

Comparison of chemical reactivity between inorganic and synthetic polymers in the treatment of AMD

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DECLARATION

I, Irvin Oupa Lesele Ntwampe, hereby declare before a Commissioner of Oaths:

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ABSTRACT

This study involves the treatment of the acid mine drainage (AMD) sample using inorganic coagulants such as FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$ and acid-free polyferricchloride (af-PFCl) of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ and acid-free polyaluminiumchloride (af-PACl) of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ in a jar test during rapid and slow mixing, for 250 and 100 rpm for 2 and 10 minutes respectively, settled for 1 hour, after which the pH, conductivity, turbidity measurements were conducted. A similar set of experiments was conducted using the AMD sample with the same dosages in a shaker using the same timing, settled for 1 hour, after which similar measurements were conducted. A third similar set of experiment was conducted with dosage without mixing, settled for 1 hour, after which similar measurements were conducted. In a few selected experiments extra measurements such as dissolved oxygen (DO) and oxidation reduction potential (ORP) were conducted.

In the first experiment, 200 mL of the AMD sample was poured into five 500 mL glass beakers. A dosage of 20, 30, 40, 50 and 60 mL of 0.043 M FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ was added in the middle of the samples respectively using plastic syringes. The samples settled for 1 hour after which the pH, conductivity and turbidity were measured. A second similar set of experiments was conducted by pouring the AMD sample into five 500 mL Erlen Meyer flasks, equal quantities of coagulants were added and the samples were placed in a shaker using similar stirring method. A third similar set of experiments were conducted in a jar test with rapid mixing for 2

minutes, settled for 1 hour, and similar measurements were done. The results showed turbidity removal in the AMD samples with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage during mixing, shaking and without mixing is similarly identical. Turbidity removal was still effective in the AMD using inorganic coagulants/flocculents. Experimental results show that the ionic concentration and charge density in the system (wastewater) during treatment determines the rate of destabilization-hydrolysis.

In a second set of experiments, 200 mL of acid mine drainage sample were poured into 5 glass beakers and dosed with FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and polymers of a mixture of FeCl_3 and $\text{Ca}(\text{OH})_2$ (af-PFCl) respectively. The samples were placed in a flocculator and stirred at 250 rpm for 2 minutes. The samples were allowed to settle for 1 hour after which the pH, conductivity and turbidity were measured. A similar set of experiments was conducted by pouring 200 mL of the sample into five Erlenmeyer flasks with the same dosage and were placed in a shaker using similar timing and measurements. A third similar set of experiments was conducted but without mixing, settled for 1 hour and the same measurement taken. The fourth and fifth sets of experiments were conducted with $\text{Ca}(\text{OH})_2$ and af-PFCl polymer respectively. The results showed that the pH and residual turbidity in the samples with Fe^{3+} salts, $\text{Ca}(\text{OH})_2$ and af-PFCl dosages in corresponding dosages are almost identical. The difference between the pH and residual turbidity in the corresponding sample dosages with mixing, shaking and without mixing exhibit is insignificant.

In a third set of experiments, 200 mL of the AMD was poured into 5 glass beakers and thereafter dosed with Fe^{3+} and Al^{3+} salts and a synthetic polymer of FeCl_3 and

Mg(OH)₂. The samples were treated in a jar test at 250 rpm for 2 minutes, settled for 1 hour after which the pH, conductivity, turbidity, dissolved oxygen (DO) and oxidation reduction potential (ORP) were measured. A similar batch experiments was conducted by placing the samples on a shaker using the same timing and measurements. A similar third batch of experiment was conducted with samples without mixing and employed similar settling time and measurements, and the fourth similar set of experiments was conducted dosing the AMD sample with 0.1 M af-PFCl of Mg(OH)₂ in mixing and shaking. The turbidity removal in the samples in the samples with FeCl₃, AlCl₃ and af-PFCl dosage was effective and comparable, whereas FeCl₃ yielded better performance. The SEM images show that the sludge in the samples with af-PFCl of Mg(OH)₂ dosage consists of a large cake-like structure, with the likelihood of optimal adsorption. The turbidity removal in the AMD sample with 0.1 M af-PFCl polymer of Mg(OH)₂ with mixing and shaking is similarly identical, and also ORP results showed that redox reaction is predominant during destabilization-hydrolysis.

The experimental results in all the AMD samples dosed with the coagulants and flocculants used in this study revealed that the concentrations, dosages, dispersion techniques (mixing, shaking and no-mixing), dosing (prior or during mixing), yielded optimal turbidity/TSS removal potential. This shows that the experiments achieved the desired objective, i.e. investigation of the reactive potential of the coagulant/flocculent in the destabilization-hydrolysis of the AMD sample without pH adjustment.

PUBLICATIONS AND PRESENTATIONS FROM THIS RESEARCH WORK

2015: Evaluating and Understanding the impact of Acid Mine Drainage (AMD) on the ecosystem (Cedar Park Hotel Conference Centre-Woodmead.

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DEDICATION

I dedicate this work to the team of research that accepted me to pursue studies towards Master's Degree in Engineering at North West University, my supervisor and co-supervisor for believing in me and the quality of work I carried out, external examiners, lab manager, Chemistry Laboratory Manager, God for providing strength and courage to strive towards success and achieve the set goal and lastly, my family

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GLOSSARY

Acid mine drainage-Acid water ric in iron, produced when pyrite (FeS_2) is oxidized in an aqueous medium in the presence of air or oxidized by bacteria.

Ca(OH)_2 -Slake lime

Ca(OH)_2 -slaked lime

Dolomite-A sedimentary rock of chemical composition of $\text{CaMg(CO}_3)_2$

Limestone-Sedimentary rock containing CaCO_3

ABBREVIATIONS

AMD : Acid mine drainage

PSD : particle size distribution

CLD : chord length distribution

TGA : Thermo-gravimetric analysis

SEM : Scanning Electrn Microscopy

XRD : X-ray diffraction

FTIR : Fourier Transform Infrared Spectroscopy

af- AlCl : acid-free polyaluminiumchloride

af- PFCl : acid-free polyaferricchloride

CHAPTER 1: LITERATURE REVIEW

1.1 Background

Wastewater treatment poses a serious challenge to the research fraternity, industries and governments world-wide. The quality of the wastewater (pH, constituents and turbidity) is a distinctive factor which characterizes its impact to the ecosystem (biota and fauna). The main issue is that the governments stipulate the requirements of specific standards and the parameters of the treated effluent, which is discharged to the water-course and the industries struggle to meet those requirements due to a lack of comprehensive information pertaining to optimal wastewater treatment. A large amount of research has been conducted, employing various techniques and technologies, but it has not successfully met the desired objectives.

The type of treatment required on a specific wastewater depends on the type of the colloids and size of particles present in the wastewater. The colloids can either be hydrophilic (water-loving) or hydrophobic (water-hating). The former is not easily destabilized due to the dipolarity effect of surrounding water molecules which form a barrier that deters any chemical reaction upon colloidal suspension. The chemically bound or dipolar water molecules which surround the colloids or the adsorbed water molecules on the particles cause stability of the colloidal suspension (Wulfsberg, 1987). Hydrophobic colloids are easy to treat because of their penetrability and less stability. Destabilization-hydrolysis is a physico-chemically influenced process which

depends on the type and electron configuration of solvated colloids, valence of metal ion, reagent dispersion technique, ionic strength of the colloidal suspension, particle size and the type of the colloids. Solids of the size that are visible to the naked eye can be separated either by settling under the influence of gravity or by flotation, depending on the relative densities of solids and water. They may also be easily separated by filtration. However, very fine particles of a colloidal nature (size $< 1 \mu\text{m}$) which have a high stability are significant pollutants. The reason for this stability is that these particles have electrostatic surface charges of the same sign (usually negative). This means that repulsive forces are created between them, preventing their aggregation and subsequent settling. It has therefore proved impossible to separate them by settling or flotation. It is not possible to separate these solids by filtration because they pass through any filter. However, separation by physico-chemical treatments is possible. In the physico-chemical treatment of wastewater the focus is primarily on the separation of colloidal particles. This is achieved through the addition of chemicals (called coagulants and flocculants). These change the physical state of the colloids allowing them to remain in an indefinitely stable form and therefore form into particles or flocs with settling properties (Menezes *et al.*, 1996).

Conventional wastewater treatment is a highly recommendable practice for water recycling, especially to both economic and environmental perspective. There is a variety of technological approaches in wastewater treatment, some of which are costly and seasonal, whereas conventional methods which are adopted in this study, bears a historic positive track-record. Apart from being the first technique to be

employed in wastewater treatment, research still identifies it as one of reputable and best approach, mainly because of its simplicity and affordability. Since most of the countries are facing water-scarcity crisis, it is therefore economical for the industries to utilize water economically and also curtail raw water abstraction from the sources, mostly rivers and oceans. Water recycling of both process and auxiliary systems is one of the practices that are essential in water conservation. This can also eliminate contamination of the rivers by industries which discharge contaminated wastewater back into the watercourse, a phenomenon which occurs regularly around the globe. Some of the steel and mining companies paid enormous penalties in the past for environmental degradation such as underground water pollution which is caused by wastewater seepage or overflow.

Conventional wastewater treatment using inorganic coagulants is common because iron and aluminium salts are in abundance and also effective. Common inorganic coagulants include FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3 . There are various types of chemicals which are dosed during wastewater remediation using a modern technological approach Billenkamp *et al.*, 2011, Drews, 2006 and Dodd *et al.*, 2006). Some are toxic, radioactive and hazardous such as cyanide, mercury and chlorine which are used for gold purification, radioactive elements in nuclear power utilities and chlorine gas for water disinfection. All these chemicals dissolve in drain water and are discharged into the rivers which also flow into the oceans and pose a danger to the ocean ecosystem and are possible causes of material degradation on ships and boats (Clark, 1997). Apart from the type of coagulants and technique, dosages,

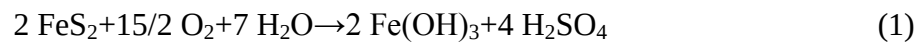
concentration of metal ions in the coagulant, the rate and duration of mixing also play a pivotal role in wastewater treatment. Electron valence, a property that determines the monoprotic, diprotic or triprotic properties of metal ions, is another factor which is an attribute to the degree of hydrolysis during wastewater treatment. Effective hydrolysis results in a high degree of turbidity removal.

1.2. Introduction

Wastewater treatment is a general term which includes the treatment all types of wastewater as classified according to their constituents, acidic, basic, toxic and radioactive. The objective of treatment can be two-folds, either to re-use or discharge back to the water-course. Acid mine drainage (AMD), which is the type of wastewater investigated in this study. It occurs when metal sulphides, e.g. ferric sulphides (FeS_x) most commonly pyrite (FeS_2) or ferrous sulphides, are oxidized in an aqueous medium or microbial activities. Microbes expedite the decomposition of these metal ions and also play a huge part in the bioremediation of AMD (Gurses *et al.*, 1997). The metal sulphides deposits which form AMD are embedded in mineral ore of coal or gold conglomerates. The former is defined by Jambor (1979) as a material that is fundamentally composed of the fossilized remains of plant debris in which progressive physical and chemical changes took place over an extended period of time. Neavel (1982) defined coal as a sedimentary rock accumulated as peat and is composed mainly out of materials and subordinately out of minerals. Water and gases

are also present within the submicroscopic pores of the coal (Neavel, 1982). Stach *et al.*, (1982) states that the general agreement in literature is that clays, sulphides, carbonates and quartz can be regarded as the most common coal minerals. The most common minerals found in this group are pyrite and marcasite and are only present in Southern African coals. Marcasite is usually limited to coals in which there is sulphur content of more than 1 wt% (Renton, 1982 and Stach *et al.*, 1982).

Another mineral ore, namely gold is extracted from one or more 1–2 m thick tabular conglomerate layers. These conglomerates consist of pebbles of quartz in a sand matrix and contain about 3% pyrite (FeS₂), as well as several other sulphide containing minerals, such as pyrrhotite (Fe_xS) and galena (PbS). Gold mining operations may continue to depths of 2.5 km or deeper after which it becomes financially unfavourable to continue. Abandoned mines are normally flooded with groundwater, which can re-enter the catchment areas by means of adits. The water is rich in sulphates and dissolved metals as it has an acidic pH due to the oxidation of the sulphide containing minerals, such as pyrite, to form sulphuric acid as shown by Equation 1.



The H₂SO₄ which has been formed (Equation 1) is detrimental to the ecosystem, biota and fauna whereas the Fe²⁺ (FeS₂) can either form unstable ferrous hydroxide (Fe(OH)₂) or it is oxidized to form stable ferric hydroxide (Fe(OH)₃) species (Feng *et*

al., 2000, Geldenhuys *et al.*, 2001, Maree, 2004a, Semerjian *et al.*, 2003, Watten *et al.*, 2005, Akcil *et al.*, 2006, Kurniawan *et al.*, 2006, Herrera *et al.*, 2007, and Sibrell *et al.*, 2009, Kempkes *et al.*, 2007, Pinto *et al.*, 2008, Navratil *et al.*, 2008, Moussas *et al.*, 2009, Suarez *et al.*, 2009, van der Graaf *et al.*, 2010 and Jiang *et al.*, 2012). Other sources of AMD include the gold mining industry arising from the sand and slime dumps which emanate from tailings (Naicker *et al.*, 2003). These dumps are subjected to oxygenated rainwater resulting in the oxidation of the residual sulphide containing minerals. The oxidation acidifies the percolating water, which is also believed to enter streams along the gold-fields (Naicker *et al.*, 2003) and it was discovered that the ground water in the mining district of the gold-fields is heavily contaminated with heavy metals and acidified due to the oxidation of pyrite containing tailings. The investigations in this study have also found that the deleterious effect of the addition of contaminated water persists for more than 10 km beyond the source.

The AMD from the coal mining industry is also periodically discharged directly into local streams (Geldenhuys *et al.*, 2001). The acidic character of a pH value as low as 2, high sulphate content and a dissolved heavy metal content in the AMD is of such detriment to the ecosystem such that it is prohibited to be discharged in public streams (Feng *et al.*, 2004). Apart from natural formation of AMD, biological formation by bacteria such as namely *Acidithiobacillus ferrooxidans* is also inevitable. These bacteria oxidize the pyrite to form sulphuric acid as shown by Equation 1. The dumping sites also act as the source of AMD which occurs when the

dumps with a high permeability are associated with a high oxygen ingress, which then contributes to higher chemical reaction rates. Higher temperatures cause increased oxygen ingress through convection. These bacteria may also accelerate oxidation of sulphides of antimony, gallium, molybdenum, arsenic, copper, cadmium, cobalt, nickel, lead and zinc; and are most active in water with a pH of less than 3.2. If conditions are not favourable, the bacterial influence on acid generation will be minimal (Diz, 1997).

AMD is distinguished by its bright orange, yellow, or brownish-red colour due to the presence of iron in the water. The pH of the mine drainage is very low (acidic) and causes it to be corrosive and toxic due to the presence of various heavy metals. The generation of AMD is unavoidable because it emerges from both abandoned and currently operating mining activities. The other sources of AMD include construction sites and other places that have been highly disturbed by geophysical and meteorological catastrophes, such as natural rock weathering processes. The greatest consequence of AMD is water pollution, which in turn results in contaminated drinking water, damage to aquatic flora and fauna, and corrosion of man-made infrastructures. AMD is affected by characteristics such as pore size, particle size, permeability, and mineral composition of the materials being oxidized. The size of particles directly influences the surface area of rock exposed to weathering and oxidation. Surface area and particle size are inversely related. Therefore very coarse grain substances expose less surface area; however, they have deeper crevices between particles. This characteristic allows ingress of air and water, thereby

exposing more substance to oxidation and ultimately generating more acid (Doymus, 2007). Conversely, fine grain substances may prohibit the flow of air and water, but also have more surface area exposed to oxidation. Another important factor is that air circulation is impacted by wind, barometric pressure changes, and perhaps convective gas flow due to the heat created in the oxidation reaction. These variables are part of a positive feedback cycle. As the substances weather over time, particle size is decreased, exposing more surface area and affecting the physical characteristics of the unit (Crawford *et al.*, 2001).

Water and oxygen availability are the most important factors though as they are essential to create acid mine drainage. Atmospheric oxygen is needed to drive the oxidation reaction, particularly to maintain the quick bacterially catalyzed oxidation at pH values less 3.5. When the concentration of oxygen in pore spaces of mining materials is less than one or two percent, the rate of oxidation is notably reduced. Water has several functions in the generation of AMD. It not only serves to transport the oxidation products, but also works as a reactant and medium for bacteria in the oxidation reaction (Gurses *et al.*, 1997)

Although AMD is not an anthropogenic phenomenon, it is compulsory for every coal and gold mine to ensure that it is contained not to flow over and pollute other areas, namely ground water, rivers or wet-lands. The treatment involves a number of factors such as the physical and chemical properties of the wastewater and coagulants, the amount and composition of natural organic matter (NOM), and chemical and physical properties of the water. The common parameters are pH, coagulant type, dose (Yan *et*

al., 2008 and Uyak., *et al.*, 2008). The physico-chemical properties of the wastewater play a pivotal role during treatment, as they interact amongst themselves to transform the compound/atoms to another phase or compounds. The modification of the surface properties of solid particles by adsorption of surface-active agents is widely used in industrial procedures. Various mineral separation processes which occur during selective coagulation and fluxing, wastewater treatment and the stabilization of colloidal dispersions in liquids involve the adsorption or deposition of suitable small molecules or polymers which are capable of forming monomolecular surface films on solid surfaces.

As the impact of AMD to the environment varies from site to site, it has to be taken into consideration that there are AMD hazards at individual sites, and that they give rise to specific risks. Where AMD is inevitable or likely, it makes sense to gear the response to the probability of serious consequences, which requires site-specific research to be undertaken. In mining regions where AMD has not yet formed, research should be carried out to identify ways in which it can be prevented. Mine technical personnel must therefore be equipped with the knowledge and tools to control AMD – specifically, to identify techniques that will minimize AMD impacts on life forms and their support systems (Morrissey, 2003).

Most of the approaches which have been exploited focus more on chemical properties whereas the effectiveness of the treatment mainly relies upon the reaction dynamics between the colloidal suspension and coagulants. There are four main processes which occur during wastewater treatment, namely destabilization, hydrolysis,

coagulation, flocculation and sedimentation. Coagulation-flocculation is a process which leads to nucleation, crystal growth and aggregation of the destabilised suspended particles in the solution (Kemmer, 1988). Nucleation is the formation of the first particles of precipitate capable of spontaneous growth into large crystals of a more stable solid phase in an unstable, supersaturated solution. Nucleation can be homogeneous or heterogeneous where the former is formed in a bulk solution in the absence of any other solid surface. Heterogeneous nucleation occurs at moderate supersaturation where particles of a material provide the nucleation sites for another material. Subsequent to nucleation is crystal growth that is (1) the diffusion of atoms or molecules of the crystallising substance through the solution or surrounding environment, (2) the diffusion of atoms over the surface of crystals to special sites on the surface, (3) the incorporation of atoms into a crystal within special sites on the surface and (4) the diffusion of heat of crystallization away from the crystal surface counter-ions. Adsorption of the coagulant is the mechanism which takes place during coagulation in wastewater to effect charge neutralization, enmeshment of interparticle bridges and agglomeration which are formed in a precipitate. The amount or concentration of coagulants added into wastewater during treatment must be sufficient to exceed the solubility of their metal hydroxides so that precipitates can be formed. There are series of hydrolytic reactions that occur after the addition of coagulants, namely simple hydroxo complexes (MOH^{2+}), colloidal hydroxometal polymers and the metal hydroxide precipitates. Coagulants can be added with a concentration that is high enough to rapidly precipitate the metal hydroxide $[\text{Al}(\text{OH})_3]$, $[\text{Fe}(\text{OH})_3]$, $[\text{Mg}(\text{OH})_2]$ or metal carbonate $[\text{CaCO}_3]$, where colloidal

particles are enmeshed in these precipitates (Moore *et al.*, 1976). Adsorption dynamics are defined in various ways by different authors. Some authors such as Kemmer (1988) and Coulson *et al.* (1999) state that the metal hydroxides (flocs) are adsorbed by colloidal particles whereas others state that colloidal particles are enmeshed in these precipitates (Moore *et al.*, 1976, Ives, 1978 and Duan *et al.*, 2002). The colloidal charge in most wastewater coagulation requires positively charged inorganic polymers. Table 1.1 shows the pH values at which common metals precipitate (Moore *et al.*, 1976).

