

# The Effect of Temperature and Agitation in AMD with $\text{FeCl}_3$ and Metal Hydroxides

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## Abstract

Acid mine drainage (AMD) from decant in Krugersdorp (South Africa) was dosed with acid-free polyferric chloride (af-PFCI) of  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  ( $\text{PFCI-Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$ ). A 200 mL sample was poured into five 500 mL glass beakers and the flocculent was added in a jar test respectively using different methods of mixing and dosing. The mechanism tests were performed employing two methods of dispersing reagents throughout the colloidal suspension, i.e., rapid mixing and shaking in order to find the removal mechanism of mineral salts and relationship between the removal and characteristics of flocculent/pollutants. The results showed that the turbidity removal efficiency exhibited by  $\text{FeCl}_3$ ,  $\text{PFCI-Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$ , and hydroxides of Ca or Mg is identical, all above 90%. It also revealed that the effective AMD treatment is not necessarily dependent upon the pH, but the ability of the coagulant to destabilize the double layer (high electronegativity) of an aqua-colloid and optimal hydrolysis. The residual turbidity of the AMD samples at 15, 25 and 35°C does not exhibit significant deviations. The turbidity removal of the samples with low temperature shows that dynamic viscosity of the colloidal suspension has an influence in the destabilization-hydrolysis reaction.

**Keywords:** AMD; Mixture; Dosing; Dispersing; Turbidity; Coagulant

## Introduction

Effective wastewater treatment has been confusedly associated with a variety of factors such as pH, temperature, mixing, retention time, dosage, reagents, feed water quality, colloids, etc. Before appropriate results were obtained, a shift towards alternative technologies, as opposed to conventional technology was advanced. Wastewater treatment works are currently facing a dual challenge, i.e., appropriate parameters and technologies leading to a cost-effective treatment methodology. A conventional wastewater treatment was a popular treatment technique world-wide where inorganic coagulant, namely Fe or Al salts are used due to their abundance on the earth's crust. Although ferric salts are more popular than other metal salts, the main challenge is their corrosive property which requires regular process plant maintenance or equipment replacement to avoid plants' failure. The use of reduced concentration of the metal ions of a coagulant and combine with other naturally occurring minerals is an ideal approach. This will also reduce the costs associated with afore-mentioned defects. pH adjustment during treatment has always been a challenge because inorganic metal salts cause extremely rapid and uncontrolled hydrolysis at approximately 6 to 8. Such conditions induce rapid hydrolysis, where hydrolysis species which are formed cannot be controlled, and the performance of the coagulants may worsen with the changes in the physical and chemical characteristics of the wastewater [1]. In order to improve the efficiency of the coagulants in wastewater treatment, pre-polymerised inorganic coagulants have been developed which were principally those of polyaluminium chloride (PACl) and polyferric chloride (PFCI). Their preparation which involves the pre-hydrolysed inorganic coagulants is costly because that is processed with partial hydrolysis of acid of their metal chloride ( $\text{MCl}_3$ ) solution using a special reactor [2]. In spite of the complex approach to conduct research on new technologies [3-7], most of them are costly and sophisticated or selective in wastewater of certain qualities.

Apart from the use of inorganic coagulants in conventional treatment, commercial polymers/flocculent were also utilized as coagulants or coagulant-aids. Advantages with polymer usage is their low inversion requirements, operation in a wide range of pH, easy

to handle, easy to dissolve in hard waters, can be used in solids dewatering including grease, oil and grease. On the contrary, polymers are expensive and incur unbearable extra costs which reduce the sustainability of the operations. Based on the fact that they are added in large volumes during wastewater treatment [2], it is therefore not feasible to reduce the concentration of the constituents during manufacturing. The main reason for the higher efficiency of organic polymers is their higher molecular weight (MW), and the increase of their molecular weight and size is thought to be the way for further improvement. That indicates that there is a need for more additives (e.g., silica) and a higher dosage of polymers to a colloidal system to achieve better adsorption, thus incurring more costs. The alternative synthetic flocculant which consists of metal salts and metal hydroxide of reduced concentrations is an ideal technique, an investigation considered in this study. The constituents include the combination of  $\text{FeCl}_3$  and  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$ , flocculants which behave as both coagulant and neutralizer concomitantly ( $\text{M}^{n+}/\text{OH}^-$  ratio). The advantage with these flocculants is their easy preparation and adaptability to all four types of destabilization (double layer compression, charge neutralization, particle bridging and entrapment in a precipitate) mainly due to metal salt and metal hydroxide components. On the contrary, commercial cationic polymers have a narrow pH operating range and it is recommended that the pH optimal performance has to be monitored in order to prevent free radical chain degradation [2]. In wastewater treatment, destabilization is the process which plays a pivotal role and influences the effectiveness of all the other subsequent reactions. Effective performance of destabilization depends primarily on the

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physico-chemical properties of the colloid-reagent and thorough chemical dispersion throughout the colloidal suspension. Other solute properties which include solute partition coefficient, polarizability and molecular structure influence organic pollutants adsorption [8]. The efficiency of a reagent is indicated by its destabilization potential, the ability to reduce the electrostatic forces of repulsion of an electrical double layer [9] (Supplementary Figure A1). Ineffective destabilization may result in poor quality of treated effluent due to a low concentration of hydrolysis species.

Settling time has normally not been addressed in wastewater treatment studies, as its significance is associated with hydrodynamic effect. The particle tend to increase in velocity due to hydrodynamic influence, where the drag force and the gravitational force reach equilibrium and causes no change in the velocity of the flocs.

Brownian motion also has an impact in settling as the colloids/flocs are always kept in suspension through random motion. The random motion of colloidal particles is induced by their bombardment against the molecules of the bulk fluid. Brownian motion is effective on the colloids/flocs of about 2 to 5 μm, where the density of colloids/flocs and viscosity of the medium allows random motion of colloids/flocs. Based on the fact that viscosity is influenced by temperature, it is therefore necessary to investigate its effect on the rate of sedimentation as Brownian motion becomes less important and sedimentation becomes favourable when the radius of suspended material increases [10]. Brownian motion is a random, diffusion-type transport, the intensity or rate of which is a function of the thermal energy of the fluid. The rate constant ( $k(r_1, r_2)$ ) for Brownian or perikinetic flocculation is expressed by Eq. 1.

$$W = 2 \frac{(\rho_p - \rho_f) g r}{9\mu} \quad [1]$$

where  $k$ =Boltzmann's constant ( $1.38 \times 10^{-16}$  erg K<sup>-1</sup>),  $T$ =absolute temperature (K),  $m$ =absolute viscosity and  $r_1$  and  $r_2$ =radii of adjacent particles.

