period, 60 s post PAC addition. The turbidity achieved was as low as 2 NTU. The mechanism is confirmed with the settling velocity tests. This confirms that the flocculant should be added during rapid mixing. It was found that it takes 30 min to form a 10 mL floc bed.

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