Table 1.1: Precipitation of metal hydroxides from dilute solutions vs. pH (Moore *et al.*, 1976)

Metal	pH	Metal	pH
Fe ³⁺	2.0	Ni ²⁺	6.7
Al ³⁺	4.1	Cd ²⁺	6.7
Cr ³⁺	5.3	Zn ²⁺	6.7
Cu ²⁺	5.3	Co ²⁺	6.9
Fe ²⁺	5.5	Hg ²⁺	7.3
Pb ²⁺	6.0	Mn ²⁺	8.5

Table 1.1 shows that the Hg²⁺ and Mn²⁺ ions precipitate in an alkaline medium whereas the rest in an acidic medium. The information can be used during wastewater treatment for pH control. The effectiveness of destabilization depends primarily on the type of colloids, hydrophilic (water-loving) or hydrophobic (water-hating), physico-chemical properties of the coagulant(s) and the intensity of the mechanical agitation for the dispersion of the coagulant(s) throughout the colloidal suspension (O'Melia *et al.*, 2001, Menezes *et al.*, 1996 and Adams *et al.*, 2002). Inclusively, the type and size of the turbid materials and the electronegativity of the metal ions of a

coagulant also play a main role (Hubell *et al.*, 2003, Meghzili, 2008, Water Specialist Technology, 2003, Aboulhassan *et al.*, 2006 and Scholtz, 2010). Contaminated water contains particles of different sizes which are classified as dissolved ($<0.08 \mu\text{m}$), colloidal ($0.08 - 1 \mu\text{m}$), supracolloidal ($> 1 - 100 \mu\text{m}$) and settleable ($> 100 \mu\text{m}$) (van Nieuwenhuijzen *et al.*, 2002). The type of treatment selected depends on the size of the particles present in the wastewater; where very fine particles of a colloidal nature (colloids of size $< 1 \mu\text{m}$) with a high stability are significant pollutants. The stability is caused by the electrostatic surface charges of the same sign, possessed by these particles (usually negative). This means that repulsive forces created between them, prevent their aggregation and subsequent settling. It has therefore proved to be impossible to separate them by settling or flotation, and physico-chemical treatment has shown to be the only option. This is because it changes the physical state of the colloids allowing them to remain in an indefinitely stable form resulting in flocs with settling properties (Dobias, 1993). The treatment occurs in two stages such as coagulation and flocculation. The aggregation of submicron particles during rapid mixing is relatively fast if their surface chemistry is ideally suited and their concentration is high enough ($>108/\text{ml}$). Their transport is brought about by Brownian motion, also known as perikinetic flocculation which is influenced by the thermal condition of the colloidal system and induced by the coagulants (Dobias, 1993). The agglomerates still stay small and cannot be removed by sedimentation or filtration until further agglomeration during flocculation termed orthokinetic flocculation occurs (Dobias, 1993). Flocculation is classified either as micro-flocculation or macro-flocculation. The former is significant for particles in the size

range 0,001-1 μm and the latter for particles of size greater than 1 or 2 μm (Metcalf *et al.*, 2003).

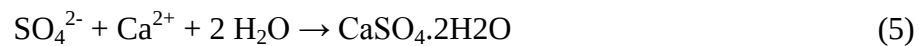
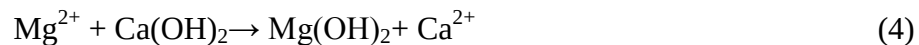
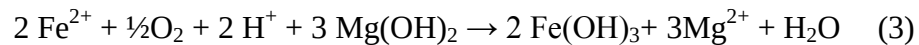
Other solute properties include the solute partition coefficient, polarizability and molecular structure influence pollutants adsorption (de Ridder *et al.*, 2010). Those which are associated with the coagulants include the electronegativity, charge per surface area, valence electron, particle size, porosity, density (Wulfsberg, 1987).

These are the main attributes to effective wastewater treatment, a process which is measured by the removal of the turbidity from AMD. Destabilization and hydrolysis are the key processes which determine the effectiveness of the treatment process. They are reactions which actually co-exist because the former occurs on the aqua-colloids whereas the latter on the metal ions of the salt as revealed in the study by Ntwampe *et al.* (2013) where it was shown that destabilization-hydrolysis occurs within 30 seconds of rapid mixing. The former includes the disturbance of the equilibrium between the van der Waals forces of attraction and electrostatic repulsive forces in the colloidal suspension whereas hydrolysis is the formation of the metal hydroxide species (Flynn, 1984), as shown by Equation 2.



AMD is the type of wastewater which is studied in this dissertation using Fe^{3+} and Al^{3+} salts, synthetic acid-free polyferricchloride (acid-free PFCl) polymers of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ dosages. The AMD is a common by-product of

the mining and mineral industries and one of the significant contributors to water pollution. Various studies conducted on AMD involve neutralization, oxidation of pyrite and gypsum crystallization. The common reagents which are used in AMD treatment include Ca(OH)_2 , Mg(OH)_2 , $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CaMg(CO}_3)_2$. The Ca(OH)_2 has shown to be popular in AMD treatment because of its gypsum crystallization ability. Wastewater treatment with Ca(OH)_2 yields improved sludge settling, dewatering characteristics, bacterial inactivation capability and sludge stability. It is also commonly used internationally in inorganic effluent treatment with a metal content higher than 1000 mg/L and the pH of 11 (Kurniawan *et al.*, 2006). Advantages of Ca(OH)_2 include the simplicity of the process, inexpensive equipment requirement, convenient and safe operation. Disadvantages with lime include the clogging of pipelines, excessive sludge production that requires further treatment, high cost of sludge disposal, slow metal precipitation, tendency to increase turbidity, poor settling, aggregation of metal precipitates and the long-term environmental impact of the sludge (Kurniawan *et al.*, 2006). The disadvantage with Mg(OH)_2 is that an over-dosage can raise the pH to 10.0 as stated by Kuyucak *et al.* (2005), a condition which deters the formation of effective hydrolysis species (Fe/Al(OH)_3) (Flynn, 1984). Both reagents react with pyrite in AMD as shown in Equations 3-5



The rate of sulphate removal by gypsum crystallization may be predicted from Equation 6 (Maree et al., 2004b).

$$d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt = k[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)[C - C_0]^2 \quad (6)$$

where $d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt$ = the rate of crystallisation, k = reaction rate constant, $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)$ = surface area of the seed crystals, C = initial concentration of CaSO_4 in solution and C_0 = saturated concentration of CaSO_4 sulphate in solution.

1.3 Types of wastewater treatment

Conventional wastewater treatment with inorganic coagulants has been the common process due to its easy operation and affordable operating costs. The other factor is its removal efficiency of organic and inorganic matter, colour, heavy metals and pathogens from the AMD. The selection of the water treatment process for a specific application depends on the physical form, chemical and biological nature of the impurities. There are various treatment processes that are considerable and coagulation-flocculation is common due to its historical background, low costs and easy maintenance. The AMD is a complex, multicomponent system which makes the treatment complex which leads to complex interactions between the ingredients of the AMD and reagents and the low pH contributes to complexity of treatment dynamics.

Waste rocks containing sulphides are a significant source of AMD; which makes the management of waste dumps of utmost importance. Within the broader definition of waste dumps lie spoil piles, tailings dams and spent heap-leach piles. Spoil piles have

the potential to be extremely acidic wastewater. Figures 1.1, 1.2, 1.3 and 1.4 show the AMD around the Krugersdorp mining areas, and there is even more AMD within the Mogale City area. Figure 1.1 shows an uncontrolled decant of acid mine drainage from the 18 Winze shaft as seen on 27 March 2014, on Mintails Mogale Gold property, near Krugersdorp. The decant is a result of heavy rains during the preceding time period, which elevated the water table and effected the decant, where thirty-million-litres of AMD has decanted from two points in March alone.

Figure 1.2 shows the discharge point for treated acid mine drainage, flowing into a retaining dam on 27 March 2014, which feeds to a depository dam at the Mintails Mogale Gold treatment plant near Krugersdorp.



Figure 1.1: The 18 Winze shaft as seen on 27 March 2014, on the Mintails Mogale Gold property. Photograph credit: Michel Bega, the Citizen newspaper.



Figure 1.2: AMD flowing into a retaining dam, 27 March 2014, Picture credit: Michel Bega, the Citizen newspaper.

Decant AMD and sinkholes are some of the main environmentally hazardous sources; and inevitably uncontrollable due to their geochemical origin. Whenever there is a geological void around a pyrite-rich ground and copious rainfall, decanting and sinkhole formation are inevitable. Excessive rainfall may result in the flooding of the area and subsequent decanting and sinkhole formation where the AMD contaminates the landscape and wetland, causing an environmental catastrophe. The worst part around this phenomenon is that there is a limited number of the AMD treatment plants in the neighbourhood for the treatment of a highly contaminated wastewater (containing toxic and heavy metals) before it is discharged to the water-course or underground seepage. Sinkholes are rated as the most catastrophic geological

phenomenon, i.e. has a potential of complete building collapse such as an incident which took place in Centurion (SA) on the 20 January 2005 (Figure 1.3).



Misfortune: This is all that remains of one Centurion townhouse's foundation after a sinkhole damaged most of the property. *Photo: Herbert Matimba, Pretoria News*

Figure 1.3: Photograph of a sinkhole which damaged buildings in Centurion
Photo credit: Herbert Matimba, Pretoria News)

Figure 1.4 shows one of 36 radiation hotspots in the Krugersdorp area which resulted in the destruction of the landscape by the AMD.



Figure 1.4: The Lancaster Dam as seen on 27 March 2014, in the Krugersdorp area. Picture credit: Michel Bega, the Citizen newspaper.



Figure 1.5: Limestone neutralization at BCL, Botswana showing a Red water lake (Commissioned: June 2002).

Scientific research claims that climate change is in the process of endangering the environment even further to an extent that water scarcity is inevitable. That will be the time wastewater treatment will no more be a statutory requirement but a

necessity. To solve the problems the wastewater minimization decision-tree adopted by Perry *et al.* (1997) and Cheremisinoff *et al.* (1989), is shown in Figure 1.6.

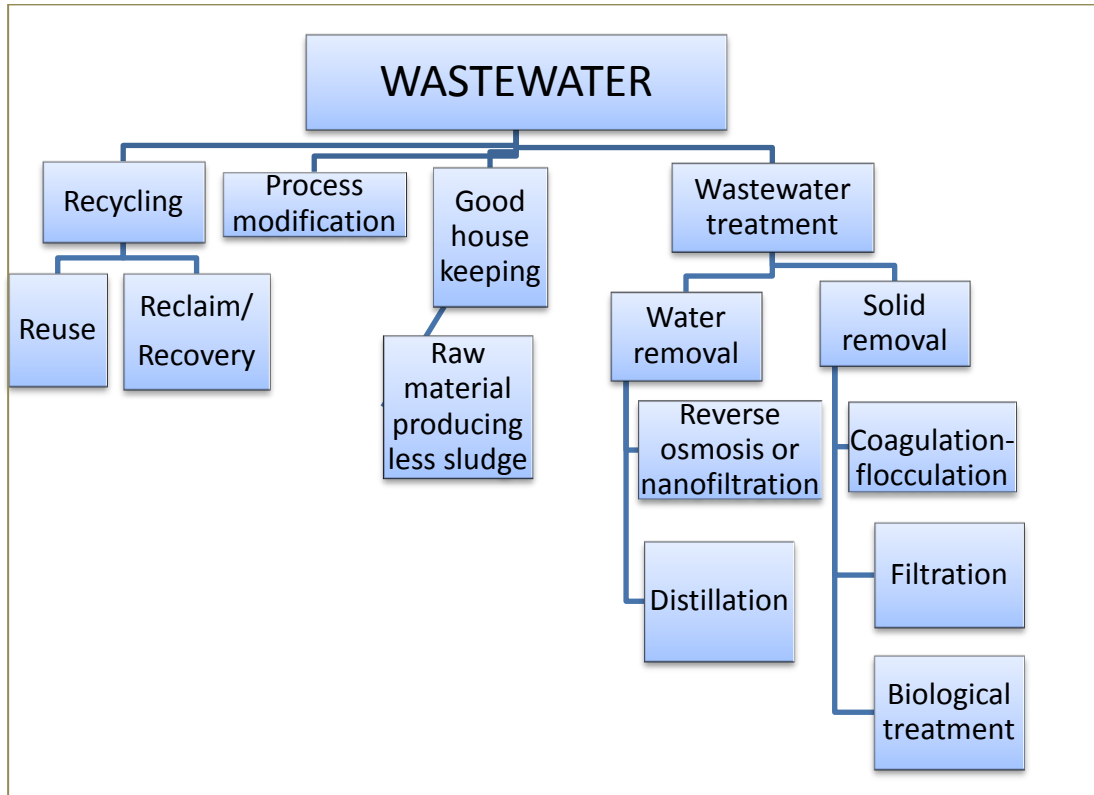


Figure 1.6: Wastewater minimization decision-tree adopted from Perry *et al.* (1997) and Cheremisinoff *et al.* (1989).

Figure 1.6 shows wastewater related processes which are divided in four main processes namely, recycling, process modification, good house-keeping and waste treatment. Conventional treatment is still regarded as the most recommendable option due to its simplicity to operate and relatively cheap chemicals utilized. Power utilities and other industries utilize wastewater of poor quality for dust suppression and further cooling of the hot coal ash so as not to damage the conveyor belts. It is also

necessary to control the pH of alkaline or acidic wastewater before it can be used in order to reduce scaling and corrosion of the pipe-work respectively (Coulson *et al.*, 1999). Another option is that the effluent can be used as neutralizing solution to other alkaline solutions or processes. This is a primary solution and entails the removal of sulphuric acid and heavy metals from the AMD and the secondary solution is to identify how the acidic effluent can be utilized.

The treatment of wastewater can be by physical, chemical or biological means. Chemical treatment is the most appropriate method in AMD treatment because it does not contain biological nutrients. The treatment includes the addition of a reagents/coagulant to destabilize the colloidal suspension (AMD). This occurs when the surface charge of the particles is decreased or neutralized by adsorbing counter-ionic property of inorganic coagulants, where repulsive forces are reduced or eliminated (Gregory *et al.*, 2001). The type of coagulant which are dosed and the time taken during mixing determine optimum velocity gradient (du/dy), change of velocity per change of distance, to disperse the reagents throughout the solution. The velocity gradient depends on the speed of the impellers during stirring and influences the type of destabilization. An excellent design of mixing devices requires a high velocity gradient, which can be as high as 1000 s^{-1} with minimum chemical dosage. The polyelectrolytes function effectively when the velocity gradient is in a range of $400\text{--}1000\text{ s}^{-1}$ (Binnie *et al.*, 2003). Fe^{3+} and Al^{3+} salts produce the best results at a velocity gradient between 20 and 70 s^{-1} (Swartz *et al.*, 2004).

In the present study the investigation of the factors which effect optimum removal of colloidal particles in the AMD using “environmentally friendly” metal hydroxide or synthetic af-PFCl polymer of $\text{Mg}(\text{OH})_2$, CaCO_3 and $\text{CaMg}_2(\text{OH})_2$ is investigated. The uniqueness in this study is that the treatment is carried out without pH adjustment, which will also proof that the morphological structure (compactness/rigidity) of the flocs plays a pivotal in the adsorption efficiency of the coagulant/flocculent. It also indicates that the non-porous structural configuration of the flocs prohibits the passage of the particles which are attributes to the turbidity in the AMD sample. Results obtained by Flynn (1984) and Kemmer (1988) explain the reactions of Ca^{2+} and Mg^{2+} hydroxide in wastewater as reagents when reacting with $\text{Ca}(\text{HCO}_3)_2$ or $\text{Mg}(\text{HCO}_3)_2$ to form a $\text{CaCO}_{3(s)}$ precipitate which is removed as sludge. In this study the effect of these metal hydroxides in hydrolysis, which is not clearly defined in the existing literature is investigated. Research has been carried out on AMD/wastewater treatment using $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ but comparison on their destabilizing-hydrolysing potential was never investigated, an investigation which is adopted in this study. They are normally dosed in wastewater treatment for pH adjustment whereas their ability to form polymers when reacting with metal salts to form $\text{FeCl}_3\text{-Ca}(\text{OH})_2$ or $\text{FeCl}_3\text{-Mg}(\text{OH})_2$ has not been determined and furthermore the turbidity removal efficiency, using Fe^{3+} and Al^{3+} salts only, Fe^{3+} and Al^{3+} salts with Ca^{2+} or Mg^{2+} hydroxide as both softeners and synthetic polymers is also investigated.

1.4 Physical and chemical factors in colloidal suspensions

1.4.1 Colloids and colloidal suspension

A colloidal system is divided into colloidal suspensions and emulsions. Colloidal suspension is when the solids are suspended in water emulsions and are insoluble liquids (oils) suspended in water. The suspended materials are divided in two categories, stable materials, which are caused by the forces of attraction between particle and water (hydrophilic) and mutually repulsive materials (hydrophobic) caused by the repulsive forces between neighbouring particles. Hydrated coagulants form hydrophobic colloids in water and the stability which occurs is as a result of electrostatic repulsion whereas stability in hydrophilic colloids (proteins, starches and fats) is caused by forces of attraction between water and particles. It is more difficult to coagulate the stable suspension formed by hydrophilic colloids than hydrophobic colloids (Suzuki, 1990). The large surface area in a given volume in a colloid allows substances to concentrate and subsequently adsorbed onto this surface or surface of a substance and come in contact with water and acquires an electrical charge to give electro-kinetic properties (Jiang *et al.*, 2003, Binnie *et al.*, 2003 and Dey *et al.*, 2004). The surface electrical charges in the colloidal system are caused by the affinity between the colloidal materials in water, ionized atoms or groups of atoms that leave the colloids. The surface charge then attracts the ions carrying opposite charges, creating a cloud of “counter-ions”. During this reaction, the adsorption decreases due to increasing repulsive forces between the particles where the colloids that carry similar charges in the medium repel one another. The presence of counter-ions in the medium complicates the repulsion between the colloidal particles and causes fall-off

in repulsive forces as distance increases. When the colloidal particles come closer, they are then subjected to van der Waals forces of attraction (Swartz *et al.*, 2004).

The hydrophilic or hydrophobic properties of the colloids play a pivotal role during the destabilization-hydrolysis (coagulation) process. Coagulation in a hydrophilic colloid occurs when the colloidal suspension is destabilised due to the reduction of the chemical energy in the system and electrical forces are weakened (Wulfsberg, 1987). Two approaches are used to explain the basic mechanisms of destabilization of colloidal particles. The first approach is based upon the coagulant which determines the solubility constants, stability constants, equilibrium constants, heat of reaction, chemical composition and the effective charge and valence type (Ives, 1978). The second approach involves the actual determination of the electrophoretic mobility of individual particles (Faust *et al.* 1967). Electrophoretic mobility is elucidated as the migration of charged colloidal particles or molecules through a solution under the influence of an applied electric field usually provided by immersed electrodes. The Schultze-Hardy rule emphasizes that the products of hydrolysis from Al^{3+} and Fe^{3+} salts are more effective in reducing or neutralizing the zeta potential of colloidal particles than the divalent cations (Lyklema, 2013). The solution can also be at a neutral point (isoelectric point), which is when the charges of the materials present in the wastewater is neutral, depending on the nature of the colloids and the concentration of other materials. At this point, there is no charge mobility and destabilization through neutralization cannot continue (Ali *et al.*, 2002).

1.4.2 Dispersion of colloidal particles

Dispersion is classified as either lyophilic or lyophobic, the former is characterized by a solid that shows affinity for water or other dispersion medium that forms sols during mixing. Lyophobic sols are formed by the addition of coagulants to a colloidal suspension or as a result of mechanical mixing. Lyophilic sols are sensitive to the addition of electrolytes into a bulk phase (Ives, 1978). Certain lyophobic colloids become unstable and flocculate when coagulants are added. Multivalent ions, such as Fe^{3+} and Al^{3+} react effectively in a medium concentrated with net negative charged particles. The Schulze-Hardy rule states that the valence ions with opposite charge to that of the sol determines the effectiveness of coagulation (Ives, 1978). Aluminium salt shows more effectiveness in floc formation at a concentration around 60 mg/L (Ives, 1978 and Meghzili, 2008). Treatment of the solid-liquid interface by chemical addition in the form of surface-active agents or electrolytes can alter colloidal dispersion, causing a change in particle size and interfacial area.