Small charged particles do not settle in stationary fluid under gravity within a reasonable time-frame due to their small mass and also subjection to other forces, hence Brownian motion is essential in promoting flocculation in order to achieve effective settling. Stoke's Law predicts the settling velocity of the flocs expression using Eq. 2.

$$W = 2 \frac{(\rho_p - \rho_f) g r}{9\mu} \quad [2]$$

$w$ =settling velocity,  $\rho$ =density (the subscripts  $p$  and  $f$  indicate particle and fluid respectively),  $g$ =acceleration due to gravity,  $r$ =radius of the particle and  $\mu$ =dynamic viscosity of the fluid.

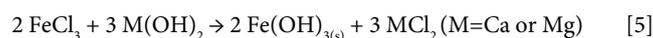
Flocs velocity includes the terminal, settling or fall velocity; and measures of the rate at which the colloids/flocs accumulate at the bottom. These forces affect the rate of flocculation as it becomes effective when gravitational force is greater than the drag force, which subsequently results in sedimentation and settling. Settling depends on the forces such as drag, gravitational and electrostatic [11]. Hydrolysis, a precursor of settling and also a process which co-exists with destabilization determining speciation and settling is expressed in Eq. 3.



The first species ( $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ) is formed when  $\text{FeCl}_3$  is added to a solution and hydrolysis commences until an insoluble hydrolysis species ( $\text{Fe}(\text{OH})_{3(s)}$ ) is formed. Eq. 3 does not indicate the molar ratio between the metal ions and the hydroxyl ions, Eq. 4.



This study focuses on the use of synthetic flocculent prepared by the mixture of reduced amounts of  $\text{FeCl}_3$  and Ca or Mg hydroxides in AMD. The disadvantage with  $\text{Ca}(\text{OH})_2$  is that it increases turbidity in a solution as stated by Kurniawan et al. [12], whereas  $\text{Mg}(\text{OH})_2$  has an ability to operate at pH above 9.0 in wastewater, giving a buffered pH control  $\text{Ca}(\text{OH})_2$  is environmentally hazardous as it has propensity to cause dust to the environment and also form clogs which block the pipeline. This study investigates the turbidity removal efficiency which occurs when metal hydroxide reacts with metal salts to form metal hydroxide species (flocs) as shown by Eq. 5.



It is evident (Eq. 5) that hydrolysis species are not only derived from hydrolysis of the metal ions by the bulk fluid (Eq. 4), but also from the dehydroxylation of the metal hydroxide. Unlike commercial polymers, the synthetic flocculent used in this study exhibit both destabilizing and hydrolysing potential (Eq. 4). The study conducted by van Nieuwenhuijzen [9] on polymers showed that there were some drawbacks in the application of (inorganic) metal salts for coagulation/flocculation to treat the AMD. The study states that the treatment increases inorganic sludge production and salinity of the effluent due to the release of counter ions by the flocculants, hence a study investigating the performance of the metal salts is conducted. Adsorption with excessive little or more amount of polymers on some particles results in incomplete coagulation or flocculation. On the other hand, adsorption with excessive amount of polymer on some particles can result in the destabilization of these particles on the positive or negative side depending upon the type of polymer used.

The objective of this study is to determine the effect of the flocculent prepared by the combination of the inorganic coagulant and metal hydroxide in the treatment of the AMD at lower and elevated temperatures. The investigation is to determine the chemical reactivity of the synthetic flocculants when the viscosity of the colloidal suspension changes from ambient conditions using mixing or shaking technique.

## Materials and Methods

In this study, coagulation-flocculation treatment has been applied to AMD samples at low and elevated temperatures using 0.043 M  $\text{Fe}^{3+}$  in  $\text{FeCl}_3$ , 0.043 M  $\text{Ca}^{2+}$  in  $\text{Ca}(\text{OH})_2$  or 0.043 M  $\text{Mg}^{2+}$  in  $\text{Mg}(\text{OH})_2$  and a combination of 0.043 M  $\text{Fe}^{3+}$  in  $\text{FeCl}_3$  and 0.043 M  $\text{Ca}^{2+}$  in  $\text{Ca}(\text{OH})_2$  ( $\text{PFCl}_{\text{Ca}}$ ) or 0.043 M  $\text{Fe}^{3+}$  in  $\text{FeCl}_3$  and 0.043 M  $\text{Mg}^{2+}$  in  $\text{Mg}(\text{OH})_2$  ( $\text{PFCl}_{\text{Mg}}$ ) using a jar test and a shaker respectively. Another set of experiments was conducted on the AMD samples adjusted to 15 and 35°C with  $\text{PFCl}_{\text{Ca}}$  and  $\text{PFCl}_{\text{Mg}}$  dosage with mixing or shaking. The aim was to compare their turbidity removal efficiencies, employing similar speed during mechanical agitation and measurements. Prior to a jar test, the pH, conductivity and turbidity of the samples were measured before the jar test. The samples were placed in a flocculator with rapid mixing (without a magnetic stirrer) at 250 rpm for 2 minutes. The samples were allowed to settle for 1 hour and thereafter the pH, conductivity and turbidity were measured. A second similar experiment was conducted and rapid mixing was replaced with shaking done at 250 rpm for 2 minutes. The samples were allowed to settle for 1 hour and thereafter the pH, conductivity and turbidity were measured. A supplementary set of experiment was conducted on the AMD samples with 20 mL of  $\text{FeCl}_3$  and  $\text{PFCl}$  of  $\text{Ca}(\text{OH})_2$  during mixing and shaking respectively, using varying speeds (50 to 300 rpm at 50 intervals) for 2 minutes.

## Acid mine water sample

The samples are collected from Western Decant in Krugerdorp in 25 litres plastic drum. The sample was air-tied and stored at room temperature as it did not contain natural organic matter. The pH, conductivity and turbidity of untreated AMD solution were 2.56, 4.43 mS/cm and 105 NTU respectively. The solid content of the sample was 6.8 g in a 200 mL solution. The constituents of the sample are shown in Table 1.

## Coagulants

Inorganic coagulants of 0.043 M of Fe<sup>3+</sup> in FeCl<sub>3</sub> and 0.043 M Ca<sup>2+</sup> in Ca(OH)<sub>2</sub> or 0.043 M Mg<sup>2+</sup> in Mg(OH)<sub>2</sub> and 0.043 M acid free polymer (PFC) using a jar test (a concentration obtained from the literature) are dosed during flocculation of the acid mine water yielded a wide range of results showing effective flocculation. The low concentrations are chosen as per a study which was conducted by [13] on paint wastewater treatment, which is low and resemble optimal concentration.