1.4.3 Intermolecular forces in a colloid

The zeta and electrical potential are the forces which are involved in the colloidal stability and exist at the edge of the agglomerate and play a major role in stabilization. Colloidal particles are always charged and the repulsive and attractive forces of particle-particle or particle-fluid influence stability of colloids. The zeta potential has a lower value in heterogeneous suspensions because of complicating

factors involved (Tebbutt, 1983). The zeta potential is based upon the diffuse-layer thickness (δ) and is a qualitative useful expression because of its measurability. The stability of a colloidal suspension decreases when the zeta potential (Z) decreases and it is expressed as:

$$Z = 4 \pi \delta q / D^* \quad (8)$$

where δ = diffuse layer thickness, q = net (apparent) particle charge, D^* = dielectric constant of water

The addition of metal salts disturbs the stability of the colloid in two ways such as their effect in the extent of the diffuse layer around the particles and by specific effect on the electric potential controlling colloid stability (Ives, 1978). The depth of the diffuse layer determines the predominance of attractive forces irrespective of whether particles of like charges are brought close to one another or not. When the ionic strength of the solution increases, the distance of effective repulsive forces decreases toward the particle surface and causes the net-charge curve between attractive and repulsive forces to drop entirely towards attraction force region as shown in Figure 1.7.

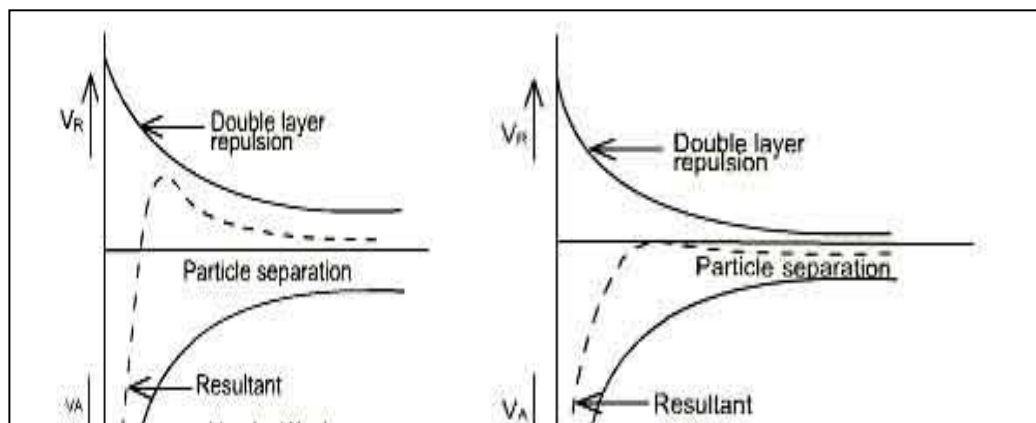


Figure 1.7: Forces exerted between the colloidal particles (Lee, 2001)

The particles are attracted to one another by van der Waals forces and the addition of electrolytes increases ionic strength of the solution which results in double-layer compression (Lee, 2001).

1.5 Destabilization process

Destabilization is a reaction which occurs after the addition of a reagent/coagulant to the solution. It is classified into four categories such as double layer compression, neutralization, particle bridging and entrapment in a precipitate (Sincero *et al.*, 2003). Although literature describes destabilization as a process which is induced by shear forces during rapid mixing, it is suggested that the strength of ionic charges between the metal ions of a salt and the diffuse layer determine its effectiveness. Destabilization of the repulsive environment requires the addition of salts which contain multi-charged ions that will change the ionic property of the colloidal particles and form aggregates (Kemmer, 1988). Destabilization by particle bridging does not require rapid mixing as that can break the chain of particles bonded by polymers whereas charge neutralization is affected at lower pH. Binnie *et al.* (2003)

stated that the type of destabilization common in a colloid with high velocity gradient around 1000 s^{-1} is double layer compression and charge neutralization, which is predominant above 5000 s^{-1} . In wastewater treatment where polymers are used as coagulants, the velocity gradient must be in the range $400\text{--}1000 \text{ s}^{-1}$ (Binnie *et al.*, 2003). The results obtained by many researchers confirm that the best treatment results are obtained when the velocity gradient in the mixer is high (Binnie *et al.*, 2003). Another advantage of the higher velocity gradient is that a lower dosage is required during the treatment process. Equation 9 shows the first hydrolysis reaction on a hydrated metal ion.

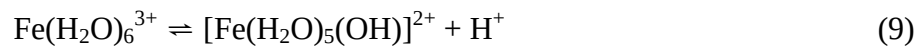


Figure 1.8 shows water molecules surrounding an Al^{3+} ion, an inner metal ion.

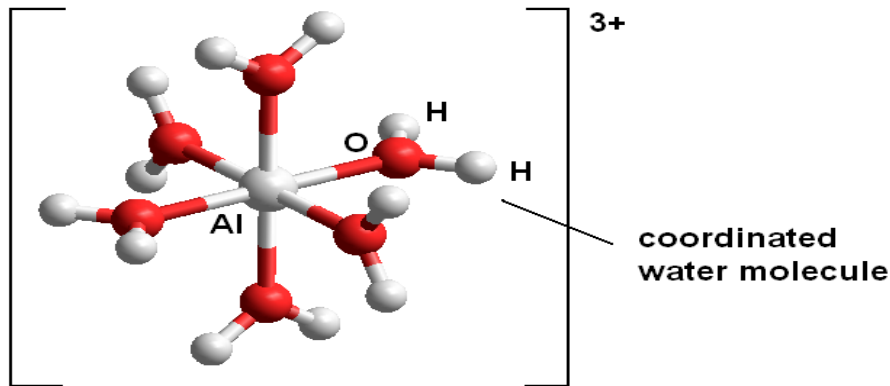


Figure 1.8: A solvated Al^{3+} ions with six water molecules (Moore *et al.*, 1978).

The speciation which results in various hydrolysis species determines the rate of adsorption, a process determined by deprotonation. The speciation occurs when the hydroxyl ions from the colloidal suspension replace the water molecules (Figure 1.8)

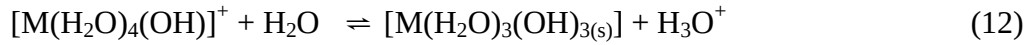
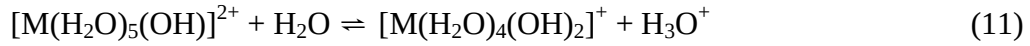
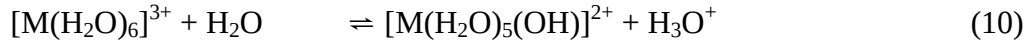
surrounding the metal ion (hydration sphere) and hydrogen ions are released into the solution. The speciation of the metal ions results in the formation of hydrolysis species, Equation 9. The hydrolysis chain for a metal ion continues until the formation of an uncharged metal hydroxide with very low solubility, $M(OH)_{3(s)}$. Other species termed dimers, trimers and polymers are also formed (Flynn, 1984 and Cheng, 2002). The type of destabilization actually plays an important role in the pH of the solution, e.g. for charge neutralization the pH must be 5 (acidic) so that the excess positive charges may neutralize negative charges in colloidal particles. The $Fe(OH)_3$ has a minimum solubility in a wide pH range of 7–10 whereas $Al(OH)_3$ is around neutral pH, giving them more flexibility during hydrolysis. Any pH outside this range increases the solubility of iron than aluminium hydroxide (Binnie *et al.*, 2003).

1.6 Hydrolysis process

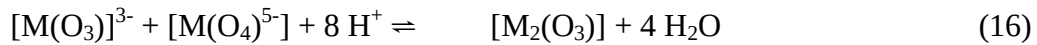
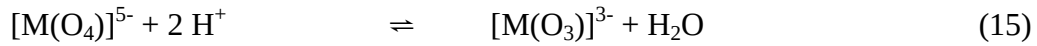
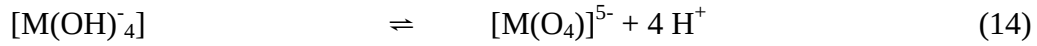
1.6.1 Factors which influence hydrolysis

Hydrolysis is a process which occurs on the metal ions of a salt (coagulant) after the addition of a reagent/coagulant. There are two coordination complexes formed during hydrolysis of a metal ion, namely octahedral and tetrahedral coordination (acidic or basic). These coordination complexes determine the adsorption potential of the reagent/coagulant added to the solution. The octahedral coordination complex is

acidic and the tetrahedral one is basic. These reactions are given by Moore *et al.*, (1978) as follows:



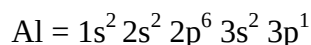
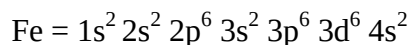
The $[M(H_2O)_3(OH)_{3(s)}]$ species starts to behave like a weak oxo acid which ionises to give oxo anions where water molecules (Figure 1.8) are separated from the hydrated metal to form:



In Equation 12 a stable metal hydroxide with maximum flocs formation is formed, which is followed by adsorption of the colloidal particles which are suspended in the solution. Equations 13-16 show the series of anionic hydrolysis reactions which result in a final metal oxide formation.

The adsorption process often dominates flocculation and aggregation in the solution. Factors that play an important role in the process are the translational and rotational motion of dispersed particles in the liquid, surface charge of particles and the interaction forces between the particles. The sign and the magnitude of the surface charge are directly related to colloidal stability and influence the adsorption characteristic of the particles. Molecules which are adsorbed on the surface change the surface charge and particle interaction through structural effects. Adsorbed layers of polyelectrolyte are affected by the long-range electrostatic repulsive forces between the surfaces of the particles and can adjust since they depend on the pH, salt concentration and surface charge (Sulkowski *et al.*, 2005). Ferric ions readily undergo hydrolysis, complexation, polymerization and precipitation in an aqueous solution. In general, the ferric ion monomers and polymers produced during hydrolysis have a stronger tendency to precipitate than aluminium. Stabilization of the iron polymers to optimal state of coagulation is always a problem when coagulant and commercial products of high quality have to be prepared. The study of Fe^{3+} hydrolysis is carried out on partially neutralized solution prepared by slow addition of a base. Despite numerous investigations, the mechanism of hydrolysis-polymerization-precipitation of Fe^{3+} and the quantitative principles have not been clearly defined (van De Woude *et al.*, 1983). The nature and behaviour of the hydrolysis products are profoundly controlled by the components and the concentration of the primary Fe^{3+} solution, pH, components of co-existing anions, temperature, time of ageing, traces of contaminants including dust particles which can seed the precipitation of the solid, preparation methods and other chemical transformation (van De Woude *et al.*, 1983).

Hydrolysis of the metal ions can also be related to the electron configuration of the metal element, which occurs during hybridization of the metals when they start reacting during chemical reactions (Wulfsberg, 1987). The structural formulae of the Fe^{3+} and Al^{3+} metal salts which are used as coagulants in the experiments are:



The electron configuration of Fe shows that it has a bigger radius than Al with two electrons in the outer 4s-orbitals. These electrons have opposite spins to reduce the forces of repulsion. On the contrary, Al shows a smaller radius and only one electron in its 3p-outer orbital. It is suggested that the six water molecules (Figure 1.8) around the former ($\text{M}(\text{H}_2\text{O})_6^{3+}$) are less attracted to a central Fe ion than in Al with a smaller radius. The hydration energy and the radii of Fe^{3+} and Al^{3+} are 4376 and 4660 kJ/mol, 78 and 67 μm respectively. Three stages of hydration occur; the first endothermic process includes a change in enthalpy (ΔH) when the water molecules overcome attractive forces in the solute particles to break chemical bonds. The second endothermic process includes the separation of the solvent molecules to accommodate the solute and the third is exothermic process which includes the formation of new attractive interactions between solute and solvent particles. Energies 1 and 2 are added and if they are greater than 3 (negative number), the process is endothermic (Wulfsberg, 1987). The precipitation rate of metal ions is determined by Equation 17:

$$\text{pH} = \text{pK}_a - (1/z) \log [\text{M}^{z+}] - 5.6/Z \quad (17)$$

$$\text{pK}_a = 15.14 - 88.16 (Z^2/r) \quad (18)$$

The pK_a values for Fe^{3+} and Al^{3+} 2.2 and 5.0 respectively. The processes that are involved in the hydration energy give a number of species which are formed from $\text{M}(\text{H}_2\text{O})_6^{3+}$, $[\text{M}(\text{H}_2\text{O})_5\text{OH}]^{2+}$, $[\text{M}(\text{H}_2\text{O})_4(\text{OH})^+]_2$, $[\text{M}(\text{H}_2\text{O})_3(\text{OH})_3]$, $\text{M}(\text{OH})_4^-$, MO_4^{5-} , M_2O_3 as shown by Equations 10-16. Such a chain of hydrolysis species reactions start from iron cations, hydroxo cations, precipitates, hydroxo anions, oxo anions. Table 1.2 shows a comparison of some of the properties for Fe and Al:

Table 1.2: Comparison between the properties of Fe^{3+} and Al^{3+} .

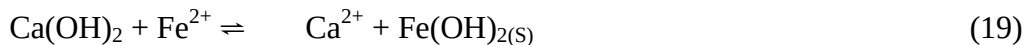
Metal	Radius (Å)	χ_p	Z^2/r	Max oxid No.	pK_a
Fe	1.25	>1.8	0.04 - 0.1	6	1 - 6
Al	1.18	1.5	0.1–0.16	3	1 - 6

The properties of Fe and Al can be used to determine their reactivity. χ_p =Pauling electronegativity and Z^2/r = charge per surface area. Wulfsberg (1987) discovered that the metal ions with electronegativity above 1.5 such as Fe are more acidic and have a higher hydrolysing potential than those less than 1.5. The ratio Z^2/r also determines the hydrolysis reactivity of a metal ion, both Fe^{3+} and Al^{3+} have ionic charge of 3 and radii 1.25 and 1.18 (ionic radii 0.64 and 0.52) respectively. Both metal ions show a high hydrolysing potential because their charge density is equal and greater than 0.1. The lower the negative logarithm of the equilibrium constant

(pK_a), the more acidic and higher hydrolysing potential the metal ion becomes (Wulfsberg, 1987).

1.6.2 Hydrolysis and formation of precipitate species

Studies have shown that hydrolysis of Fe and Al salts are more sophisticated than the expression of the formulae as they can only be useful as approximations of reaction products and quantitative relationships. This is caused by some hydrolysis species which are formed at very low pH values. Hydrolysis of Al^{3+} ions in solution is complicated and undefined. It forms various complex species in solution with varying pH values. It appears as Al^{3+} in pure water with low pH and forms $Al(OH)_4^-$ or $Al(OH)_5^{2-}$ in alkaline solution. It forms $Al(OH)_3$ precipitates in a dilute solution near neutral pH only when there are not any anions other than hydroxide (Lottermoser, 2010). The treatment is less successful in the presence of some coordinating ligands since they form soluble metal complexes such as hydrous metal oxide which are largely adsorbed by the floc at lower pH values below that customarily is used in water treatment (Freeze *et al.*, 2001). These metal salts are also used in coagulation-flocculation processes together with $Ca(OH)_2$ to precipitate iron as shown by Equation 19.



Some of the heavy metals which are precipitated by Ca(OH)_2 include Zn^{2+} , Cd^{2+} , Mn^{2+} . This also hastens the speed of reaction and subsidence of the precipitate, but the problem is that too little Ca(OH)_2 allows iron to remain in solution whereas an excess of Ca(OH)_2 may promote growth in the sand filter. Ferric salt has advantages over aluminium salt because of manganese removal, shorter reaction time, wider pH range and insolubility of flocs at higher pH values. However, the use of iron is critical since $\text{Fe}_2(\text{CO}_3)_3$ that normally occurs has no coagulant value. The advantage with iron compounds is that they produce heavy flocs that settle easily under favourable conditions at low costs. Another disadvantage is the tendency of iron flocs to pass the filter or settlement tank and stimulate bacterial growth (Eremektar, 1998). Dyer *et al.*, (1998) conducted experiments to determine the behaviour of the iron in aqueous solution forming different species. Various ferric hydroxide solids were formed at varying pH values of the medium with the concentration of the iron in the solution below 0.05 mol/L. The results of their work revealed that Fe(OH)_3 is dominant at pH 6.5- 7.0 whereas Fe(OH)_4^- at pH above 7.0. Figure 1.9 shows ferric hydroxide species formed during coagulation process at different pH of the solution.

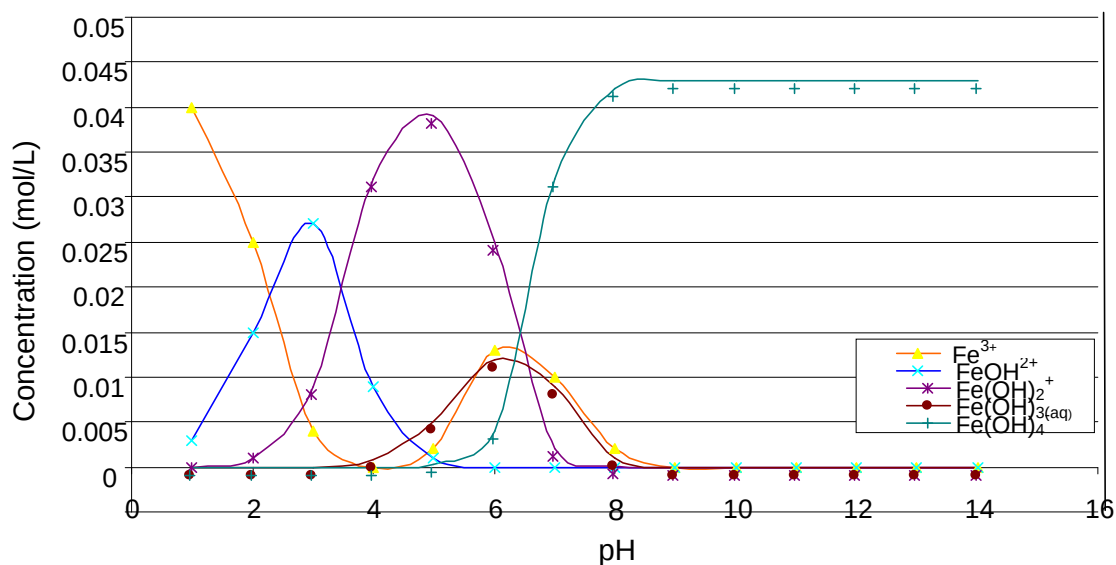
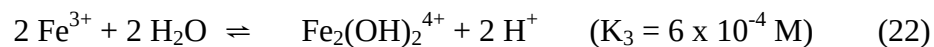
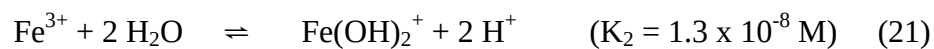
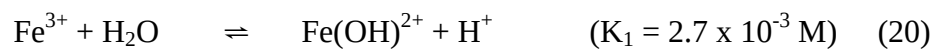


Figure 1.9: Ferric hydroxide species distribution curve (Flynn, 1984).

Figure 1.9 shows that there are at least four species that co-exist in aqueous solution in the pH range less than 5, namely Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and a very small fraction of dimer $\text{Fe}_2(\text{OH})_2^{4+}$. The species distribution is controlled by equilibrium equations of the low molecular weight hydrolysis species (Flynn, 1984, Faust *et al.*, 1983) shown as:



Each species has an area of dominance with some overlap as elucidated by Peavy (1985). $\text{Fe}(\text{OH})^{2+}$ is the first species to form due to decreasing concentration of Fe^{3+} .

It covers an area in the pH range 1 to 5, which is followed by Fe(OH)_2^+ in a pH range of 2-7, and follows $\text{Fe(OH)}_{3(\text{aq})}$ which covers the pH range of 4-8. The last species is Fe(OH)_4^- which covers the pH range of 4-14. The degree of hydrolysis process is determined by an equilibrium state between coagulants and colloidal suspension. The shift in equilibrium reaction depends on factors such as the activity coefficient of metal ion (M^{n+}), ionic potential of metal salts and the temperature of the medium. The more ionic charge on the metal ion, the more effective it becomes (Flynn, 1984). The temperature does not show any significant effect on hydrolytic reactions of metallic coagulants. Most of the studies show that metal hydroxides are formed between pH 4 and 10 (Jiang *et al.*, 1997 and Flynn, 1984).