The calculations of the mass of metal salt to obtain 0.043 M of M<sup>3+</sup> (M<sup>3+</sup>=Fe or Al) follow:

Monoprotic metal salts (MCl<sub>3</sub>)

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6H_2O \text{ (} M^*=Fe \text{)} \quad [6]$$

FeCl<sub>3</sub>-Ca(OH)<sub>2</sub> or FeCl<sub>3</sub>-Mg(OH)<sub>2</sub> (af=acid free)

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6M(OH)_2 \text{ (} M^*=Fe \text{ or } Ca/Mg \text{)} \quad [7]$$

Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*(OH)_2 \text{ (} M^*=Ca \text{ or } Mg \text{)} \quad [8]$$

## Performance evaluation

The pH was used as a determinant to assess the rate of hydrolysis and hydrolytic potential of the coagulants at different mixing duration, whereas turbidity was used to determine the removal of colloidal particles from the samples.

**pH measurement:** A MettlerToledo Seven Multimater (*made in Germany*) pH meter with an electrode filled with silver chloride solution, and the outer glass casing with a small membrane covering at the tip was used. The equipment was calibrated with standard solutions with the pH of 4.0 and 7.0 before use.

**Turbidity measurement:** A Merck Turbiquant 3000T Turbidimeter (*made in Japan*) was used to determine turbidity or the suspended

particles in the supernatant using NTU as a unit of measurement. It was calibrated with 0.10, 10, 100, 1000 and 10000 NTU standard solutions.

**Inductively Coupled Plasma (ICP):** A Perkin Elmer Optima DV 7000 ICP-OES Optical Emission Spectroscopy (*made in USA*) was used to determine the metals in the supernatant using ppm as a unit of measurement. It was calibrated with the standard solution between 2-50 ppm of the salts mentioned under sub-section 2.1.

**Scanning electron microscopic analysis:** A KYKY-EM3200 Digital Scanning Electron Microscope (model EM3200) equipment (*made in China*) was used to produce the SEM photomicrographs.

**X-ray diffractometric analysis:** The x-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku Miniflex II Desktop x-ray diffractometer (Japan) with Cu K $\alpha$  radiation. A step size of 0.02° at a speed of 4° (2 $\theta$ )/min over 10-80° was applied. The minerals in VM treated between 950 and 1300°C were quantified by Siroquant software.

## Experimental procedure

**Jar test procedure:** The equipment used for a jar tests was a *BIBBY Stuart Scientific Flocculator (SW1 model)*, which has six adjustable paddles with rotating speeds between 0-250 rpm. The AMD solution containing 6.8 g colloid in 200 mL of the solution was poured in each of the five 500 mL glass beakers for the test. Different dosages of 0.043 M Fe<sup>3+</sup> in FeCl<sub>3</sub> were added to the AMD samples. The experiments were conducted employing rapid mixing (250 rpm for 2 mins.), with mixing and shaking (250 rpm for 2 mins). The rationale was to determine correlation between the pH changing trend and turbidity removal when the treatment is conducted in acidic wastewater without pH adjustment.

**Experimental procedure:** In the first set of experiments, the samples were treated with varying dosages of FeCl<sub>3</sub> and treated in two different methods such as a jar test and shaker. A second similar set of experiments was carried out by replacing FeCl<sub>3</sub> with Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>. A third similar set of experiments was carried out by replacing FeCl<sub>3</sub> with acid free PFCl<sub>Ca</sub> or PFCl<sub>Mg</sub> flocculent. The fourth set of experiments was conducted on the AMD samples at 15 and 35°C with Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> during mixing and shaking respectively. The samples in all sets of experiments were allowed to settle for 1 hour, after which the pH and turbidity were measured.

## Results and Discussion

Effective wastewater treatment is controlled by two processes such as the degree of destabilization and the rate of flocs formation. On the other hand, wastewater treatment is controlled by three processes, i.e., destabilization-hydrolysis, coagulation and flocculation. In effective treatment, the reagents which are added must have an optimal destabilizing potential to reduce the electrostatic forces of repulsion and proliferate van der Waals forces of attraction (destabilization). When that has been successfully accomplished, the formation of primary flocs must continue uninterrupted until it reaches a stage of secondary flocs formation. When the secondary flocs are well-developed with a deterrent such as rupture due to shear stress (rapid mixing). Destabilization-hydrolysis is classified as a single process because both reactions co-exist as they are induced by the reagent(s) added to the colloidal suspension; where the first reaction occurring on the colloidal suspension and the latter on the metal ions of the coagulant. Subsequent to that, coagulation starts to occur when the

Element	Conc (ppm)
Al	2.1844
Ca	187.9
Co	0.138
Cu	0.059
Fe	23.685
K	5.209
Mg	68.396
Mn	34.428
Na	46.44
Ni	0.375
Pb	0.189
Sb	0.27
Se	0.795
Zn	0.315

**Table 1:** Printout of ICP-EOS results of the untreated AMD sample.

hydrolysis species (precipitates) are formed and latter develop into larger flocs during collision due to velocity gradient and differential velocity. The pH of the solution changes when hydrolysis occurs because of dehydroxylation of the hydration sphere around the central metal ions (Supplementary Figure A1) as represented in Figure 1.

The pH values of the samples with Ca(OH)<sub>2</sub> are slightly lower than those of the corresponding samples with Mg(OH)<sub>2</sub> mixing. The pH values of the samples with both Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> shaking are slightly higher than their corresponding samples with mixing (Figure 1).

This may be attributed to high intensity of mechanical agitation during mixing which ameliorated the rate of destabilization, thus increasing the rate of hydrolysis. The study [14] has proven that there is a strong correlation between the pH and the turbidity when basic wastewater is treated with Fe and Al salts. Invariably, Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> have also been used in wastewater with adjusted pH [15], an approach which was not followed in this study. Although the determination of the turbidity removal of the AMD samples between Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> has been conducted [16], their usage in this study is to compare their performance with that of the combinations of FeCl<sub>3</sub> and Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>. The experimental results show that the turbidity removal efficiencies exhibited by corresponding samples between Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> during mixing and shaking are similarly identical (Figure 1), a case which is similar between the samples with PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> mixing and shaking. According to Eqs. 1 and 2, the former explains the speciation and the latter the products of hydrolysis. The former is indicative of the type of destabilization which occurred whereas the latter indicates the acidity of the solution. The former shows that neutralization was a predominant reaction during the process, i.e., Fe(OH)<sup>2+</sup> and Fe(OH)<sup>+</sup> were active species as they exist within the pH range of the AMD (1-5). The pH changing trend in the samples with PFCl<sub>Ca</sub> or PFCl<sub>Mg</sub> dosage (Figure 1) exhibits a similar decreasing pH trend, hydrolysis process. According to hydrolysis kinetics, it has to be noted that the amphoteric nature of water can influence the pH of the wastewater, thus influencing the rate of hydrolysis.