There are also other solid species which are derived from the stable metal hydroxide species ($\text{(M(OH)}_{3(\text{aq})}$). The first solid species to be formed are unstable amorphous ferric hydroxides ($\text{am-Fe(OH)}_{3(\text{s})}$) which are formed due to very low solubility of the ferric hydroxide. Ageing converts unstable amorphous ferric hydroxide to a stable alpha ferric hydroxide ($\alpha\text{-FeO(OH)}_{(\text{s})}$), which is formed at the lowest Fe^{3+} concentration. Other species such as beta ferric hydroxide ($\beta\text{-FeO(OH)}_{(\text{s})}$) are also possible depending on the compound used in the wastewater treatment process (Faust *et al.*, 1983). Faust *et al.* (1983), O'Melia *et al.* (2001) and Casas *et al.* (2000) discovered further formation of other hydroxide species such as gamma hydroxide ($\gamma\text{-Fe(OOH)}_{(\text{s})}$) which can be converted to stable alpha ferric hydroxide when heated in the presence of an alkaline solution. Polasek *et al.* (2002) discovered that crystal growth from hydrolysis of FeCl_3 is directed to particular minerals, mainly a

β -FeOOH because of a lack of suitable nuclei for the growth to other more stable mineral species. This species is formed from aqueous FeCl₃ solutions under a wide range of hydrolysis including dilute or concentrated solution with base of up to 2.8 OH/Fe mole ratio even at elevated temperatures (Polasek *et al.*, 2002).

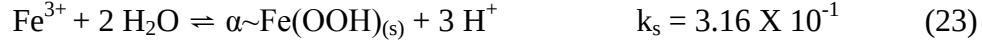
Flynn (1984) discovered that the deposition of precipitates in hydrolysed Fe³⁺ solutions begins in days to weeks and continues for months. All ferric species appear in octahedral coordination to O²⁻, OH⁻ and H₂O. X-rays and infrared spectroscopy reveals that precipitates formed by nitrate and perchlorate solutions consist of α -FeO(OH)_(s) whereas some of the γ -FeO(OH)_(s) is formed by solutions with low concentration of Fe³⁺ and OH/Fe ratios. The quantities and the formation rate of α -FeO(OH)_(s) indicate that it is a product of the ageing of the polymer and γ -FeO(OH)_(s); which is formed by the low molecular weight species. An increase in ionic strength accelerates the precipitation rate of goethite and inhibits lepidocrocite formation. Ruf *et al.* (2000) discovered that the precipitation rate is faster in solutions of polymer separated by gel filtration than solutions which are not separated. The pH change during ageing is accelerated by Cl⁻ (Flynn, 1984). The X-ray diffraction and infrared spectroscopy revealed that precipitates formed by hydrolysed Fe³⁺ in nitrates and perchlorate solutions consist of goethite and lepidocrocite formed by solutions with low concentration of Fe³⁺ and OH/Fe mole ratios. Increasing ionic strength accelerates the precipitation rate of β -FeO(OH)_(s) and inhibits the formation of lepidocrocite. This indicates that goethite is the product of ageing polymer whereas lepidocrocite is derived from low molecular weight species (Ruf *et al.*, 2000). Flynn

(1984) also identified ferric oxides and hydrous oxides, Fe_2O_3 and $\text{FeO}(\text{OH})_{(\text{s})}$ as polymorphic. The phases that are important during hydrolysis of Fe^{3+} and Al^{3+} are α - Fe_2O_3 (hematite), α - $\text{FeO}(\text{OH})_{(\text{s})}$ (goethite), β - $\text{FeO}(\text{OH})_{(\text{s})}$ (akaganeite) and γ - $\text{FeO}(\text{OH})_{(\text{s})}$ (lepidocrocite).

Aluminium metal ion yields α - Al_2O_3 (corundum), α - $\text{AlO}(\text{OH})$ (diaspore), $\text{M}'_x\text{MnO}_2$ (hollandite) and γ - $\text{AlO}(\text{OH})_{(\text{s})}$ (boehmite) (Flynn, 1984). The structures of α -, β - and γ - $\text{FeO}(\text{OH})_{(\text{s})}$ are composed of double chains of edge-shared $\text{Fe}(\text{O},\text{OH})_6$ octahedral. Feng *et al.* (2000) explains the formation of these hydroxide species as a complicated time dependent process defined as hydrolysis-polymerization-precipitation. Three classes of products are formed during hydrolysis from different species such as low molecular weight complexes, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$, hydrolytic polymer $(\text{Fe}_n(\text{OH})_m (\text{HO}_2)_x^{(3n-m)+})$, precipitated hydroxides, am- $\text{Fe}(\text{OH})_3$, precipitated oxides, FeOOH and Fe_2O_3 are produced (Flynn, 1984). Electron microscopy showed faster agglomeration of the spheres on polymer in chloride solutions with appearance of rods at 3-4 hours unlike in nitrates and perchlorate solutions. The main effect of Cl^- on the ageing of the polymer is that the final species formed during precipitation is α - $\text{FeO}(\text{OH})_{(\text{s})}$.

The ionic strength of the solution also plays a major role in the rate of precipitation. A higher ionic strength leads to a higher rate of precipitation and vice versa. This is because a solution with high ionic strength has lower electrostatic potential and

higher van der Waals forces of attraction, thus causing higher rate of precipitation (O'Melia, 1997). The solubility products of iron precipitates are as follows:



Equations 23 and 24 show that amorphous ferric hydroxide is formed at a lower solubility product than alpha ferric and ferric hydroxide species. Matijevic *et al.* (1966) conducted further studies on the hydrolysis of ferric ions in an aqueous solution. They focused on the instability of partially hydrolysed Fe^{3+} solutions that are manifested during the increasing and decreasing intensity of coloration of the solution. The novel techniques enabled them to distinguish four steps which lead to hydrolysis-precipitation process. These steps include the hydrolysis of monomer and dimers, reversible rapid growth to small polymers, the formation of slowly reacting large polymers and precipitation of solid phase. As Flynn (1984) stated that hydrolysis species consist of monomers, dimers, trimers and polymers, each species can be by applying Smoluchowski equation (Holthoff *et al.*, 1997) which is as follows:

$$\frac{dN_n}{dt} = \frac{1}{2} \sum_{j=n-i} K_{ij} N_i N_j - N_n \sum_{i=1}^{\infty} K_{in} N_i \quad (26)$$

where $N_n(t)$ = time-dependent number concentration of n-fold clusters, t = time, and K_{ij} = elements of the rate kernel which control the rate of coagulation between an i-

fold and an j-fold clusters. However, from Smoluchowski approximation, the coagulation is entirely controlled by Brownian diffusion and the coagulation rate constant for dimer formation of an initially monodisperse suspension is then given by Holthoff *et al.* (1997).

$$K_{11} = \frac{8K_B T}{3\eta} \quad (27)$$

where K_B = Boltzmann constant, T = temperature, and η = viscosity of the medium. It has been reported that assuming a constant kernel i.e $K_{ij} = K_{II}$, the Smoluchowski Equation 26 can be solved to obtain the expression.

$$\frac{N_n(t)}{N_0} = \frac{(K_{11}N_0t/2)^{n-1}}{(1+K_{11}N_0t/2)^{n+1}} \quad (28)$$

N_0 initial particle concentration. For $n = 1$, i.e monomer, the following linear functions in time for the inverse square root of monomer concentration N_1 is obtained.

$$\frac{1}{\sqrt{N_1}} = \frac{1}{\sqrt{N_0}} \left(1 + \frac{K_{11}N_0t}{2} \right) \quad (29)$$

From Equation 26, a plot of inverse square root of monomer concentration N_1 vs t should give a straight line graph. The coagulation rate constant can be evaluated from the slope provided the initial concentration, N_0 , is known.

Equation 28, for a monomer is expressed as:

$$N_1 = \frac{2N_0}{(2+K_{11}N_0t)^2} \quad (30)$$

For a dimmer, Equation 28 becomes:

$$N_2 = \frac{2 K_{11}N_0^2t}{(2+K_{11}N_0t)^3} \quad (31)$$

For a trimmer, Equation 28 derives:

$$N_3 = \frac{2N_0^3 (K_{11}t)^2}{(2+K_{11}N_0t)^4} \quad (32)$$

Also, the rapid coagulation rate constant, K_R is given by Smoluchowski (1917) as:

$$K_R = \frac{4K_BT}{3\eta} \quad (33)$$

Combining Equation 27 and 33 gives:

$$K_R = \frac{1}{2} K_{11} \quad (34)$$

Furthermore, from the constant kernel solution of Equation 28, it becomes necessary to introduce a coagulation time, when the total number concentration is reduced by a factor of 2,

$$\tau_{1/2} = \frac{2}{K_{11}N_0} \quad (35)$$

This coagulation time represents a useful time scale for the identification of the early stages in the coagulation process. Denoting the number of concentration of n- fold aggregates at reduced time, $\tau_{1/2}$ as, $N_n(\tau_{1/2})$ and $\tau_{1/2} = \frac{2}{K_{11}N_0}$, Equation 30 – 32 becomes;

$$N_1 = N_0 \left[\frac{1}{(\tau_{1/2} + t)^2} \right] \quad (36)$$

$$N_2 = 2N_0 \left[\frac{t/\tau_{1/2}}{(\tau_{1/2} + t)^3} \right] \quad (37)$$

$$N_3 = 4N_0 \left[\frac{(t/\tau_{1/2})^2}{(\tau_{1/2} + t)^4} \right] \quad (38)$$

Turbidity (NTU) was converted to TSS (mg/L) using Equation 39 and Coag-flocculation performance was evaluated using Equation 40.

$$\text{TSS (mg/L)} = (\text{TSS}_f) \cdot T \quad (39)$$

T = Turbidity in NTU; (TSS_f) = Conversion factor to TSS = 2.35 (Nnaji, 2012)

$$E(\%) = \left(\frac{N_o - N_1}{N_o} \right) \times 100 \quad (40)$$

E = Coag-flocculation Performance in percentage.

The process which gives rise to these species consists of (1) the formation of the low molecular weight species; (2) the formation of red cationic polymer; (3) ageing of polymer to form oxide phases and (4) precipitation of oxide phases directly from low molecular weight precursors. The reaction rate of Fe^{3+} has been conducted on ferric chloride, ferric nitrate or ferric perchlorate at room temperature and 0.001–0.1 M. The results showed that Fe^{3+} solutions depend on the nature and mode of the basic reagents such as alkali hydroxide or ammonia. The reaction of the Fe^{3+} solution with these basic reagents forms precipitates, and re-dissolves only if the amount of the base is equal or less than 2.5 mol of base per mole of iron.

The addition of $\text{Al}_2(\text{SO}_4)_3$ to water with bicarbonate compounds produces hydrated aluminium hydroxide which carries down organic substances. Eremektar (1998)

reported the effectiveness of alumino-ferric in water treatment. Water was free from CO_2 by running it over Ca(OH)_2 to form CaCO_3 which precipitated. The coagulant also precipitated after the addition of caustic soda or soda ash prior to alumino-ferric dosage. The $\text{Al}_2(\text{SO}_4)_3$ showed a strong coagulating power by attaining maximum precipitation at pH 5.5 compare to AlCl_3 which was at pH 8. Unlike ferric flocs, $\text{Al}_2(\text{SO}_4)_3$ flocs dissolve at pH 10 to 11 (Eremektar, 1998). Hydrolysis of Al^{3+} ions tends to form stable aluminium hydroxide species. Al^{3+} ions form an acidic medium in water and exhibits less solubility than Fe^{3+} ions (Crozes *et al.*, 1995). Coagulants with low solubility can achieve very high turbidity removal efficiencies. The performance of the species is identical to those of ferric hydroxide species, which dominates at different pH values shown as:

- $\text{Al(OH)}_{3(\text{aq})}$ dominates at pH 5.5 – 8.0
- $\text{Al(OH)}_{4^{-}(\text{aq})}$ dominates at pH above 8.0

Aluminium hydroxide species which are formed during coagulation process of Al^{3+} salts with a concentration less than 0.09 mol/L, are shown in Figure 1.10.

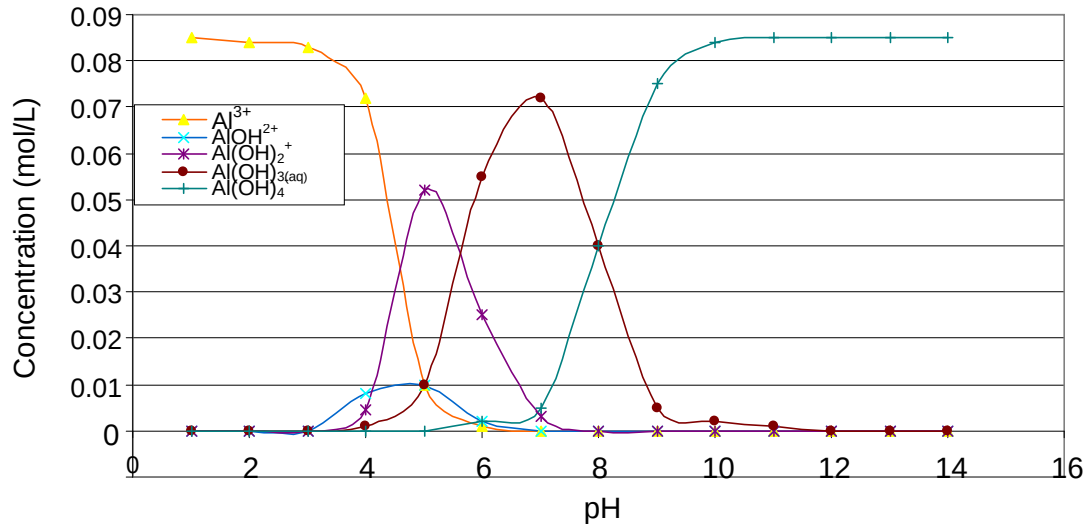
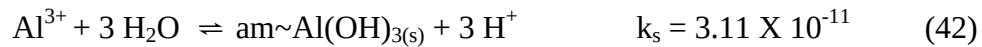
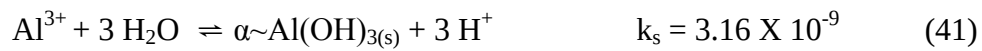
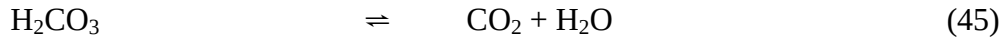


Figure 1.10: Aluminium hydroxide species distribution curve (Flynn, 1984).

Since their formation depends on the pH of the solution, the first species, a small fraction of $\text{Al}(\text{OH})^{2+}$ is formed at pH range 3 to 6; then $\text{Al}(\text{OH})_2^+$ that dominates within pH 4 to 7 followed by the most dominant species, $\text{Al}(\text{OH})_3$ in a pH range 4 to 9 and $\text{Al}(\text{OH})_4^-$ formed at pH above 8. Aluminium hydroxide also form different species that involve hydrolysis of ions such as destabilization before solid-liquid interface, flocculation, ageing process of the floc and the formation of aluminium hydroxide (O'Melia, 1997). Equations 41–42 show solubility products of the species.



Equations 41–43 show that amorphous aluminium hydroxide is formed at a lower solubility product than alpha aluminium and aluminium hydroxide species. It shows that amorphous aluminium hydroxide is formed at a lower solubility product than alpha, amorphous and ferric hydroxide species as shown by Equations 41–44. The $\text{Al}_2(\text{SO}_4)_3$ is commonly used in most wastewater treatment works to avoid Alzheimer disease by forming complex reactions as follows (Binnie *et al.*, 2003).



In the reaction where 1 mg/L of $\text{Al}_2(\text{SO}_4)_3$ is dosed, 0.5 mg/L of alkalinity is destroyed during the production of 0.44 mg/L of carbon dioxide. The $\text{Al}_2(\text{SO}_4)_3$ has low solubility at pH range of 5.0–7.5 and any water or wastewater pH outside this range yields unsuccessful coagulation (Tebbutt, 1983).

1.7 Theory of coagulation and flocculation

Coagulation and flocculation are processes which occur during the hydrolysis reaction. The former involves the formation of precipitates during hydrolysis reaction and the latter is the formation of larger flocs due to the velocity gradient and differential velocity which later settle due to a high settling velocity (Aboulhassan *et al.*, 2006, Aguilar *et al.*, 2002, Aguilar *et al.*, 2005). The velocity gradient is elucidated as the partial derivative of velocity with reference to position within a

continuous medium, usually fluid (dv/dx)) whereas the differential velocity is the formation of larger flocs due to Brownian motion of the fluid. During the coagulation process, the electrostatic forces of repulsion are reduced and the van der Waals forces of attraction increase. The coagulation process depends on the dosage whereas flocculation on the mixing effect (Dao *et al.*, 2001). Coulson *et al.* (1999) describe flocculation as the formation of large conglomerates of particles with occluded liquid and the flocs which are enlarged particles of higher density intermediate between that of constituent particles and liquid. The formation of flocs during coagulation-flocculation has been a subject usually explained by dividing the process in three steps such as coagulation/precipitation, flocculation and particle separation (sedimentation, filtration). Flocs are formed in all three steps but with different particle sizes. The size of particles leaving the first step is formed in seconds in the range 0.5–5 μm and they are referred to as primary particles. Floc formation is the second step which occurs when primary particles collide and form bigger settleable flocs of the size range 100–5000 μm . The first step deals with the chemistry of the process while the last two with the physical aspects (Li *et al.*, 2005, Li *et al.*, 2006a and Li *et al.*, 2006b).

The flocculation process is further explained as the agglomeration of small particles which are dispersed throughout a colloidal suspension to form larger particles, namely flocs. The dispersed particles carry charges and create either attractive or repulsive forces amongst the neighbouring particles. When the attractive forces

exceed repulsive forces, the particles coalesce and yield aggregates that settle under gravitational or centrifugal forces. The forces of repulsion from particles that carry the same charge prevent the settling. Flocculation can also be explained in terms of particle and fluid dynamics. According to the flocculation-rate theory, the rate of flocculation depends upon the order of mixing, the extent of adsorption of the coagulant and the character and the extent of the subsequent agitation which determines the size of the floc which has been formed (Goldberg *et al.*, 2002). This occurs when the particles are completely destabilised, but there could be some suspensions not affected due to partial stabilization, hence only a fraction of collision is effective. The partial stabilization of the suspended particles is caused by an energy barrier which is caused by the interaction between the electrical double layer and van der Waals forces. These barriers can be reduced by the addition of electrolytes as they will destabilize the fraction that stabilized. Another factor that retards the rate of flocculation is the thinning of the films of liquid between the particles. The film flows radially under laminar conditions and exerts a viscous resistance that impedes the contact between two neighbouring particles surfaces (Ives, 1978). Brownian motion also plays a pivotal role in flocculation by causing collision between the particles to stick together as they move randomly. The probability for collisions to occur to any single particle is proportional to the concentration of the particles. At this stage, particles grow to such an extent that Brownian motion no longer plays a role due to the collision frequency of the particles in the medium (Amirtharajah *et al.*, 1982 and Thomas *et al.*, 1996). Brownian motion can disrupt settling indefinitely in colloidal sized (less than 1 μm) particles under stable colloidal suspension. Minute particles

have to be induced and come together to form large particles before they could settle rapidly and ready to be removed by sedimentation process (Barnes *et al.*, 1983 and Thomas *et al.*, 1996). Since there are many descriptions about the coagulation-flocculation process; it is necessary to conduct a study which explains them in the form of their destabilization-hydrolysis potential. Flocculation is classified into three categories, perikinetic, orthokinetic and differential settling.

1.7.1 Perikinetic flocculation

Brownian motion causes collision of the particles and they stick together by moving randomly during the perikinetic flocculation stage. Transportation and attachment are dynamic reactions that cause perikinetic flocculation through the collision of two particles by virtue of variation in fluid-particle velocities. Most of colloidal sols (colloidal suspension of very small solid particles) which cause stability of dispersion are based upon perikinetic phenomena. Those phenomena originate from Brownian translation and rotation of the dispersed particles or their aggregates. Perikinetic flocculation is influenced by the thermal condition of the colloidal system and is induced by the addition of coagulants which reduce or eliminate repulsive barrier. Sometimes unstable sols tend to be slow in perikinetic flocculation due to low concentration of particles and that requires the introduction of large concentration of other particles to enhance flocculation kinetics (Dobias, 1993). There are two classes in this flocculation, namely micro-flocculation and macro-flocculation, the former is significant for particles in the size range from 0.001 to 1 μm and the latter for

particles of size greater than 1 or 2 μm . Micro-flocculation is also referred to as aggregation of particles occurring due to random thermal motion of fluid molecules, (i.e. Brownian motion) whereas macro-flocculation as influenced by the induced velocity gradient and differential settling (Metcalf *et al.*, 2003).

1.7.2 Orthokinetic flocculation

Orthokinetic flocculation is the second stage caused by movement of particles close together by gentle water motion. It occurs due to imposed velocity gradients during mixing and differential sedimentation of differential settling velocities of particles (Thomas, 1996). The contact occurs either by random Brownian motion or forced collision of colloidal particles due to velocity gradients caused by fluid mixing. The rate of this flocculation depends on the particle nature, size, concentration and the velocity shear gradient of the water. Mathematical models have been constructed to determine the effectiveness of some of parameters but could not be validated (Suzuki, 1990). In one of the models by Suzuki (1990) it is assumed that if two or more particles come close together, they collide and form a larger particle. The closeness that determines the collision of the particles to occur is defined as “zone of influence” and if the zones between two particles overlap, then the particles will agglomerate. In the model the assumption is also that the particles are so small (below 0.001 μm) that they have negligible settling velocity and will travel with the same velocity as water. If the water moves at uniform velocity or is stationery, the relative motion of particles

must be established in order to cause collision. This will keep the inter-particle distance unchanged for a long period without any chance of larger floc formation. Some collisions will only occur when there is a velocity shear gradient that will cause relative motion between particles (Suzuki, 1990). It is during this stage that larger particles and flocs are formed where relative motion by velocity gradient of the particles creates a high shear rate in the liquid phase (Faust *et al.*, 1983 and McCurdy *et al.*, 2004). Large particles impart their velocity to the neighbouring particles and the inter-particle bridging within particles in the colloidal system occurs during macro-flocculation stage. Perikinetic and orthokinetic flocculation can occur at equal rates depending on the radius of the particles. These measurements were done at various velocity gradients in water at temperature 25 °C as shown in Table 1.3:

Table 1.3: Particle radii for equal perikinetic and orthokinetic flocculation (Ives, 1978).

Velocity gradient, $G \text{ (s}^{-1}\text{)}$	Radius of particles (μm)
1	1.05
10	0.5
20	0.4
50	0.3
100	0.23

Table 1.3 shows that orthokinetic flocculation co-exists with the perikinetic flocculation when particles sizes are between 0.23 to 1.05 μm which corresponds to a velocity gradient in a range of 1-100 s^{-1} (Ives, 1978).

1.7.3 Differential settling

This type of flocculation occurs when particles of different sizes are found in the solution, as in a sludge blanket or solid contact clarifier. Relative motion occurs between particles when large particles settle faster than smaller particles. Large particles move downwards to settle and collide with the smaller particles that move randomly due to Brownian motion, thus causing flocculation. The movement of large particles can also cause a localized velocity shear gradient that can hasten orthokinetic flocculation of very small particles around that area (Suzuki, 1990). Guibal *et al.*, (1991) and Thomas *et al.*, (1996) stated that the interactions between particles in sufficiently dilute systems are treated as binary collisions between rigid spheres in perikinetic and orthokinetic flocculation. In this analysis it is assumed that the relative motion between pairs of particles is described by the superposition of isolated particle motion. Each particle behaves profoundly in an individualistic manner and the only interactions are from combined attraction and repulsion of electrostatic fields. The force field is caused by van der Waals forces and electrical double layer repulsion. Settling is the last process that influences kinetics of the system as it allows the flocs to settle by gravity due to their high settling velocity. There are three important parameters considered during settling/sedimentation process, namely, sedimentation velocity, degree of flocculation (β) and sedimentation volume (f) or height (H) of flocculated suspension as shown by Equation 47.

$$f = V_u / V_O \quad (47)$$

V_u = final or ultimate volume of sediment, V_O = original volume of suspension before settling.

The settling/sedimentation volume is a ratio of the final or ultimate volume of the sediment (V_u) and the original volume of the sediment (V_O) before settling. When a measuring cylinder is used to measure the volume, Equation 48 is employed:

$$f = H_u / H_O \quad (48)$$

H_u = final or ultimate height of sediment, H_O = original height of suspension before settling

The sedimentation volume can have values ranging from less to greater than 1; f is normally less than 1; If $f = 1$, such product is said to be in flocculation equilibrium and it does not show clear supernatant on standing sedimentation volume (f_v) for deflocculated suspension

$$f_v = V_v / V_O \quad (49)$$

f_v = deflocculated suspension, V_v = deflocculated volume of suspension (Martin *et al.*, 1966). Figure 1.11 shows the processes that occur during flocculation.

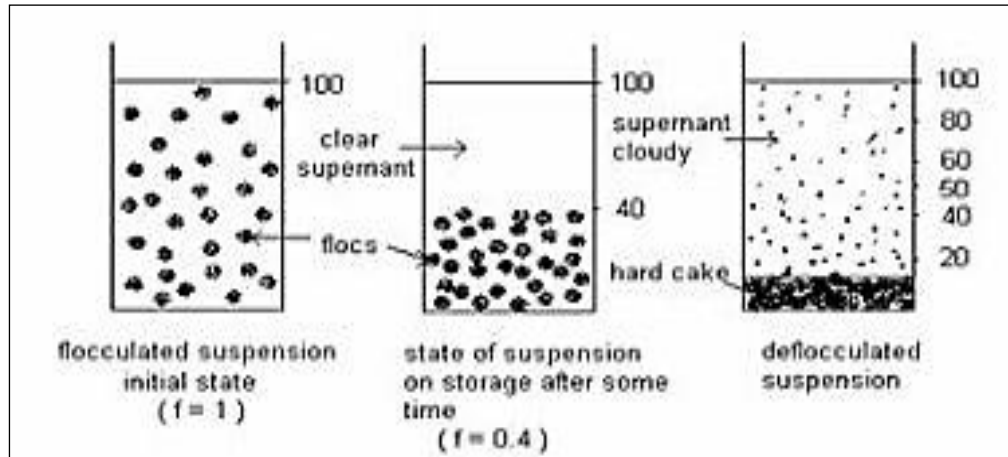


Figure 1.11: Suspensions quantified by sedimentation volume (f), Martin *et al.* 1966.

Figure 1.11 shows three glass beakers containing flocs formed before settling, after settling for a certain period and dispersed colloidal particles which did not form flocs (de-flocculation) respectively. This is one area that is studied in the present investigates, i.e. direct flocs count using a microscopic observation unlike a jar test where turbidity measurements are used; which does not depict the visual representation of the flocs formed in the beakers.

Equation 50 is an equation of a very useful parameter for flocculation:

$$\beta = f/f_{\infty} \quad (50)$$

$$= V_u/V_o \quad (\beta = V_{\infty}/V_o = V_u/V_{\infty})$$

$$= \frac{\text{ultimate sedimentation of flocculated suspension}}{\text{ultimate sedimentation of deflocculated suspension}}$$

After the coagulation-flocculation process, sedimentation follows, based upon the degree of flocculated and deflocculated suspensions. Flocculated suspensions form flocs that settle due to increasing particle size. Porosity of the flocs also plays a pivotal role in sedimentation as liquid is entrapped and the suspensions settle due to larger and heavier size. The settling rate of individual particles is slow and prevents entrapment of liquid medium which also impairs the formation of larger flocs in deflocculated suspensions. The larger flocs settle faster and smaller particles remain dispersed in the supernatant, forming a cloudy appearance whereas in flocculated suspension which are larger and smallest, particles form flocs and settle (Martin *et al.*, 1966). Brownian motion prevents sedimentation by keeping the dispersed material in random motion. The Brownian motion depends on the density of the dispersed phase, density and viscosity of the colloid. Kinetic bombardment of the colloidal particles by the molecules of the medium will keep the particles suspended, provided their size is below a critical radius, a radius which is below the settling velocity. Brownian motion can be observed when the particle size is about 2 to 5 μm where the density of the particles and viscosity of the medium allow random motion of colloidal particles. Brownian motion becomes less important and sedimentation becomes favourable when the radius of suspended material increases (Martin *et al.*, 1966). 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. Increasing the mass of the particle such that gravitational force is greater than drag force and neutralizing the charge causes settling of the particles. Flocculation becomes effective when the gravitational force is greater than the drag force. When

the density of the suspended particles is greater than that of the dispersion medium, they float above medium. Settling and sedimentation do not occur when the density of the dispersed phase equals to the density of dispersion medium. An increase in viscosity of the medium decreases the settling of particles because sedimentation velocity becomes inversely proportional to viscosity of the dispersed medium. The viscosity is the opposing force to fluid flow which is a characteristic of a medium (Martin *et al.*, 1966). Viscosity is proportionality constant between the shear rate and shear stress for Newtonian fluid is expressed by Equation 51.

$$\eta = S/D \quad (51)$$

where η = viscosity, S = shear stress and D = shear rate (η has units g/cm-sec or N-sec/m²)

Aysegul *et al.* (2002) revealed that mixing dynamics show that there is no uniformity of dispersion during mixing. The velocity of the medium decreases as the medium comes closer to the boundary wall of the vessel. The fast-moving particles overtake slow-moving particles in a velocity field, collide and stick together to form larger particles that are removed by settling or gravity separation. Particles move in a curved path in an induced velocity gradient towards the settling point and differential settling particles move perpendicularly with different settling times (Metcalf *et al.*, 2003). Settling plays a major role during the separation of impurities from wastewater. The settling velocity is the most important parameter during wastewater treatment in this regard. The shape of the particles and viscosity of the liquid play the less significant role in determining the settling velocity in the colloidal suspension. Under a laminar

flow, the settling velocity of the particles which causes turbidity is directly proportional to the square of its diameter, the shape of the particles and viscosity of the liquid (Barnes *et al.*, 1983 and Thomas *et al.*, 1996).

1.8 Types of reagents used as coagulants and coagulant-aids

1.8.1 Common reagents in wastewater treatment

The Fe^{3+} and Al^{3+} salts are affordable reagents dosed to wastewater during treatment world-wide. However, the latter has a disadvantage as it is associated with Alzheimer's disease. In addition, $\text{Fe}_2(\text{SO}_4)_3$ was superior to $\text{Al}_2(\text{SO}_4)_3$ because of its effectiveness over a wide range of pH values. Another advantage with the former is its use for water decolourization at low pH, removal of manganese at high pH and clarification of water with low temporary but high permanent hardness. FeCl_3 can also be used but the problem is its corrosive properties and difficulty in handling, storage and dosing (Binnie *et al.*, 2003). Some wastewater treatment works dose a combination of coagulant(s) and coagulant aids to improve turbidity removal. Coagulant aids have a tendency of forming polymeric chains (polyelectrolytes) which have opposite charge to the colloidal particles. Polyelectrolytes, which are identified by high molecular weight interact with the surface of opposite charged particles, resulting in charge neutralization (Ives, 1978). Polyelectrolytes are cationic, anionic and the heaviest non-ionic with a molecular weight of a million, four million and thirty million respectively. Cationic coagulants react similarly to metallic coagulants

due to their positive charge and hydrolysis reactions to yield hydroxide ions at high pH and become neutrally charged in nature. Anionic polyelectrolytes carry a carboxyl functional group (-COOH) and they ionise in water to yield hydrogen ions, turning non-ionic at low pH (Droste, 1997). FeCl_3 and coagulant aids are recommended for complex wastewater treatment due to their ability to effectively remove turbidity, COD, colour and sludge production (Eremektar *et al.*, 2006). The complexity of the AMD is attributed to the presence of heavy metals such as Cu, Zn, Ni, Cd and other metal sulphites. Acids are also found in natural water in the form of humic and fulvic acid. They form complexes with the ions such as Fe^{3+} and many metals in natural water exist largely as organically-bound species. Complexation which is caused by metal ions can have a strong effect on flocculation and adsorption behaviour of metal hydroxides, hence polyelectrolytes are necessary.

Another approach, namely pre-polymerisation of inorganic coagulants was developed on Fe^{3+} and Al^{3+} salts since the 1980 (Jiang *et al.*, 1997). Polymers such as polyaluminium chloride (PACl) and polyferric chloride (PFCI) are used in the process. The preparation involves partial hydrolysis of acidic AlCl_3 and FeCl_3 solution in special reactor. The polymeric species formed, depend on the concentration of the M^{3+} ion, ratio of moles of the base added and moles of Al^{3+} or Fe^{3+} ions $[\text{OH}]/[\text{Al}]$ or $[\text{OH}/\text{Fe}]$ mole ratio, duration on hydrolysis of M^{3+} solution, anions in the solution, mixing mode of base with the M^{3+} solution and nature and strength of the base. The most predominant parameters which govern the nature of the species are the basic ratio, temperature and time (Jiang *et al.*, 1997). PACl and

PFCI have been used in wastewater treatment and their use in drinking water has been researched and the results showed that they have a high treatment efficiency for heavy metals, COD, turbidity, and reflect superior performance in wastewater at low temperature. FeCl_3 showed superior performance in colour removal and organic matter in the surface water than PFCI; and the advantage with PFCI is its lower sensitivity to water temperature variation (Jiang *et al.*, 1997). Apart from the use of metal salts and pre-polymerisation of inorganic coagulants to remove heavy metal in wastewater, neutralizing agents such as metal hydroxide were explored, mostly in AMD treatment. Further investigations of alternative polymerised coagulants in drinking water were conducted in 1990 by Jiang *et al.* (1997). The research on polyaluminium silicate sulphate (PASS) was used in drinking water in Europe, North America and Asia. The comparison between conventional coagulants and PASS showed that the latter requires less pH adjustment and a lower dose to achieve the equivalent treatment performance. It also showed a better performance at low temperature, improved natural organic matter removal and low concentration of residual coagulant in treated water (Jiang *et al.*, 1997). Although there were some advantages associated with the technique, it is labour-intensive and costly to prepare the coagulants compared with the conventional wastewater treatment.

A study was carried out by Amuda *et al.*, (2006) to flocculate sludge from chemical industrial wastewater using FeCl_3 and non-ionic polyacrylamide. It was found that some municipalities prefer activated carbons for treatment of wastewater; where COD and some volatile organic compounds (chloroform, benzene and

carbontetrachloride) are adsorbed onto the carbon surface. Their study revealed the best COD, TP and TSS removals of 73, 95 and 97 % occurred at pH 9.0 with a FeCl_3 dosage of 300 mg/L respectively. The addition of 25 mg/L polyelectrolyte to 100 mg/L FeCl_3 resulted in 91, 95 and 97 % COD, TP and TSS removal respectively. Sludge production was higher in the FeCl_3 dosage alone compared to 60 % reduction when both FeCl_3 and polyelectrolyte were added. It is concluded that coagulation-flocculation may be a useful pre-treatment process in chemical wastewater treatment prior to biological treatment (Amuda *et al.*, 2006)

1.8.2 Polyelectrolytes in wastewater treatment

Polyelectrolytes are organic coagulants that serve as alternative coagulants to Fe^{3+} and Al^{3+} salts (Droste, 1997). They are linear or branched polymers that can be used as principal coagulants or coagulant-aids in wastewater treatment. These are formed by monomers that contain an ionisable group such as carboxyl, amino or sulfonic and identified by their high molecular weight. They are cationic, anionic and the heaviest non-ionic with a molecular weight of 1, 4 and 30 million respectively. Cationic coagulants react similarly to metallic coagulants as both are positively charged and hydrolysis reactions yield hydroxide ions at high pH and become charge neutral. Anionic polyelectrolytes carry carboxyl functional group ($-\text{COOH}$) and ionise in water to yield hydrogen ions, turning non-ionic at low pH (Droste, 1997). The ability of the polymer to flocculate depends on the molecular weight and degree of branching. Common polyelectrolytes recommended in flocculation are cellulose

compounds, polysaccharide gums, proteinaceous materials, starch and starch derivatives (Faust *et al.*, 1983). The use of polyelectrolytes as coagulants is critical, as coagulants overdosing can result in re-stabilization. This occurs when the flocs are re-dispersed back into the recovered water due to mutual repulsion. Polyelectrolytes are therefore suitable only for the treatment of wastewater of a uniform quality and yield good results in wastewater with low turbidity (Freeze *et al.*, 2001). The flocs formed by organic polymers are stronger than those formed by Fe^{3+} or Al^{3+} and can withstand higher shearing stresses. Organic polymers perform poorly when polymer segments are detached to form monomers, thus causing re-stabilization of particles (Swartz *et al.*, 2004). The disadvantage of the use of polymers in wastewater treatment is that they operate effectively within a limited pH range. They also do not affect the pH of the wastewater as compared with the metallic coagulants (Nozaic *et al.*, 2001). They produce less sludge in comparison to metallic coagulants; hence turbidity removal is relatively ineffective. One of the sub-objectives of the present investigation is to determine the effectiveness of synthetic polymers on turbidity removal in AMD as replacement of commercial electrolytes. Pratt *et al.* (2007) and Chang *et al.*, (2004) stated that turbidity removal in wastewater treatment occurs through adsorption of colloidal particles by the flocs which have been formed during hydrolysis. Adsorption cannot be explained only in terms of increased electrical repulsion or decreased van der Waals forces. The process also involves the steric repulsive forces. When two particles collide, the outer layers interact in several possible ways as detailed by Ives (1978).

- Adsorption equilibrium is affected and causes either increase or decrease in the amount adsorbed. Increasing adsorption correlates to the increase in forces of attraction between the surfaces whereas repulsive forces lead to desorption. Adsorption and desorption are processes that are relatively slow for polymeric materials and that creates uncertainty about their role during the collision of particles.
- Adsorbed layers might be compressed and reduce the volume of the particles, hence limit the number of possible configurations for adsorbed polymer chains. A reduced number of configurations is a sign of decreased entropy, where increasing free energy and repulsion between the particles become apparent. This phenomenon is sometimes called volume restriction or the elastic effect.
- Adsorbed layers may interpenetrate and increase the concentration of the polymer molecules bridged between the particles that are responsible for either attraction or repulsion. This process is known as mixing or the osmotic effect.

Ali *et al.*, (2002) conducted a further study on the wastewater treatment focusing on electrical phenomena occurring at the surface. They stated that wastewater contains microscopically visible colloidal particles which possess a high electrophoretic mobility or high zeta potential. It was also discovered that the electrophoretic mobility decreases in $\text{Al}_2(\text{SO}_4)_3$ to zero at optimum coagulation proportions where charge reversal is possible. The removal of organic colour coincides with zero electrophoretic mobility during flocculation with $\text{Fe}_2(\text{SO}_4)_3$. It was later confirmed that the complex art of water treatment should use the measurement of electrophoretic

mobility or zeta potential to predict correct dosage of coagulant for best treatment results. However, the considerations for electrophoretic characteristics of colloids and their stability apply only to hydrophobic colloids. Detergents are “hydrophilic colloids” that may or may not coagulate and are also soluble at their isoelectric point and therefore may not coagulate over any range of electrophoretic mobility or zeta potential. This type of problem is common in water purification.

1.8.3 Effect of dissociation of acids in wastewater treatment

When FeCl_3 is added to wastewater, the Cl^- released reacts with a proton (H^+) from the dissociation of the water molecule to form HCl , which dissociates completely (strong acid) to form aqueous H^+ and Cl^- . In the case of $\text{Al}_2(\text{SO}_4)_3$, the protons combine with SO_4^{2-} from $\text{Al}_2(\text{SO}_4)_3$ to form H_2SO_4 which dissociates to form H^+ and HSO_4^- . A further dissociation occurs to form H^+ and SO_4^{2-} which can also shift backwards to H^+ and HSO_4^- , thus behaving as a buffer (Ghaly *et al.*, 2006). A study conducted by Ntwampe *et al.*, 2013 revealed that diprotic metal salts ($(\text{M}_2(\text{SO}_4)_3)$) are more effective in the turbidity removal from paint wastewater than monoprotic metal salts ($(\text{MCl})_3$). The presence of basic compounds in water depends on the pH of the wastewater and reacts to neutralize acids as flows:

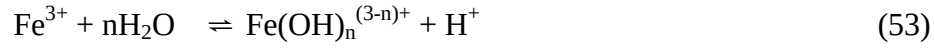
$0.5 \text{ CO}_3^{2-} + \text{HCO}_3^-$: neutralizes acids at pH range 4.5–8.3 (p-alkalinity)

$0.5 \text{ CO}_3^{2-} + \text{OH}^-$: neutralizes acids at pH range 8.3–12.8 (m-alkalinity)

In a study by Byrne *et al.*, (2000) it is stated that there is a poor understanding of the inorganic complex behaviour of Fe^{3+} even after extensive studies were conducted for many years. The poor or incomplete characterization of Fe^{3+} hydrolysis is attributed to the inherent complexity of its chemistry present at high concentrations and analytical challenges at low concentrations. The results and discussion were based upon the evaluation of consecutive hydrolysis constants which is expressed by Equation 52:

$$\beta_n = [\text{Fe}(\text{OH})_n]^{3-1} [\text{H}_6^{+}] [\text{Fe}^{3+}]^{-1} \quad (52)$$

The equilibrium state of Fe hydrolysis is expressed by Equation 52.