As the metal ions in aqueous solution behave as Lewis acids, it shows that the valence of the metal ion (Fe<sup>3+</sup>, Ca<sup>2+</sup> or Mg<sup>2+</sup>) pulls a lone pair of electrons from the O-H of the bipolar water molecules. This increases the polarity of the bond, causing the cleavage of the H<sup>+</sup>-O-H and the release of a proton to the colloidal suspension and metal hydroxide species.

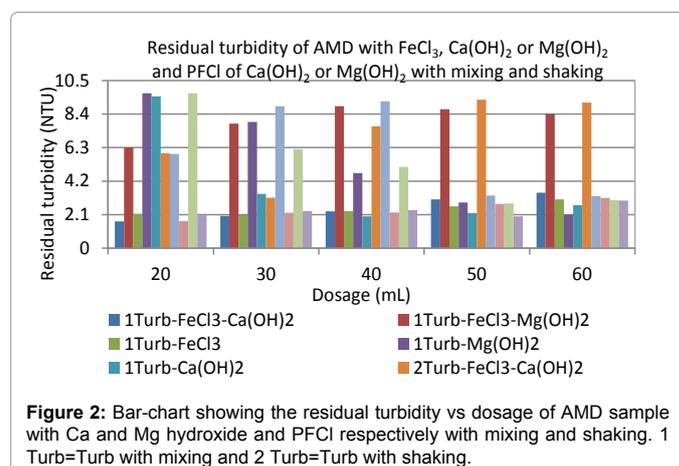
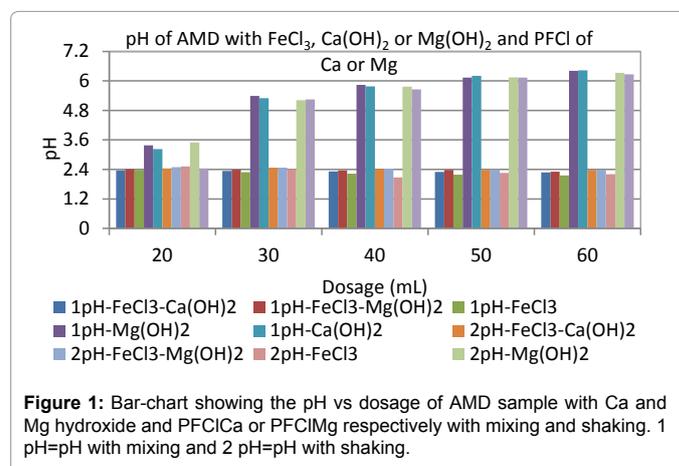
Another observation (Figure 1) from the pH values between mixing and shaking indicate that the type of the mechanical agitation does not influence destabilization-hydrolysis reaction considerably, but the rate of collision and vibration which results in shear stress [17] and energy respectively.

The effectiveness of the destabilization-hydrolysis is reflected by the residual turbidity (Figure 2), which is a determination of the destabilization-hydrolysis potential of a reagent. The residual turbidity of the AMD samples (Figure 2) with Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> (mixing and shaking) is in a range of 6.0-10.3 NTU, a reduction efficiency above 94.4%. The samples with mixing show residual turbidity in a range of 6.6-10.3 NTU. The samples with mixing exhibit a slightly higher residual turbidity than the samples with shaking, which can be attributed to uniform dispersion of the reagents throughout the colloidal suspension during shaking. According to the amphoteric property of water molecules and the OH<sup>-</sup> ions released by the metal

hydroxide, it is plausible that the residual turbidity would exhibit a consistent changing trend; the changing trend of the residual turbidity values suggests that the reagents have buffering potential which retained the pH, an indication of speciation. However, the behaviour shown by the PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> is in agreement with Ntwampe et al. [18], which state that the changing trend of the pH does not always have to correlate with the turbidity values. The treatment conducted in this study is more directed, but not restricted to the AMD of low heavy metal content (Table 1). The results of the treated AMD samples measured by ICP-OES are shown in Supplementary Table A1.

The residual turbidity of the samples with PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> (mixing) does not show a consistent changing trend, instead it fluctuates between 2.0 and 4.3 NTU. Invariably, the residual turbidity of the samples with PFCl<sub>Ca</sub> shows a fluctuating trend between 2.8 and 6.2 NTU, whereas it is between 2.0 and 3.7 NTU in the samples with PFCl<sub>Mg</sub>. The values obtained with PFCl<sub>Mg</sub> are slightly lower than those in the samples with PFCl<sub>Ca</sub>.

The synthetic PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> are exhibited an optimal turbidity removal efficiencies when compared with FeCl<sub>3</sub>, Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> because they contain common metal ions, which also show similar destabilization-hydrolysis behaviour. One of the advantages with the use of these flocculent in AMD treatment is their flexibility to withstand turbulence by mechanical agitation as they do not form a highly viscous compound. As the flocculent contain constituents of both the coagulants (Fe<sup>3+</sup>) and the neutralizing agents (Ca<sup>2+</sup> and Mg<sup>2+</sup>), destabilize is by charge neutralization and particle bridging [19], as



afore-mentioned (Eq. 3). The pH of the AMD (2.56) was attemperate for destabilization by neutralization as it is known that the Fe<sup>3+</sup> ions are active in a medium with a pH range of 1.0-5.0 (Flynn).

Figure 3 shows the residual turbidity of the AMD samples at 15 and 35°C with Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, PFCI<sub>Ca</sub> or PFCI<sub>Mg</sub> dosage respectively during mixing or shaking. The viscosity of the AMD at 15°C is low and it is therefore expected that the reaction rate (destabilization-hydrolysis) will be slower and faster at elevated temperature.

The residual turbidity of the samples with 20 mL PFCI<sub>Ca</sub> and PFCI<sub>Mg</sub> at 15°C is higher (6.4-7.9 NTU) than the other samples which in a range of 4.22-5.34 NTU, and the values fluctuate. The samples with 40 mL dosage of both flocculants with mixing have slightly lower residual turbidity than the other samples (Figure 3). It is suggested that the internal energy (enthalpy) and the viscosity of the samples with 20 mL dosage (15°C) are very low; hence it was difficult for the flocculent to destabilize the colloidal suspension [20]. The residual turbidity values of the samples with 30 mL are lower than those of the samples with 20 mL but higher than the other samples, this indicates that the internal energy and the viscosity of the former experienced a slight increase of the internal energy and viscosity. Mechanical agitation (mixing or shaking) disperse the reagents throughout the system by inducing eddies which appear in the form of turbulent dissipation length, the measure of the size of the turbulent eddies. Turbulent eddies may become destructive when propagated severely as they may cause breakage of the flocs. Mixing is the only type of mechanical agitation between the two, which is characterized by turbulent eddies. A system which has high ionic strength and a dosage of reagent(s) with high destabilizing potential is prone to react spontaneously using internal thermal energy. On the contrary, dynamic viscosity of the colloidal suspension, which is a function of temperature, affects the system's reactions, i.e., particles collision and vibration. Colloidal suspension of such a low temperature will react insignificantly with the chemicals and therefore mixing is then necessary (Eq. 9)

$$G = \sqrt{P/\mu V} \quad (9)$$

where G=average velocity gradient for mixing, P=dissipated power in water, W μ=dynamic water viscosity (N·s/m) and V=volume of mixing tank,

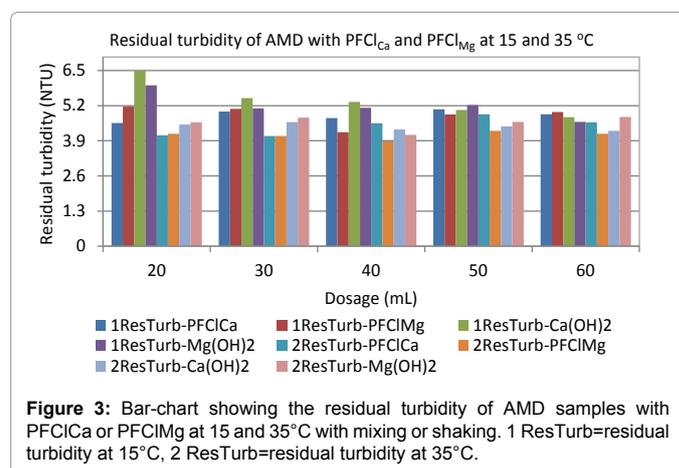
Under normal circumstances, mixing can be disadvantageous due to its selectivity character on the types of destabilization when polymers are used, i.e., unsuitable for particle bridging as it breaks the chain of particles bonded by polymers [21]. This also occurs with coagulants or flocculants by also breaking the flocs which agglomerated during flocculation. In some other instances, mixing can impair turbidity removal despite the dosage, as exhibited by higher residual turbidity of the samples with 50 and 60 mL of PFCI<sub>Ca</sub> and PFCI<sub>Mg</sub> at 35°C (mixing and shaking) compared to that of the other samples (20, 30 and 40 mL). In this case, it is suggested that the samples possess high internal energy and the viscosity is high, thus causing excessive collision and vibration of the electrons. When the electrons are in an excited stage (thermal energy), they move to the highest energy level during hybridization and induces hydrolysis. Based on the excitement of the electrons and the fast hydrolysis reaction due to high thermal energy, re-stabilization is inevitable more especially that the concentration of the Fe and Ca or Mg is high (73 and 0.88 mol/L for PFCI<sub>Ca</sub>, 0.69 and 0.83 mol/L for PFCI<sub>Mg</sub>). Thermal energy of the system is also an attribute to collision rate (Figure 1) as Brownian transport increases with increasing temperature, thus fastening reaction rate. It is vital that nucleation has to take place so that a system must have particles of

different sizes; otherwise minimum collision rate will occur between particles of identical sizes. The Brownian motion enhances diffusional motion of the particles induced by thermal energy of the fluid, thus increasing the rate of agglomeration (Figure 3). The observations also reveal that low water temperature impairs the floc strength and virtually floc formation efficiency, which causes bad settling. There is a need for prolonged flocculation time which will break larger flocs into smaller sizes and reduces settling efficiency (Figure 3).

The residual turbidity of the samples with 20-40 mL PFCI<sub>Ca</sub> and PFCIMg mixing at 35°C exhibits an inconsistent changing trend in a range of 4.08-4.55 NTU, whereas the residual turbidity of the corresponding samples with shaking exhibit a similar behaviour in a range of 4.12-4.76 NTU, slightly higher compared to the samples with mixing. The viscosities (low and high) which are influenced by the temperature of the samples are the main attributes to the reactivity of the colloidal suspension, i.e., the chemical reactions of the sample at elevated temperature are faster and slower in the samples with low viscosity [22]. The residual turbidity results shown by the samples with 15 and 35°C indicate that mechanical agitation does not influence the turbidity removal efficiencies of the reagents but mainly disperses it throughout the solution. However, the turbulent eddies play a pivotal role during the destabilization-hydrolysis reaction, i.e., severe turbulent eddies can cause poor performance in a solution which possesses a high chemical energy (Figure 3).

Figure 4 shows the pH of the AMD sample with 20 mL of FeCl<sub>3</sub> and FeCl<sub>3</sub>-Ca(OH)<sub>2</sub> dosage respectively, at varying speed during mixing and shaking between 50 and 300 rpm at 50 intervals. The rationale was to determine the effect of velocity gradient on the destabilization-hydrolysis.

According to the results of set of experiment of the AMD with 20 mL of FeCl<sub>3</sub> and PFCI of Ca(OH)<sub>2</sub> during mixing and shaking (Figure 4); the pH of the samples with FeCl<sub>3</sub> mixing exhibits a decreasing trend in a range of 2.37-2.49, and the samples with shaking in a decreasing inconsistent range of 2.35-2.48. The pH if the samples with Ca(OH)<sub>2</sub> during mixing and shaking decreases in a range of 3.23-3.51 and 3.20-3.48 respectively. The changing trend shows decreasing pattern with increasing mixing or shaking speed, indicating that velocity gradient influences hydrolysis. The results reveal that the pH of the system decreases with increasing speed of mechanical agitation, i.e., higher velocity gradient enhances the rate of hydrolysis. Although the pH values between the samples with mixing and shaking are insignificant, the former is slightly higher than the latter; which indicates that shear



stress (rapid mixing) has an influence on hydrolysis reaction, which is more likely to result in re-stabilization [17,23].