Where $n \leq 3$, the solubility behaviour of $\text{Fe}(\text{OH})_3$ is expressed as K_{s0} which describes the relationship between the concentrations of Fe^{3+} and H^+ in equilibrium with hydrous ferric oxides expressed as:

$$K_{s0} = [\text{Fe}^{3+}] [\text{H}^+]^3 \quad (54)$$

Metal ions such as Al^{3+} and Fe^{3+} are strongly hydrated by six water molecules (Figure 1.8) in an octahedral configuration as represented by $\text{M}(\text{H}_2\text{O})_6^{3+}$. According to Equations 10-13, simple unhydrolyzed ions such as Fe^{3+} and Al^{3+} are found in aqueous solution at low pH. As the pH of the solution increases, the equilibrium starts shifting to the right until uncharged species ($\text{M}(\text{OH})_{3(\text{aq})}$) are produced. Their low

solubility in water forms precipitate such as gelatinous $M(OH)_3$ and increasing pH may re-dissolve the precipitate when $M(OH)_4^-$ ions are formed (Equation 14). The advantage of using iron and aluminium salts in wastewater treatment is their high electron valence which enables them to adsorb soluble species and cause particles-charge reduction. These metal salts form hydroxide precipitates as fine colloidal dispersion during the initial stage. The particles aggregate to form hydroxides which enmesh the colloidal particles present in wastewater during “sweep flocculation” (Ives, 1978). Hydroxide precipitation can also lead to sweep flocculation when the colloidal particles are enmeshed in the growing precipitate and removed (Duan *et al.*, 2002). Duan *et al.* (2006) stated that although results on the research about the flocculation were well elucidated in terms of established ideas, a clear understanding of the ‘sweep flocculation’ mechanism did not supplement the work.

1.9 Factors which influence effective wastewater treatment

1.9.1 Effect of the pH in coagulation-flocculation

The pH is one of the significant parameters that determine the reduction efficiency of minerals in the wastewater (Pratt *et al.*, 2007). The addition of Fe^{3+} or Al^{3+} salts at pH of 6-8 fastens the rate of hydrolysis, leading to very rapid precipitation (Jiang *et al.*, 1997) which is caused by the presence of a high concentration of OH^- ions which replace the water molecules (Figure 1.7) surrounding the central metal ions (M^{3+}). This reduces the charge on the hydroxo-ferric complex and the reduction of repulsive

energy allows easier adsorption of hydroxo-ferric complexes (Duan *et al.*, 2002). The problem encountered during hydrolysis is the inability to control the nature of coagulant species formed, as they exist at specific pH values and some do not play any role in adsorption (Jiang *et al.*, 1997).

According to Zhang *et al.*, (2006), adsorption can be considered as a division of the reagent species between the interface and the bulk and can occur if the interface is energetically favoured by the coagulant in comparison to the bulk solution. They defined adsorption as a reaction which is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding or non-polar interactions between the adsorbed species, lateral associative interaction, solvation and desolvation. This indicates that the total adsorption is usually the cumulative result of some or all of the above forces. The driving force for adsorption is therefore the sum of a number of contributing forces as mentioned above and the standard free energy of adsorption ΔG^0_{Ads} (Paria *et al.*, 2004), and can be written as Equation 55

$$\Delta G^0_{\text{Ads}} = \Delta G^0_{\text{elec}} + \Delta G^0_{\text{chem}} + \Delta G^0_{\text{c-c}} + \Delta G^0_{\text{c-s}} + \Delta G^0_{\text{H}} + \Delta G^0_{\text{H}_2\text{O}} + \dots \quad (55)$$

The adsorption of non-ionic reagent/monomers is attributable to hydrogen (ΔG^0_{H}), $\Delta G^0_{\text{c-c}}$ = hydrophilic bonding and hydrophobic bonding ($\Delta G^0_{\text{c-s}}$). It should be mentioned that for adsorption due to hydrogen bonding to occur, the bond that is formed between the monomers functional groups and mineral surfaces must be stronger than the bond that is formed between the mineral and interfacial water molecules (Zhang *et al.*, 2006).

An adsorption on solids that possess a fully or partially hydrophobic surface takes place mainly due to hydrophobic bonding. In addition, this kind of chemical bonding is important for adsorption on solids that were originally hydrophilic but have acquired some hydrophobic features due to the interactions with organic species in solution (Somasundaran *et al.*, 2000).

The rate of coagulant-colloid interaction has to be faster than the rate at which the hydroxides precipitate in order to yield maximum flocs formation. This condition is only possible with a low dosage of metal cations when the pH of the wastewater is lower than 6 and the concentration of the colloid is moderate to high (Jiang *et al.*, 1997). When the dosing is restricted to a narrow range, it becomes very hard to dose the correct amount due to changing wastewater quality randomly. The ratio between the concentration of the metal ion (M^{3+}) and the mass of the colloidal particles in wastewater is important. A high chemical dosing is required when the pH is above 6 in order for treatment to produce effluent of good quality (Juttner *et al.*, 2000).

A study was conducted by Amuda *et al.*, (2006) on textile wastewater in Pakistan dosing different coagulants and reagents such as $FeCl_3$, $Al_2(SO_4)_3$, $Ca(OH)_2$ and their combinations. The $Ca(OH)_2$ and polyelectrolyte magnoflocs were used as coagulant aids. The results found that optimum pH in textile wastewater to yield effective coagulation was within 5-6 (Amuda *et al.*, 2006). Since the wastewater was alkaline, H_2SO_4 and HCl acids were dosed for pH adjustment. The second observation revealed that $FeCl_3$ with or without lime/polyelectrolyte could not coagulate

suspended particles in the wastewater whilst $\text{Al}_2(\text{SO}_4)_3$ yielded a reduction efficiency of 90 % suspended solids, 20-50 % BOD and COD within 60 minutes. The reduction efficiency of $\text{Al}_2(\text{SO}_4)_3$ dosage alone was less compared to its combination with $\text{Ca}(\text{OH})_2$ and polyelectrolyte (magnofloc) (Amuda *et al.*, 2006).

Maree *et al.*, (2004b) conducted a study on AMD and discovered that ferric ions are removed as a ferric hydroxide precipitate in the presence of hydroxide, carbonate or oxide containing materials, up to a pH of minimum solubility (pH value about 4.0). It was also revealed that ferric ions are relatively easy to remove from AMD because they start to precipitate at a pH as low as 3.0. The experiment where the AMD was dosed with 100 g/L of $<150 \mu\text{m}$ $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ or 500 g l^{-1} of fly ash took a minimum of 6 h contact time to reduce the levels of ferric ions to below 0.1 mg l^{-1} (near complete removal of ferric ions), obtained at pH values of 7.4 and 7.8, respectively.

In another investigation, Maree *et al.*, (2003) noticed that the fluidised-bed reactor process required a pH of 7.5 to be maintained for effective treatment of ferric ion rich water. Petrik *et al.* (2003) investigated the removal of total iron from an AMD sample with fly ash as dosage agent. There was a decrease of total iron from 3500 mg/L to 70 mg/L for low dosages and below detection limits for a 500 mg l^{-1} fly ash dosage. It indicated that the actual composition of the iron species in solution is highly dependent on the pH of the wastewater and more ferrous ions are found at the very low pH values than ferric ions. As in the case of the ferric ion, removal of *ferrous ions* takes place due to the precipitation of ferrous hydroxide. Although the molar solubility product constant of ferrous hydroxide is relatively small, removal is

dictated by the pH (Maree *et al.*, 1996). At pH values that were less than 7.5, precipitation became slow and incomplete. The $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CaMg}(\text{CO}_3)_2$ are relatively insoluble at pH values greater than 7, and therefore, pre-oxidation of ferrous ions to ferric ions is necessary for effective removal of iron from AMD (Maree *et al.*, 2003).

Kuyucak (2001) and Kuyucak (2002) treated AMD with $\text{Ca}(\text{OH})_2$ and the effluent was discharged directly into a rapid mix chamber where hydrated lime was added and the low ferrous iron concentrations ($<50 \text{ mg/L}$) were treated to a pH of 6.5–8.0 and then diverted directly to a settling chamber. The higher concentrations had a pH of 8–10 and were passed through an aeration tank, where the $\text{Fe}(\text{OH})_2$ precipitate was converted to $\text{Fe}(\text{OH})_3$. The water then flows to a settling chamber, where heavy metals are precipitated from the solution. The $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ is not widely used because the CO_2 buffers the reaction, therefore making it difficult to raise the pH above 6.

1.9.2 Mixing

Rapid mixing is more preferable in some water treatment plants operations because it disperses the coagulants throughout the colloid. Agitation is done in a turbulent regime and the chemicals are dosed in a most turbulent zone near the impellor. Mechanical agitation (mixing or shaking) plays a pivotal role during destabilization-

hydrolysis of wastewater by inducing velocity gradient (du/dy), a change of velocity per change of distance and disperses the reagents throughout the solution. The type of coagulant (physico-chemical properties) which are dosed and the time taken during mixing determine optimum velocity gradient (Ives, 1978, Faust *et al.*, 1983, Dao *et al.*, 2001, Duan *et al.*, 2002, Gregory *et al.*, 2002, Metcalf *et al.*, 2003, Sincero *et al.*, 2003, McCurdy *et al.*, 2004, Swartz *et al.*, 2004, Molony, 2005, Amuda *et al.*, 2006, Ghaly *et al.*, 2006).

Since rapid mixing influences destabilization-hydrolysis, it is important to have an ideal dosage to produce the best results (Swartz *et al.*, 2004). There are two types of dispersion processes, one consists of fragile particles with re-agglomeration and the other is a process that requires both dispersion and coalescence. The average and maximum shear rates caused by mixing determine the ultimate particle size produced. When the material is kept long enough in the mixing tank, the size of the particles is determined by maximum shear rate around the impeller as they will subsequently move towards that area. The maximum shear rate includes gas-liquid and liquid-liquid dispersion where equilibrium between dispersion and coalescence is established in the mixing tank. Figure 1.12 shows the fluid direction during mixing.

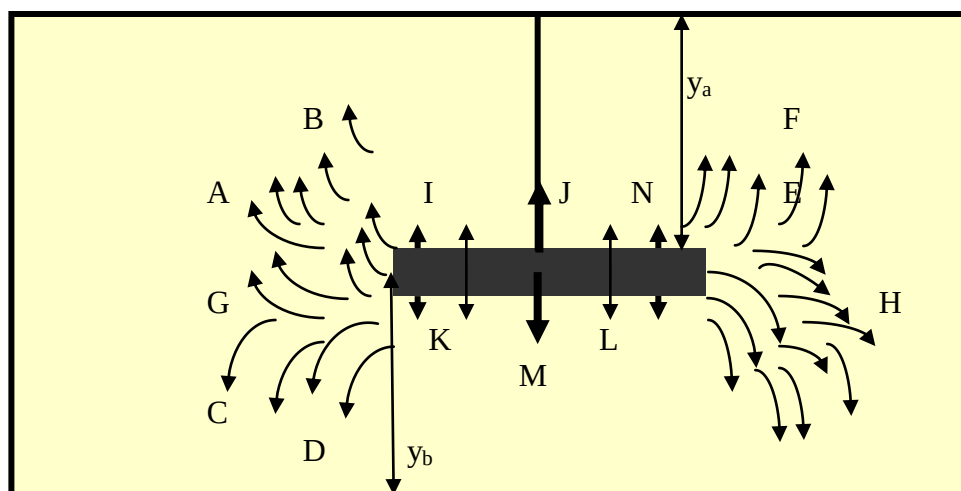


Figure 1.12: Movement of colloid during rapid mixing. (Oldshue, 1983)

A - H = direction of flow, area inside I - N = void created by impeller during turning, y_a and y_b = area not directly affected by impeller.

Figure 1.12 shows the directions of the movement of the colloidal suspension during rapid mixing. The liquid near the impeller experiences maximum kinetic energy whereas above and below is forced upwards and downwards by the shear forces respectively. The shear rate plays a pivotal role during dispersion of the metal ions (Oldshue, 1983). The speed of the impeller creates turbulent motion of the colloidal suspension, thus increasing the rate of destabilization-hydrolysis, causing increasing the rate of adsorption. The shear rate at high speed breaks the flocs and reduces the surface area of the flocs (Oldshue, 1983). The time taken for mixing relates to shear work, the product of the shear rate and the duration of time taken for mixing and is termed the shear rate of strain (shear flow or distortion ratio) expressed as m/m of strain induced in the process. It is therefore essential to determine whether a lower shear rate and longer time may give equivalent results to other patterns of shear rates

and the durations of time (Oldshue, 1983)., Intensive extensive mixing for a longer period seems to be an attribute to poor effluent quality by causing rupturing of the flocs (high shear rate) at high speed. The research does not indicate the effective time frame within which maximum flocs are formed. In the present work an investigation of the optimal time within which effective flocs are formed to achieve maximum adsorption is conducted.

Turbulent dissipation length, the measure of the size of the turbulent eddies is another quantity that plays a role in mixing dynamics. These turbulent eddies are responsible for the energy utilised during mixing. Shear rates are classified into macro- and micro-scale, where the former is responsible for particles size greater than 500 μm or larger and the latter for particles less than 100 μm . There are four considerable quantities in the mixing tank during wastewater treatment namely, maximum velocity at the impeller zone, average velocity gradient in the impeller zone, average velocity gradient in the entire batch zone and minimum velocity gradient in the batch volume (Oldshue, 1983). Clark *et al.*, (1993) conducted studies on the effect of mixing conditions on aluminium precipitation and were based upon the neutralization of AlCl_3 solutions in a mixing tank reactor where the kinetics of hydrolysis reactions was investigated with respect to mixing time-scale. The research showed that there is competition between the formation of polynuclear hydrolysis products and precipitated solids. The findings of the research on the formation of flocs by binary encounters through the perikinetic and orthokinetic mechanisms do not clearly define the cause of the flocs break-up in an agitated system. The flocs break-up poses a

problem in wastewater treatment as it affects the distribution of floc sizes throughout the flocculating colloidal suspension. The break-up influences the performance of solid-liquid separation processes. Flocs break-up in dilute agitated suspensions is influenced by the interaction of individual flocs with fluid forces (Heath *et al.*, 2002).

1.9.3 Hydrodynamic interaction between particles

Hydrodynamic forces also play a role in the collision of particles during mixing and occur when the fluid in the decreasing space between them is squeezed out. Hydrodynamic interactions arise mainly from the distortion of the fluid flow when the particles are present. Such distorted fluid flow causes the particles to deviate from their linear path and start rotating relative to one another and subsequently collide. The prevailing inter-particle colloidal forces in an unstable suspension become attractive and enhance the colloidal efficiency, defined as the ratio of actual coagulation frequency and collision frequency. In Table 1.4 a comparison of the particle size and settling velocity with specific gravity of 2.8 in water at 10 °C is given (Tebbutt, 1983).

Table 1.4: Particle size and settling velocity, Smoluchowski (1917).

Particle size (µm)	Settling velocity (m/s)
1000	6×10^2
100	2×10
10	3×10^{-1}
1	3×10^{-3}
0.1	1×10^{-5}
0.01	2×10^{-7}

Smoluchowski (1917) postulated that the most rapid coagulation occurs when every contact of particles in a colloidal system causes the adherence of one particle to another. There is an assumption from Smoluchowski's (1917) research which states that all collisions lead to attachment irrespective of other forces such as electrostatic repulsion, van der Waals or hydrodynamic forces (Flynn, 1984).

Adler (1981) conducted an investigation relating to the theory of hydrodynamic interactions in hetero-dispersed systems using equations for laminar flow conditions. The findings show that collision frequencies were the highest when colliding particles subjected to hydrodynamic, electrostatic and van der Waals forces were of the same size. Thomas *et al.* (1996) calculated the collision efficiencies of hydrodynamic forces for various size ratios of particles which collide, showing a comparison on curvilinear and rectilinear models with the following conditions:

- Collision frequencies are less or equal to 0.5 s^{-1} in perikinetic flocculation.
- Collision frequencies are less or equal to 5 s^{-1} in orthokinetic flocculation.
- Collision frequencies are less or equal to $2 - 3 \text{ s}^{-1}$ for differential sedimentation.

Han *et al.* (1992) presented the numerical expressions which relate the correction factors for the conversion of the rectilinear model to the curvilinear model. The expressions showed a direct relation as the functions of the size ratio of colliding particles and the ratio of the hydrodynamic shear forces to van der Waals forces between colliding particles. Han *et al.*, (1992) compared curvilinear collisions between particles of all sizes in the range $1\text{-}1000 \text{ }\mu\text{m}$ and developed the following:

- Orthokinetic flocculation not being important in the curvilinear than rectilinear model.
- The curvilinear model predicts a lower collision frequency than in the rectilinear model and the reduction in collision frequency becomes less when the particles are of same size.
- Orthokinetic flocculation is no longer directly proportional to local velocity gradient (G), as predicted by Camp *et al.*, (1968) as shown by Equation 56.

$$G = (\varepsilon/\nu)^{1/2} \quad (56)$$

ε = energy dissipation

ν = kinetic viscosity

A high velocity gradient has been recommended for the dispersion of the coagulant (Binnie *et al.*, 2003). However, rapid mixing induces turbulence which is regarded as a cascade of eddies which increases in size when mixing intensifies. In a flocculator stirred with an impeller these high values of G will occur close to the tip of the impeller. It is probable that breakage occurs in these regions of high shear intensity rather than in the more quiescent areas way from the impeller. This condition of breakage occurs due to rapid mixing of the impellor, which forms part of the investigations in this study about an alternative mechanical agitation (shaking).

The collision of the colloidal particles which is induced by mechanical agitation was extrapolated by Han *et al.*, (1992) in a mathematical expression. The expressions showed a direct relation as the functions of the size ratio of colliding particles and the

ratio of the hydrodynamic shear forces to van der Waals forces between colliding particles. The two precepts are most succinctly expressed mathematically as a rate of successful collision between particles of size i and j in Equation 57.

$$\text{rate of flocculation} = \alpha\beta(i, j)n_in_j, \quad (57)$$

α = collision efficiency, $\beta(i, j)$ = collision frequency between particles of size i and j , and n_i, n_j = particle concentrations for particles of size i and j , respectively.

The collision frequency β is a function of the mode of flocculation, i.e. perikinetic, orthokinetic or differential sedimentation. The collision efficiency, α (taking values from 0 to 1), is a function of the degree of particle destabilisation. The greater the degree of destabilisation, the greater is the value of α . Thus, in effect, β is a measure of the transport efficiency leading to collisions, whilst α represents the percentage of those collisions leading to attachment. Smoluchowski (1917) developed the following analytical expressions for the collision frequency for both perikinetic and orthokinetic flocculation:

$$\beta_{\text{perikinetic}} = (2kT/3\mu)(1/d_i + 1/d_j)(d_i + d_j), \quad (58)$$

$$\beta_{\text{orthokinetic}} = (1/6)(du/dy)(d_i + d_j)^3, \quad (59)$$

k = Boltzmann's constant, T = absolute temperature of the fluid, μ = fluid viscosity, and du/dy = velocity gradient of the fluid.

Eqs. 58 and 59 are based upon the fact that the collision efficiency factor (α) is unity for all collisions, a fluid motion undergoes laminar shear, the particles are monodispersed (all of the same size), there is no breakage of flocs, all particles are spherical in shape and remain so after collision and the collisions involve only two particles. Smoluchowski (1917) produced solutions to the set of differential equations for both perikinetic and orthokinetic flocculation, the solution for orthokinetic flocculation as:

$$N_t = N_0 \exp(4/\pi)(du/dy)\phi t, \quad (60)$$

N_t = total particle count at time t , N_0 = the initial particle count and ϕ = volume fraction of the particles, which is assumed to be constant and given by $(4/3)a^3 N_0$, a = particle radius.