The residual turbidity in the samples with FeCl<sub>3</sub> during mixing and shaking (Figure 4) decreases with increasing mechanical agitation in an inconsistent trend of a range 7.08-8.89 and 6.35-8.44 NTU respectively. On the other hand, the residual turbidity of the sample with flocculent of FeCl<sub>3</sub>-Ca(OH)<sub>2</sub> during mixing and shaking also decreases with increasing mechanical agitation in an inconsistent trend of a range 7.11-9.03 and 6.62-8.84 NTU respectively. The results show that both FeCl<sub>3</sub> and FeCl<sub>3</sub>-Ca(OH)<sub>2</sub> dosage yielded optimal turbidity removal efficiencies in the samples with 150-250 rpm in both mixing and shaking techniques. The samples with 50, 100 and 300 rpm show a slightly higher residual turbidity, indicating inadequate chemical dispersion with lower mechanical agitation and re-stabilization with 300 rpm. However, the samples with shaking show a lower residual turbidity compared to corresponding samples with mixing. This invokes the findings by Ntwampe et al. [14], stating that velocity gradient in the system treated in a shaker is not prone to shear stress which is associated with flocs rupture; hence there is no indication of re-stabilization. Figures 5 and 6 show the comparison between the turbidity removal efficiency and the concentration (mass%) of PFCl<sub>Ca</sub> or PFCl<sub>Mg</sub> in each of the 200 mL AMD samples respectively.

The turbidity removal efficiencies of PFCl<sub>Ca</sub> of the samples with low concentrations of combined Fe<sup>3+</sup> and Ca<sup>2+</sup> in a flocculent (Figure 5) of 0.29, 0.44 and 0.58 mol/L are high, i.e., 94.1, 95.2 and 92.4% respectively, whereas the samples with higher concentrations (0.73 and 0.88 mol/L) show lower efficiencies (90.7 and 90.9% respectively). It is suggested that it might be due to over-dosage which resulted in re-stabilization of the particles [17,23]. Another cause of poor turbidity removal with the flocculent occurs in wastewater with the pH lower than 6 is due to adsorption of the hydrolysis products onto the colloidal surfaces for charge neutralization [24]. They may also interact with dissolved components in the colloid, thus resulting in re-stabilization due to charge reversal at the colloidal surface [25].

The turbidity removal efficiency of the samples with PFCl<sub>Mg</sub> is high in the samples with low and high concentrations, i.e., 0.27, 0.69 and 0.83 mol/L (94.1, 95.1 and 95.3% respectively). Only two samples with the concentrations of 0.42 and 0.56 mol/L (30 and 40 mL) have removal efficiencies of 91.1 and 90.8% respectively. Figure 7 shows the polynomial graph of the pH vs E% of AMD sample with PFCl<sub>Ca</sub> dosage with shaking. Figure 8 shows the polynomial graph of the pH vs E% of AMD sample with PFCl<sub>Mg</sub> dosage with shaking.

Figure 9 shows the SEM images of AMD sludge with PFCl<sub>Ca</sub> and PFCl<sub>Mg</sub> with shaking at the magnification of 2500X. Both SEM images of the AMD sludge (Figure 9) with PFCl<sub>Ca</sub> (left) and PFCl<sub>Mg</sub> (B) show almost identical crystal morphological matrix, i.e., the flocs are distributed throughout the area of bigger and smaller sizes, with spongy-like structure. The micrograph of the sludge with PFCl<sub>Ca</sub> (A) shows a hard fused sponge-like structure at the base with small fused non-spherical floc-like structures on top. The structure is spread all over the slide, showing no voids for any particle to pass through. On the other hand, the micrograph of the sludge with PFCl<sub>Mg</sub> (B) shows a highly compacted smooth-spongy-cake structure on the top part without any voids. The small non-spherical fused flocs occupy the bottom part of the slide, with very small voids on the top which disappear as moving downwards.

Supplementary Figure A2 shows the SEM images of AMD sludge with Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> with rapid mixing at the magnification

of 2500X. The micrograph of the sludge with Ca(OH)<sub>2</sub> (A) in Supplementary Figure A2 shows a porous sponge-like structure occupying around 80% of the slide with some small and big voids which are indicative of rupture due to rapid mixing. On the other hand, the sludge with Mg(OH)<sub>2</sub> (right) also shows a similar crystal morphological structure with cluster of dense sponge-like structures joined by longitudinal flocs. The slide also shows some small and big voids.

The PFCl<sub>Ca</sub> or PFCl<sub>Mg</sub> show high hydrolysing potential compared to Fe<sup>3+</sup> salt of charge density which is equal and greater than 0.1. The lower

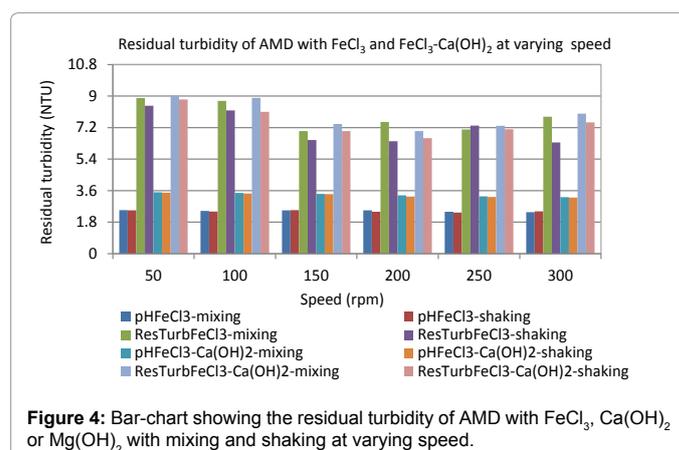


Figure 4: Bar-chart showing the residual turbidity of AMD with FeCl<sub>3</sub>, Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub> with mixing and shaking at varying speed.

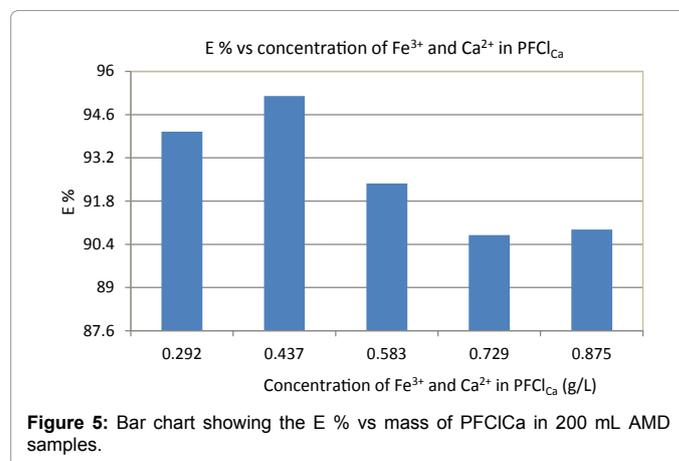


Figure 5: Bar chart showing the E % vs mass of PFClCa in 200 mL AMD samples.