Camp *et al.*, (1968) extended Smoluchowski's equation for orthokinetic flocculation by substituting the fluid shear velocity, du/dy , with the authors' definition of the fluid's root-mean-square velocity gradient, G :

$$\beta(i, j) = (G/6)(d_i + d_j)^3 \quad (61)$$

The same authors found the collision frequency for differential sedimentation to be given by Eq. 62.

$$\beta(i, j) = g\pi/72\mu)(\rho_p - \rho_1)(d_i + d_j)^3 |d_i - d_j|, \quad \text{Eq. 62}$$

g = gravitational constant, ρ_p and ρ_1 = particle and fluid densities respectively.

1.10 Research Overview

A sample of AMD with various coagulant dosages added, was used in all experiments of this study, using a jar test during rapid mixing and shaking at a constant speed respectively as well as coagulation-flocculation without mixing. The supernatant was extracted to measure the pH, conductivity and turbidity and the coagulants which were used include Fe^{3+} or Al^{3+} salts, Ca^{2+} and Mg^{2+} hydroxides, polymers consisting of FeCl_3 and Ca^{2+} or Mg^{2+} hydroxides. The AMD and treated samples were analysed by means of TGA, SEM, XRD and FTIR for characterization of the metal salts present. The sludge of the samples with Fe^{3+} and Al^{3+} salt dosages were heated in an oven to determine their water holding capacity.

Experiment 1

AMD samples were poured into glass beakers. The samples were dosed with varying amounts of Fe^{3+} and Al^{3+} salts. The samples were treated in a jar test and a shaker at constant speed, for 2 minutes, settled for 1 hour after which the pH, conductivity and turbidity were measured. Another batch of experiments was conducted whereby wastewater was dosed with the same coagulants and dosages but there was no mixing or shaking. The samples were allowed to settle and the same measurements were conducted. A third batch of similar experiments was conducted where the dosages were done before and during mixing or shaking respectively. Similar settling time

and measurement were conducted as mentioned before. A forth batch of experiments was conducted on an AMD sample dosed with FeCl_3 and treated in a jar test with rapid mixing for various time periods respectively. Similar settling time and measurements were conducted as before.

Experiment 2

A batch of experiments was conducted using AMD samples with varying dosages of synthetic polymers prepared by a mixture of FeCl_3 and $\text{Ca}(\text{OH})_2$ to form af-PFCl of $\text{Ca}(\text{OH})_2$. The samples were treated in a jar test or a shaker for 2 minutes at constant speed, then settled for 1 hour after which the pH, conductivity and turbidity were measured. A similar batch of experiments was conducted using the same dosages with shaking at constant speed for 2 minutes and the other batch of experiment was without mixing, and similar measurements were conducted. A third batch of experiments was conducted using Ca^{2+} in $\text{Ca}(\text{OH})_2$ with shaking at 250 rpm for 2 minutes and the other batch of experiment was without mixing with similar measurements conducted.

Experiment 3

A batch of experiments was conducted with AMD with varying dosages of Fe^{3+} in FeCl_3 in a jar test and a shaker at constant speed for 2 minutes, after which the samples settled for 1 hour and then the pH and turbidity were measured. A similar

batch of experiments was conducted with synthetic polymers prepared by a mixture of FeCl_3 and Mg^{2+} in $\text{Mg}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ to form a af-PFCl of $\text{Mg}(\text{OH})_2$ polymers. The samples were treated in a jar test and a shaker at constant speed for 2 minutes and allowed to settle for 1 hour after which the pH and turbidity were measured. A third similar batch of experiments was conducted with different concentrations of af-PFCl of $\text{Mg}(\text{OH})_2$ respectively, with measurements done in the manner as described previously.

1.11 Objectives

In this study the objective of is to investigate and determine the following factors:

- The optimal dosage of Fe^{2+} , Fe^{3+} , Al^{3+} salts and synthetic polymers of FeCl_3 and metal hydroxides of Ca or Mg for effective destabilization-hydrolysis in AMD without pH adjustment.
- The time-frame within which optimal flocs are formed during rapid mixing.
- Obtain a comparison of turbidity removal efficiency between Fe^{2+} , Fe^{3+} , Al^{3+} salts and the polymers of the combination of synthetic polymers of FeCl_3 and $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ in the AMD with mixing, shaking and without mixing.
- Determination of the destabilization potential and the neutralizing effect of Ca^{2+} or Mg^{2+} ions in their respective metal hydroxide (using pH and turbidity as determinants).

- Determining of the rate of flocculation (flocs formation-adsorption) at varying time intervals.
- Determining the effect of bivalent and trivalent metal ions (M^{2+} or M^{3+}) on a double layer of the aqua-colloids.

1.12 Benefits of the study

The findings in this study will encourage the coal and gold mining industry to focus on AMD treatment during and after operations by dosing cost effective synthetic polymers. Although the capital costs to erect an AMD treatment plant could be high, there is a good return-on-investment to re-use treated effluent or avoid penalties against contamination of AMD to the ecosystem. In this work the focus was on the synthetic polymers which can replace the costly commercial polymers and also attributes to optimal and affordable AMD treatment, mainly to remove the toxic and heavy metals. Unlike the acid content in AMD which can be neutralized by adding metal hydroxide reagents, toxic and heavy metals pose serious detrimental consequences to the rivers and eco-system, hence it is imperative to focus on the treatment techniques to ensure their removal. The correlation between pH and hydrolysis during coagulation-flocculation, determine the most effective metal salt(s) and ideal concentration of metal ion that can adsorb a considerable amount of colloidal particles (turbidity removal), determine optimal dosages, mixing dynamics to produce water effluent of good quality without re-stabilization or flocs rupture,

identify proper retention time during treatment to achieve a better sedimentation, determine metal hydroxide which can be used for pH adjustment without any harm, identify a convenient and fast laboratory testing technique for the production of good quality effluent, effect of rapid and slow mixing in flocs formation, effect of monoprotic and diprotic reagents in wastewater treatment.

It must also be understood that the study include some of the reagents/coagulants such as $\text{Ca}(\text{OH})_2$ and Al^{3+} salts which have shown some short-comings. This does not indicate that they are ideal for the applications but are used for comparison as they have shown desirable effectiveness. The former is known for its environmental hazardousness and blockage of the pipeline whereas the latter for its association with Alzheimer disease.

Since coal and goal mining requires an enormous amount of process water, the treatment of the AMD and recycling of the effluent can be a better option as that will also eliminate the accumulation of AMD after operation. Adopting such an approach may be useful more especially in the abatement of raw water abstraction from the rivers, which would reduce the risk of water shortage.

1.13 Challenges in AMD treatment

A number of cases which has been reported on AMD spillages and contamination emanated from closed mines, which is a clear indication that mining operations do not generate AMD but expose the FeS_2 to any immediate oxygen and flowing water

attack. The reaction of the three components results in ferrous ions and sulphuric acid as shown by Equation 2. The other problem is that many coal and gold fields do not have wastewater treatment facilities to treat their AMD during operations so that on-going treatment may proceed. However, even if such facilities are available, some AMD result from the reaction of FeS_2 , O_2 and H_2O as mentioned (Equation 2), a situation which is unavoidable. A vast amount of research has been conducted on coagulation-flocculation focussing more on neutralization, oxidation of Fe^{2+} and crystallization of gypsum. The electrochemistry element has not been investigated, to determine the reactivity between aqua-colloid and solvated metal ion. Adsorption stays an unclear concept because some researchers stated that the hydrolysis species (flocs) are adsorbed onto the colloidal particles whereas others stated that the colloidal particles are embedded in the agglomerates (Ives, *et al.*, 1978, Jiang *et al.*, 1997, Peavy *et al.*, 1995).

1.14 Findings

In the study the following observations were found:

1.14.1 Reactivity of Fe^{3+} and Al^{3+} salts in AMD sample with mixing or shaking

Chemical reactivity between hydrated metal salts and colloidal particles is a spontaneous process and not influenced by mixing. The pH adjustment is unimportant

when treating highly acidic AMD with trivalent Fe^{3+} and Al^{3+} salts. Shaking is an ideal technique to disperse coagulant throughout the colloidal suspension to eliminate high shear forces which cause rupturing of the flocs.

1.14.2 Effect of dosing prior or during mixing or shaking on turbidity removal in AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$.

The results obtained also indicated that the addition of coagulants to AMD prior or during mixing or shaking does not affect the rate of the turbidity removal. Similarly equal turbidity removal values of FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ indicate that the flocs which are formed consist of a filter-cake structure which is an adsorption substrate.

1.14.3 Comparison of turbidity removal from the AMD sample with FeCl_3 or $\text{Ca}(\text{OH})_2$ and af-PFCl polymer of $\text{Ca}(\text{OH})_2$.

A synthetic af-PFCl polymer yielded a better turbidity removal which is comparable to that of FeCl_3 or $\text{Ca}(\text{OH})_2$, indicating that all three coagulants have the same destabilization potential. The pH and residual turbidity in the corresponding sample with mixing, shaking and without mixing exhibit an insignificant difference. The af-PFCl polymer of $\text{Ca}(\text{OH})_2$ is an ideal replacement of both reagents due to their corrosive and environmental degradation implications. The af-PFCl polymers also show a high spontaneous reactivity as it yielded a better turbidity removal in the samples without mixing and with shaking.

1.14.4 Comparison of turbidity removal from the AMD sample with AlCl_3 and af-PFCl polymer of $\text{Mg}(\text{OH})_2$.

The AlCl_3 and af-PFCl polymer of $\text{Mg}(\text{OH})_2$ yield high turbidity removal in the AMD samples treated without pH adjustment, with FeCl_3 showing slightly lower values. The formation of the precipitates does not depend on the pH but the ionic strength of the metal ion to destabilize the colloidal suspension. The turbidity removal efficiency in af-PFCl polymer of $\text{Mg}(\text{OH})_2$ shows that it can be used as a replacement coagulant for metal salts. The SEM images show that the sludge in the samples with af-PFCl polymer of $\text{Mg}(\text{OH})_2$ dosage consists of a large cake-like structure which is symbolic of optimal adsorption.

1.14.5 Reaction dynamics

The experimental results (turbidity removal) revealed that dosing prior or during rapid mixing is immaterial as the results are identical. The rate of destabilization determines the rate of hydrolysis, both are dependent on the ionic strength of the reagent/coagulant (electro-negativity or -positivity). Turbidity removal in both rapid mixing and shaking for 2 minutes indicates that optimal floc formation occurs during coagulation process.

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CHAPTER 2: Reaction dynamics of iron and aluminium salts dosage in AMD using shaking as an alternative technique in the destabilization-hydrolysis process

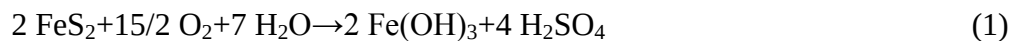
Abstract

The experiments were conducted in the AMD samples using Fe^{3+} and Al^{3+} salts as coagulants in a jar test (mixing), shaker (shaking) and without mixing. A 200 mL solution of acid mine drainage (AMD) was poured into five 500 mL glass beakers. A dosage of 20, 30, 40, 50 and 60 mL of 0.043 M FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ was added in the middle of the samples respectively using plastic syringes. The samples settled for 1 hour after which the pH, conductivity and turbidity were measured. A second similar set of experiments was conducted by pouring the AMD sample into five 500 mL Erlen Meyer flasks, equal quantities of coagulants were added and the samples were placed in a shaker using similar stirring method. A third similar set of experiments were conducted in a jar test with rapid mixing for 2 minutes, settled for 1 hour, and similar measurements were done. The results showed turbidity removal in AMD samples with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage during mixing, shaking and without mixing is similarly identical. Turbidity removal was still effective in AMD using inorganic coagulants without pH adjustment. Experimental results show that the ionic concentration and charge density in the system (wastewater) during treatment determines the rate of destabilization-hydrolysis.

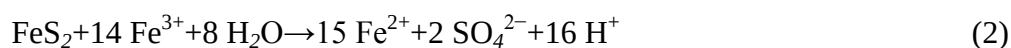
Key words: AMD, pH, turbidity, mixing, shaking, coagulants

2.0 INTRODUCTION

Wastewater treatment is a complex process which is integrated into a variety of physical and chemical reactions. The choice of the reagents used in the treatment plays a crucial role as their reaction efficiency of determines the effectiveness of the reactions. Both physical and chemical processes play a pivotal role and are also complementary due to their electrochemical characteristics. A lot of research has been conducted on AMD to determine an appropriate technique and reagents (organic and inorganic) which can produce wastewater effluent of good quality. The main problem encountered in AMD treatment is its complexity due to its mineral content. The AMD consists mainly of ferric/ferrous sulphites (FeS_x), mainly pyrite (FeS_2). This compound is oxidized in aqueous solution to form sulphuric acid (Eq. 1), and a lot of other salts dissolve due to the acidic state of the medium.



A further oxidation of pyrite by the Fe^{3+} is inevitable, generating more AMD as shown by Eq. 2.



A lot of research has been conducted on AMD employing various technologies, but more study still needs to be conducted. The main challenge is to identify the appropriate coagulants/flocculents, dosage (mol/L), dispersion technique to achieve

optimal turbidity removal. Labeschagne *et al.* (2005), Geldenhuys *et al.*, (2001), Johnson *et al.*, 2006a, Johnson *et al.*, 2006b, Sibrell *et al.*, (2009), Wei *et al.*, (2009) and Wei *et al.*, (2010) employed conventional method using lime-, dolomite-neutralization, iron oxidation, gypsum crystallization and activated carbon treatment techniques. Some diversified employing more complicated technologies such as co-treatment of AMD solution with the municipality wastewater using activated sludge (Bratby, 2006 and Santos *et al.*, 2011). Sewage effluent with relatively high concentrations of suspended solids may enhance iron oxyhydroxide precipitation by encouraging iron, which is often present in high concentrations in AMD, to form flocs (Johnson *et al.*, 2006, Neto *et al.*, 2010 and Winfrey *et al.*, 2010). Further research was extended by Feng *et al.*, (2004) using blast furnace slag, whereas Petrik *et al.*, (2003) and Xenidis *et al.*, (2000) used fly ash and fly ash leachate without liming agents. New technological approach was such as distillation, reverse osmosis, carbon nanotubes, Fenton's reagent, wet oxidation, advanced oxidation, coagulation-electro oxidation was also explored. These techniques are complex, incur high costs and do not cover a wide range of the wastewater poor quality. This study employed the use of inorganic coagulants, Fe^{3+} and Al^{3+} salts in AMD sample without pH adjustment. The choice of these salts in this study is based on their abundance and the easy and an affordable technique when using them. Another aspect is that their chemical reactivity in AMD sample has not yet been elucidated, an approach intended in this study. Although a research on these salts has been accomplished, it was on a normal water/wastewater treatment with a pH adjustment, a condition which is different in this study. Another varying aspect is the dispersion technique which is

employed in this study, i.e. comparison between mixing, shaking and no-mixing. The ideal objective of using Fe^{3+} and Al^{3+} salts is not only to determine their reactivity in AMD sample, but to compare their turbidity removal efficiencies when AMD sample is treated with mixing, shaking and without mixing. It also covers their turbidity removal efficiencies when added to highly acidic wastewater for treatment without pH adjustment. The comprehensive study will identify the factors which contribute towards effective destabilization/diffusion to achieve optimal hydrolysis and adsorption.

Mixing plays a principal process which plays a pivotal role in a chemical reaction as it disperses the reagent(s) throughout the system in order to induce chemical reaction(s). Some authors such as Freeze *et al.* (2001), Swartz *et al.* (2004) and Aboulhassan *et al.* (2006) identified rapid and prolonged mixing as the cause of re-stabilization by rupturing of flocs due to shear forces, resulting in poor turbidity removal as will be discussed later. Experiments in our study are conducted without mixing and the other are with shaking, mainly to determine a treatment approach which will eliminate breakage of flocs. A lot of studies by Amuda *et al.*, (2006), (1997), Gregory *et al.*, (2006) and Bolto *et al.* (2007) recommended mixing (rapid or slow) for chemical dispersion throughout the solution. On the contrary, Jiang *et al.*, (1997), Molony, 2005, Amuda *et al.*, (2006) and Ghaly *et al.*, (2006) stated that rapid mixing and over-dosing can result in re-stabilization and de-flocculation. According to Law of diffusion, the ionic metal salts (Fe^{3+} or Al^{3+}) are added to a highly acidic AMD sample and ionic diffusion (destabilization) occurs (Figure 2.1)

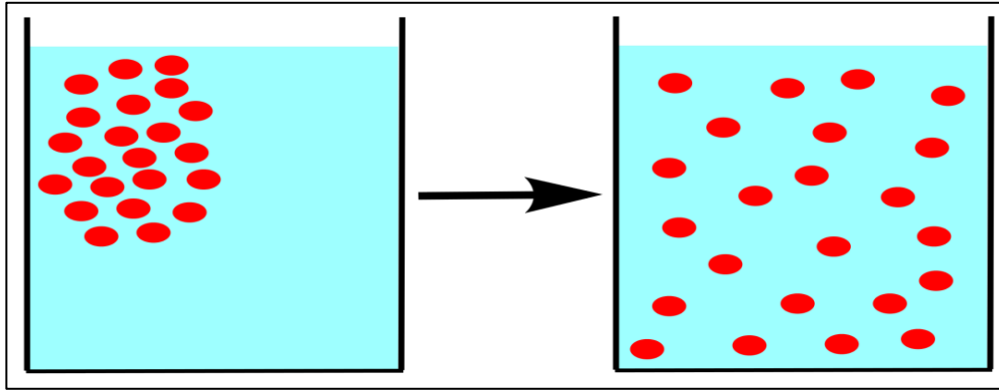


Figure 2.1: Diagram showing diffusion of the ions in the solution (Smith, 2004)

The first diagram of Figure 2.1 shows the addition of an ionic reagent, where ions are concentrated within a confined volume. The second diagram of Figure 2.1 shows the ions dispersed throughout the solution, a similar situation occurring with diffusion during destabilization reaction. It can be postulated that the dispersion of the ions is activated by the thermal energy within the system, including other energies such as bond energy, chemical energy, enthalpy.

Recent research has shown that mixing in non-turbulent flows can be greatly enhanced by complicated particle behaviour which is caused by chaotic advection. Chaotic advection is derived from non-linear dynamics and used to investigate transport and mixing problems in fluid flows. The motion of the individual particles can be described by ordinary differential equations as shown by Equation 3.

$$\frac{dx}{dt} = u(x,y,t), \quad \frac{dy}{dt} = v(x,y,t), \quad (u \text{ and } v = \text{two dimensional flow fields}) \quad (3)$$

The above two-dimensional advection equations are integrable if the flow is steady, while for unsteady flow they may be non-integral. Integrable solutions of the advection equations lead to regular advection, and the non-integrable cases are characterized by chaotic advection which can be described as particle motion sensitive to initial conditions, i.e., initially nearby trajectories diverge at an exponential rate.

Mixing induces the chain reactions such as destabilization-hydrolysis during coagulation-flocculation process. Coagulation is the destabilization of the colloid after the addition of the coagulants when the electrostatic forces of repulsion are reduced and van der Waals forces of attraction increase. Flocculation is a subsequent reaction which occurs when larger flocs are formed through velocity gradient and differential velocity of colloidal particles (Kemmer, 1988). The former is explained as the partial derivative of velocity with reference to position within a continuous medium, usually fluid (dv/dx) whereas the latter is the formation of larger flocs due to Brownian motion of the fluid. Coagulation process depends on the dosage whereas the latter depends on the mixing effect (Dao *et al.*, 2001). Coagulation-flocculation leads to nucleation, crystal growth and aggregation of the destabilized suspended particles in the solution (Kemmer, 1988, Wu *et al.*, 2006, Sharp *et al.*, 2006a and Sharp *et al.*, 2006b). The type of particles such as hydrophilic (water-loving) or hydrophobic (water-hating), in the colloidal suspension determines the effectiveness of a coagulant to be dosed. Natural organic material (NOM) in water controls the dosages and selection of coagulant (Fabris *et al.*, 2008). NOM contains hydrophobic

compounds (humic and fulvic acids) and hydrophilic fraction (Wall *et al.*, 2003). Hydrophilic colloids are difficult to treat because electrostatic forces which surround hydrophilic colloids induced by dipolarity of water molecules form a barrier which deters any chemical reaction upon colloidal suspension. The chemically bound or dipolar water molecules (which surround the colloids), or adsorbed water molecules on the particles, causes stability of the colloidal suspension (Wulfsberg, 1987). Apart from the dipolar effect of water molecules, there are some other forces which attributes to stability through their counter-ionic nature. This occurs as a result of the interaction between positive and negatively charged ions due to electrical forces of repulsion and van der Waals forces of attraction in a colloidal suspension (dipole-dipole force, dipole-induced dipole force and dispersion forces (Kurniawan *et al.*, 2006, Ives, 1978, Goldberg *et al.*, 2002 and Sulkowski *et al.*, 2005). Apart from the nature of colloids, particles size, degree of stability of colloids, mineral/salts content, pH, valence of coagulant also play pivotal role.