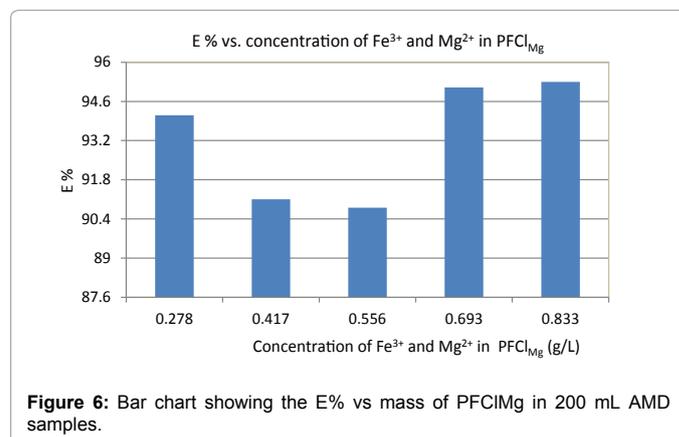


Figure 6: Bar chart showing the E% vs mass of PFClMg in 200 mL AMD samples.

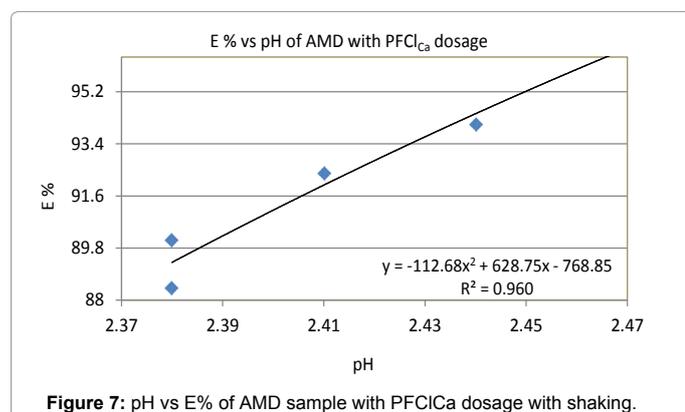


Figure 7: pH vs E% of AMD sample with PFCICa dosage with shaking.

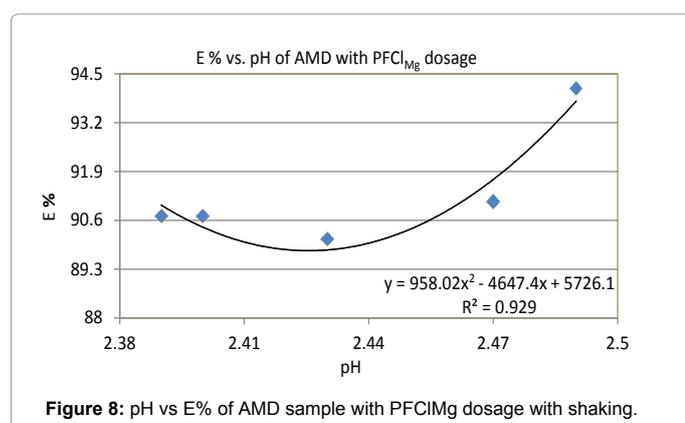


Figure 8: pH vs E% of AMD sample with PFCIMg dosage with shaking.

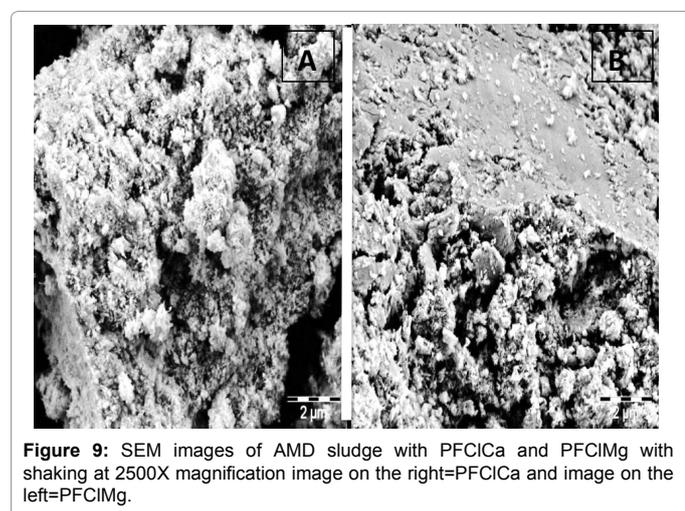


Figure 9: SEM images of AMD sludge with PFCICa and PFCIMg with shaking at 2500X magnification image on the right=PFCICa and image on the left=PFCIMg.

the negative logarithm of equilibrium constant ( $\text{p}k_a$ ), the more acidic and higher hydrolysing potential the metal ion becomes weaker [26]. The experimental results showed that the best turbidity removal, which is an indication of high rate of hydrolysis is achieved mainly in the samples with low dosages, which suggests that effective destabilization is not only dependent on the dosage, but the concentration of metal ions and their valence cations ( $M^{3+}$ ) in the solution.  $\text{Fe}^{3+}$  has a tendency of becoming weakly hydrolysed and appears as monomeric, dimeric or trimeric species within the colloids. This suggests that the monomers, dimers and trimers conglomerate to form a massive filter-cake structure which consists of larger and dense (sponge-like) flocs. This enables the

polymer to achieve maximum mass transfer of the colloidal particles. It is therefore concluded that optimal turbidity removal in AMD solution with  $\text{PFCl}_{\text{Ca}}$  or  $\text{PFCl}_{\text{Mg}}$  is of a physical nature. Ionic strength of metal ions, a parameter which determines the destabilization potential of the reagents is illustrated in Tables 2 and 3.

Figure 10 represents XRD curves of the sludge of the AMD sample with a combination of  $\text{FeCl}_3$  and  $\text{Mg}(\text{OH})_2$  flocculent during mixing, whereas Supplementary Figure A3 shows the XRD curves of the sludge of the sample with the same flocculent during shaking.

The XRD curves Figure 10, where the AMD sample was treated with a combination of  $\text{FeCl}_3$  and  $\text{Mg}(\text{OH})_2$  ( $\text{PFCl}_{\text{Mg}}$ ) flocculent during mixing. On the other hand, Supplementary Figure A3 is the same samples and dosage during shaking, the reason being to compare the concentration of the minerals or metals sorbed onto the flocs. In the Figure 10 showed two peaks representing crystalline materials at  $2\theta$  positions of  $22^\circ$  and  $38^\circ$ , respectively, with an intensity slightly below 500 counts.

The peaks (Supplementary Figure A3), where the AMD sample was treated with a combination of  $\text{FeCl}_3$  and  $\text{Mg}(\text{OH})_2$  ( $\text{PFCl}_{\text{Mg}}$ ) flocculent during shaking also appeared at  $2\theta$  positions of  $20^\circ$  and  $37^\circ$  respectively, with about the same intensity as with the previous case, slightly below 500 counts. Pearson correlation coefficient ( $r$ ) is used to calculate the relation between pH and residual turbidity. The equation is also used to determine the reliability of the experimental results, i.e., comparison between  $r$  and  $R^2$  (Figures 5 and 6). Correlation coefficient of 0.70 or higher is a very strong relationship, 0.40-0.69 is a strong relationship, and 0.30-0.39 is a moderate relationship. The results of the experiments are used in the calculations below:

$$x_{\text{PFCl-Ca}} = \text{pH of PFCl and } x_{\text{PFCl-Mg}} = \text{pH of PFCl}$$

$$y_{\text{PFCl-Ca}} = \text{turbidity of PFCl and } y_{\text{PFCl-Mg}} = \text{turbidity of PFCl}$$

$$\Sigma x_{\text{PFCl-Ca}} = 10.7, \Sigma x_{\text{PFCl-Ca}}^2 = 23.46, \Sigma y_{\text{PFCl-Ca}} = 10.09, \Sigma y_{\text{PFCl-Ca}}^2 = 24.5 \text{ and } \Sigma xy_{\text{PFCl-Ca}} = 25.03$$

$$\Sigma x_{\text{PFCl-Mg}} = 9.1, \Sigma x_{\text{PFCl-Mg}}^2 = 25.36, \Sigma y_{\text{PFCl-Mg}} = 10.7, \Sigma y_{\text{PFCl-Mg}}^2 = 28.07 \text{ and } \Sigma xy_{\text{PFCl-Mg}} = 26.02$$

### Ca-polymer of $\text{Ca}(\text{OH})_2$ and Mg-polymer of $\text{Mg}(\text{OH})_2$

Using the results obtained with the AMD sample containing  $\text{PFCl}_{\text{Ca}}$  and  $\text{PFCl}_{\text{Mg}}$  dosage respectively, yielded the  $r$ -values of 0.895 and 0.748 (89.5 and 74.8%) respectively. The range of the correlation coefficient is from -1 to 1. The correlation coefficients in samples with shaking fall within a range of strong relationship. This is validated by  $R^2$  of the pH of  $\text{PFCl}_{\text{Ca}}$  and  $\text{PFCl}_{\text{Mg}}$  vs. residual turbidity in AMD samples with shaking respectively as shown in Figures 5 and 6 of 0.960 and 0.923 respectively [27-32].

### Conclusion

The turbidity removal efficiency exhibited by  $\text{FeCl}_3$ ,  $\text{PFCl}_{\text{Ca}}$  or  $\text{PFCl}_{\text{Mg}}$  and Ca or Mg hydroxide is identical, all above 90%. Effective wastewater treatment is not necessarily dependent upon the pH, but the ability of the coagulant to destabilize the double layer (high electronegativity) of an aqua-colloid and optimal hydrolysis, precursor to adsorption. A colloidal suspension high in charge density is highly reactive to the metal salts with a high electron valence. Effective destabilization is not only dependent on the dosage, but also on the concentration of metal ions and their valence cations ( $M^{3+}$ ) in the solution. The photomicrograph (SEM) of the AMD sludge samples indicates that optimal turbidity removal occurring with  $\text{PFCl}_{\text{Ca}}$  or

Salt	Mass of salt (g)	Conc <sup>n</sup> (mol/L)	M <sup>n+</sup> conc <sup>n</sup> (M)
FeCl <sub>3</sub>	16.3	0.1	0.1
AlCl <sub>3</sub>	23.3	0.1	0.1
Mg(OH) <sub>2</sub>	5.8	0.1	0.1

Table 2: Mass of FeCl<sub>3</sub> and metal hydroxide for preparation of standard solutions.

Species	Ionic strength
Fe <sup>3+</sup>	0.193
Ca <sup>2+</sup>	0.086
Mg <sup>2+</sup>	0.086
Fe <sup>3+</sup> +Ca <sup>2+</sup> /Mg <sup>2+</sup>	0.322

Table 3: Ionic strength of FeCl<sub>3</sub>, Ca<sup>2+</sup> or Mg<sup>2+</sup> hydroxides.

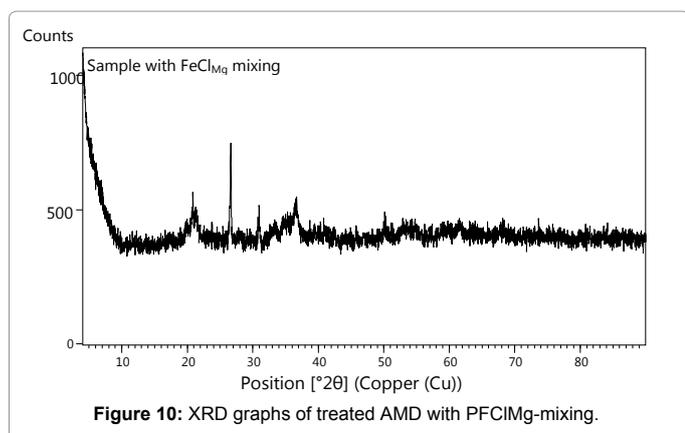


Figure 10: XRD graphs of treated AMD with PFCIMg-mixing.

PFCIMg is of a physical nature. The residual turbidity of the AMD samples at 15, 25 and 35°C does not exhibit significant deviations. The turbidity removal of the samples with lower temperature revealed that dynamic viscosity has an influence in destabilization-hydrolysis. A colloidal suspension with a high charge density (AMD) is highly reactive to metal salts with a high electron valence, thus indicating that effective destabilization is not only dependent on the dosage but also on the concentration of metal ions and their valence cations (M<sup>2+</sup>) in the solution.

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