In this study destabilization, which is influenced by the physico-chemical properties of the reagents and the dispersion dynamics as the key process to effective coagulation-flocculation, has been identified. This is coupled by the electrovalence of the reagents which are dosed in the wastewater (Hubell *et al.*, 2003, Meghzili, 2008, Water Specialist Technology, 2003, Aboulhassan *et al.*, 2006 and Scholtz, 2010). Heavily concentrated wastewater AMD contains different minerals and also has a high ionic movement, which results in a highly reactive tendency (Tayler *et al.*, 1990, Niesen *et al.*, 2005, Edwards *et al.*, 2007, Nielsen *et al.*, 2008a, Nielsen *et al.*, 2008b,

Firer, 2008 and Sinha *et al.*, 2013). The transport of ions may also be affected by various chemical reactions that occur within the material. Ions can react with other species present in the pore solution to form new compounds (Tayler *et al.*, 1990). They can also interact with other ions found in the double layer at the surface of the pores, or eventually be bound to the various solid phases forming the skeleton of the porous material. The chemical reactions can also be very important since highly concentrated colloidal suspensions are very reactive (Tayler *et al.*, 1990 and Skalny *et al.*, 2001). The reactivity of the coagulant is determined by its strength to compress an electrical double layer (EDL). von Helmholtz (1879) discovered EDL and stated that it is formed by a layer of positive ions which surround the central negative ions and the mixture of positive and negative ions bound together by coulomb forces in a diffuse layer (Lee, 2001, Haselberg, 2009, Kosmulski, 2004, Cosgrove, 2005, Crittenden *et al.*, 2005, Ananikov *et al.*, 2005, Bratby, 2006 and Scholtz, 2010). Figure 2.2 is a schematic diagram of a colloidal particle showing charged layers.

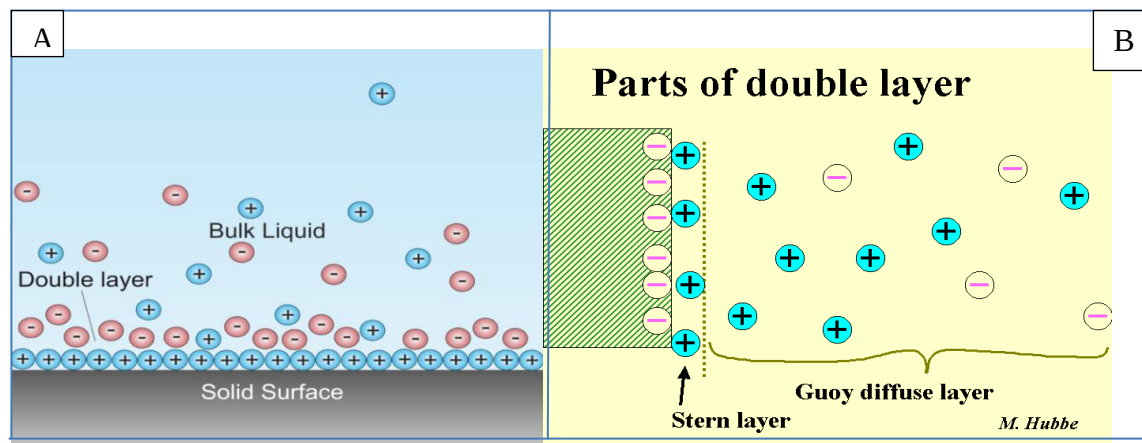


Figure 2.2: Double layer showing electrical charges (von Helmholtz *et al.*, 1879).

When charged particles move relative to a liquid due to sedimentation, ions from the bulk flow into the lower part of the double layer tangentially around the particle and return to the bulk solution via the upper half of the double layer. This is the area which has an impact in double layer compression during destabilization (Ives, 1978, Duan *et al.*, 2002 and Meghzilli, 2008). The interface of a charged surface has been explained by the models of Helmholtz, Gouy and Chapman (Field *et al.*, 1988). Stern later combined these models and further developed the model of the EDL. In this model there is an inner region and an outer diffusion region. In the inner layer ions are tightly bound to the surface, and move about under the influence of diffusion in the outer layer. According to the Gouy-Chapman model, the potential distribution in a flat double layer can be described by Equation 4:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\rho}{\varepsilon} \quad (4)$$

ψ = potential at a point in the diffuse layer versus infinity at the bulk solution, ρ = charge density at the same point and ε = permittivity.

During the process, the electrostatic potential in shear plane (i.e. potential that exists between bulk liquid and an envelope of water that moves with particle), as in Figure 2.1 and it is expressed by Equation 5.

$$Z_n = \frac{4\pi qd}{D} \quad (5)$$

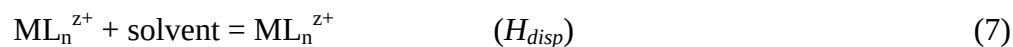
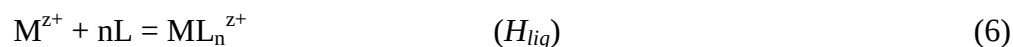
q = charge on the particle, d = thickness of the layer surrounding the shear plane and D = dielectric constant of liquid.

As mentioned above, a lot of researchers recommended mixing as one of the factors which influences effective destabilization. It disperses coagulants throughout the colloidal suspension by inducing shear forces through a velocity gradient (du/dy), change of velocity per change of distance. Velocity gradient is induced by the speed of the impellers during mixing and determines the rate of destabilization (Sincero *et al.*, 2003 and Metcalf, 2003). Binnie *et al.* (2003) stated that an excellent design of mixing devices requires a high velocity gradient, which can be as high as 1000 s^{-1} with minimum chemical dosage. Fe^{3+} and Al^{3+} salts produce best results at a velocity gradient between 20 and 70 s^{-1} (Swartz *et al.*, 2004). An EDL, (Figure 2.1), plays a pivotal role during destabilization-hydrolysis during the coagulation process (Cheng, 2002, Sincero *et al.*, 2003, Eikebrokk, 2007 and Widderska-Broz *et al.*, 2009). The scope of this study is to investigate the destabilization-hydrolysis process focusing on the physical and chemical properties as shown in Table 2.1.

Table 2.1: Chemical and physical properties of iron and aluminium atoms

Description	Iron	Aluminium
Electronegativity	1.8	1.5
VanderWaals radius	0.126 nm	0.143 nm
Ionic radius	0.076 nm (2+)	0.05 nm (3+)
Ionic radius	0.064 nm (3+)	0.05 nm (3+)
Electronic shell	[Ar] $3d^6 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^1$
Density	7800 kg/m^3	2700 kg/m^3
1 st ionization energy	761 kJ/mol	577.4 kJ/mol
2 nd ionization energy	1556 kJ/mol	1816.1 kJ/mol
3 rd ionization energy	2951 kJ/mol	2744.1 kJ/mol
Standard potential	-0.44 V (Fe^{2+})	-1.67 V (Al^{3+})
Standard potential	0.77 V (Fe^{3+})	

Table 2.1 shows properties which play a pivotal role during the destabilization process. Energy and double layer, among others, are very influential factors which cannot be marched. According to Suzuki (1990), the metal ions are attracted to six water molecules to form a hexagonally hydrated metal ion molecule using enthalpy of hydration. When the atomic number increases, the ionic size also increases, leading to a decrease in the absolute values of enthalpy of hydration. Atomic number and enthalpy of hydration in Fe and Al is 26 and 13, -4430 and -4665 kJ/mol respectively. Enthalpy of hydration is a combination of energy of ligation (H_{lig}) and dispersion (H_{disp}). The former is the amount of energy released when the solvent forms a coordination compound with the ions, and the latter is energy released when the hydrated metal ion is dispersed into the solvent (Rodriguez-Cruz *et al*, 1999). Equations 6 and 7 show the reactions leading to the release of both energies.



During the formation of a compound or a solution, enthalpy is the type of energy in the process. It is then converted to potential energy and is stored in the chemical bonds of the compound. During a chemical reaction, the chemical bonds break and potential energy stored is released (Rodriguez-Cruz *et al*, 1999). The amount of enthalpy of formation correlates with the potential energy released during a chemical reaction, the concept we predict in this study. Arrhenius theory states that chemical

energy is utilized during the self-exchange system $\text{Fe}^{2+}/\text{Fe}^{3+}$ on the vibration of the six water molecules around the iron ions thereby inducing vibration of the nucleus and jumping of electrons during redox. The overall enthalpy change in forming a solution is the sum of the energy changes for each of these processes, and it is represented in Equation 8.

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_{n-1} \quad (8)$$

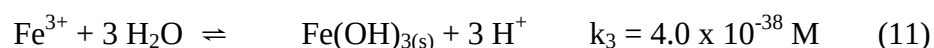
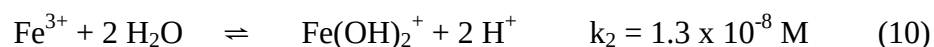
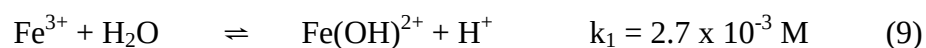
In our context, we would assume that the same energy utilization applies during hydrolysis, as the metal ions are reduced throughout speciation. Solubility is another factor which plays a major role during the formation of hydrolysis species. Table 2.2 shows the solubility constant of Fe^{3+} and Al^{3+} which can be used to determine the pH range at which a particular metal hydroxide is formed.

Table: 2.2: Hydrolysis and solubility constants for Al^{3+} and Fe^{3+} for zero ionic strength and 25 $^{\circ}\text{C}$. (Wesolowski *et al.*, 1994 and Flynn, 1984)

Metal ion	pK ₁	pK ₂	pK ₃	pK ₄	pK _{Sam}
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6.0	10.0	33.0

The experiments in this study involves treatment of AMD using FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$. A lot of research has been conducted on AMD using metal salts and metal hydroxide in aqueous solution such as lime neutralization, pyrite oxidation and gypsum crystallization. The uniqueness in our study is that inorganic coagulants (metal salts) dosage is done in AMD without pH adjustment in order to investigate chemical

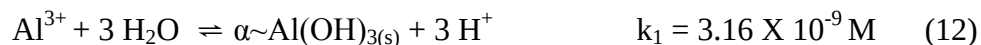
reactivity in solvation. The pH of wastewater during treatment changes inconsistently and that disrupts the rate of hydrolysis remarkably. The addition of acid or base for pH adjustment is not ideal because over-dosage may result in excess H^+ or OH^- in wastewater. Excess OH^- will take part during hydrolysis by competing with OH^- from the solution as shown in Eqs. 9-11, thereby disturbing the equilibrium state, which may result in the re-stabilization or de-flocculation. This will also occur with acid neutralization, whereby excess protons will decrease the pH to more acidic. There are two coordination complexes formed during hydrolysis of a metal ion, namely octahedral and tetrahedral, the former are acidic and the latter basic (Moore *et al.*, 1978). The structure of the octahedral complexes is shown in Eqs. 9-11.



Equations 10 and 11, revealed that that more precipitates are formed during hydrolysis, thus causing optimal adsorption of turbid material. The species shown in Equation 11, a stable species shows the highest adsorption efficiency (low solubility). This is an indication of the adsorption potential of the ferric hydroxide species.

Aluminium mainly occurs as $Al^{3+}_{(aq)}$ under acidic conditions, and since the formation of hydrolysis species in Equations 12-14 depends on the pH of the solution, the first

species, a small fraction of Al(OH)^{2+} is formed at pH range 3 to 6; the other species exist at pH values above 6.



Similar to Equations 10 and 11, all the species shown by Equations 12-14 have low solubility, which indicates that adsorption in Al^{3+} salt occurs in all three species. Duan (2003) stated that adsorption occurs in several steps such as hetero-coagulation, sweep-flocculation and further charge neutralization of natural organic compounds (NOC), a comparison of the reactions between Fe^{3+} and Al^{3+} salts will be investigated using turbidity removal. The correlation between the anionic components (Cl^- and SO_4^{2-}) of the aqua-metal salts and protonation (H^+) during hydrolysis has not been investigated, that will be investigated in this study. Percentage turbidity removal is calculated in the Eq. 15.

$$\text{Removal efficiency (E \%)} = \frac{C_0 - C_i}{C_0} \times 100 \quad (15)$$

Where C_0 and C_i are the initial and residual concentration of the wastewater effluent (mg/L) respectively.

2.1 MATERIALS AND METHODS

In this study, coagulation-flocculation treatment has been applied to AMD using 20, 30, 40, 50 and 60 mL of 0.043M Fe^{3+} in FeCl_3 and 0.043 M Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ dosages respectively. The pH, conductivity and turbidity in the samples are measured before and 1 hour after treatment. A 200 mL sample of AMD was poured into five 500 mL glass beakers. Dosages of 20, 30, 40, 50 and mL coagulants were added to the samples using 100 mL plastic syringes respectively. The samples settled for 1 hour, and then the pH, conductivity and turbidity were measured. A similar set of experiments was conducted by putting the samples on a shaker at 250 rpm for 2 minutes, the samples settled for 1 hour before the pH, conductivity and turbidity were measured. A third similar set of experiments was conducted using a jar test at 250 rpm for 2 minutes, settled for 1 hour and pH, conductivity and turbidity were measured.

2.1.1 Acid mine water sample

The samples were collected from the Western Decant in Krugerdorp in a 25 litres plastic drum. The sample was air-tied and stored at room temperature. The pH, conductivity and turbidity of the AMD sample was 2.56, 4.43 mS/cm and 100 NTU respectively. The solid content of the sample was 6.8 g in a 200 mL of AMD.

2.1.2 Coagulants

Inorganic coagulants of 0.043 M of Fe^{3+} and Al^{3+} ions (a concentration obtained from the literature) are dosed for coagulation-flocculation of the AMD. The concentrations are chosen as per a study conducted by Fasemore (2004) on paint wastewater treatment.

The calculation of the mass of metal salt to obtain 0.043 M of M^{3+} ($\text{M}^{3+} = \text{Fe or Al}$) is as follows:

Monoprotic metal salts (MCl_3)

$$0.043 \text{ M of } \text{M}^{3+} \times \text{mass of } \text{M}^*\text{Cl}_3 \cdot 6\text{H}_2\text{O} \quad (\text{M}^* = \text{Fe or Al}) \quad (16)$$

Diprotic metal salts ($\text{M}_2(\text{SO}_4)_3$)

$$0.043 \text{ M of } \text{M}^{3+} \times \text{mass of } \text{M}^*_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} / 2 \quad (\text{M}^* = \text{Fe or Al}) \quad (17)$$

Table 3 shows monoprotic and diprotic metal salts dosed into acid mine water samples.

Table 2.3: Monoprotic and diprotic metal salts dosed into acid mine water samples

Salt	Mass of salt (g)	Concentration (mol/L)	M^{3+} concentration (M)
FeCl_3	7.00	0.043	0.043
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	13.6	0.022	0.043

2.1.3 Procedure in jar tests.

The equipment used for the jar tests was a *BIBBY Stuart Scientific Flocculator (SW1 model)*, which has six adjustable paddles with rotating speeds between 0–350 rpm. A 200 mL sample of AMD containing 6.8 g of solid particles was poured in each of the five 500 mL glass beakers for the test. Rapid mixing was set at 250 rpm for 2 minutes, followed by slow mixing at 100 rpm for 10 minutes, a normal standard.

2.2 EXPERIMENTS

2.2.1 Experiment A: Treatment with mixing-Jar test

The pH, conductivity and turbidity of the sample were measured. Five 500 mL glass beakers were filled with 200 mL samples of AMD with a pH, conductivity and turbidity of 2.56, 4.43 mS/cm and 100 NTU respectively. The samples were dosed with 20, 30, 40, 50 and 60 mL of 0.043 M Fe^{3+} in FeCl_3 or 0.043 M Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ respectively, placed in the jar test and were stirred at 250 rpm for 2 minutes to disperse the reagents throughout the solution and thereafter settled for 1 hour. After settling the pH, conductivity and turbidity were measured.

2.2.2 Experiment B: Treatment without mixing

The same parameters were measured before treatment. Five 500 mL glass beakers

were filled with 200 mL samples of AMD with a pH, conductivity and turbidity of 2.56, 4.43 mS/cm and 100 NTU respectively. The samples were dosed with 20, 30, 40, 50 and 60 mL of the FeCl_3 or $\text{Al}_2(\text{SO}_4)_3$ respectively (the concentrations are given in Table 2.1). The samples were allowed to react with the coagulant for 1 hour (same duration as above) and the same parameters were measured.

2.2.3 Experiment C: Treatment with shaking

The same parameters were measured before treatment. Five 500 mL glass beakers were filled with 200 mL samples of AMD with a pH, conductivity and turbidity of 2.56, 4.43 mS/cm and 100 NTU respectively. The samples were dosed with 20, 30, 40, 50 and 60 mL of the FeCl_3 or $\text{Al}_2(\text{SO}_4)_3$ respectively. Samples were poured into a shaker with 250 rpm rapid mixing for 2 minutes. The samples settled for 1 hour and the same parameters were measured.

2.3 PERFORMANCE AND EVALUATIONS

The pH was used as a determinant to assess the rate of hydrolysis and hydrolytic potential of coagulants (Fe^{3+} and Al^{3+} salts) at different mixing duration, whereas the concentration and turbidity were measured to determine the ionic potential and removal of colloidal particles from the samples respectively.

2.3.1 pH measurement

A MettlerToledo Seven Multimetric (*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 pH of 4.0 and 7.0 before use.

2.3.2 Conductivity

A EDT instrument FE 280 conductivity-meter (*made in Japan*) was used and calibrated with 0.1 KCl standard solution.

2.3.3 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 measure. It was calibrated with 0.10, 10, 100, 1000 and 10000 NTU standard solutions.

2.3.4 Scanning electron microscopic analysis

KYKY-EM3200 Digital Scanning Electron Microscope (model EM3200) equipment (*made in China*) was used.

2.3.5 X-Ray Diffractometry analysis

A XRD (Model Rigaku) diffractometer with CuK radiation at 150 mA and 50 kV were used in this study.

2.4 EXPERIMENTAL RESULTS

Figures 2.3 and 2.4 show the pH of AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing, and the conductivity in AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing respectively.

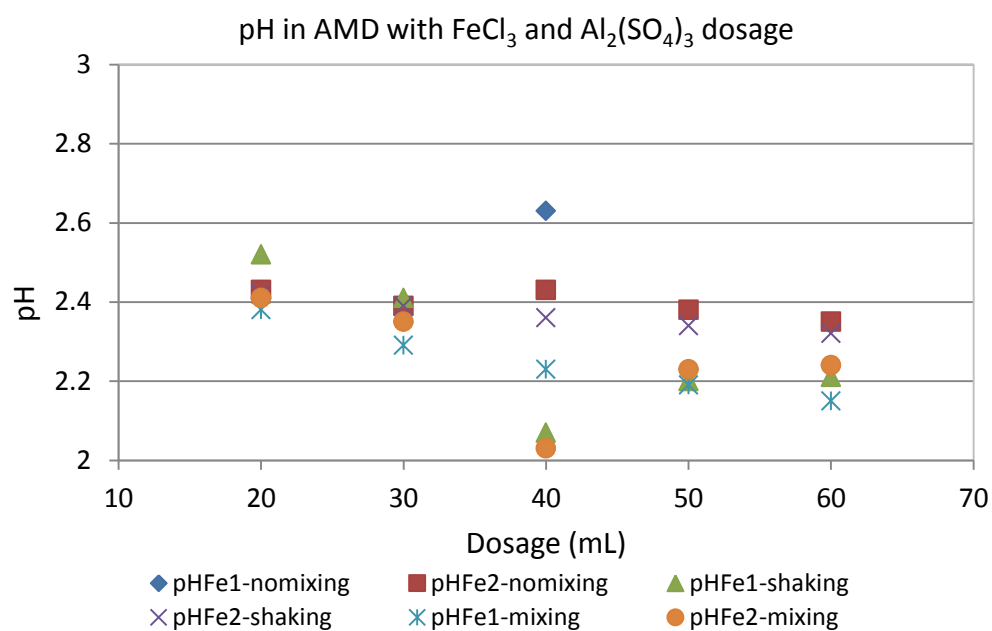


Figure 2.3: pH of AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing.

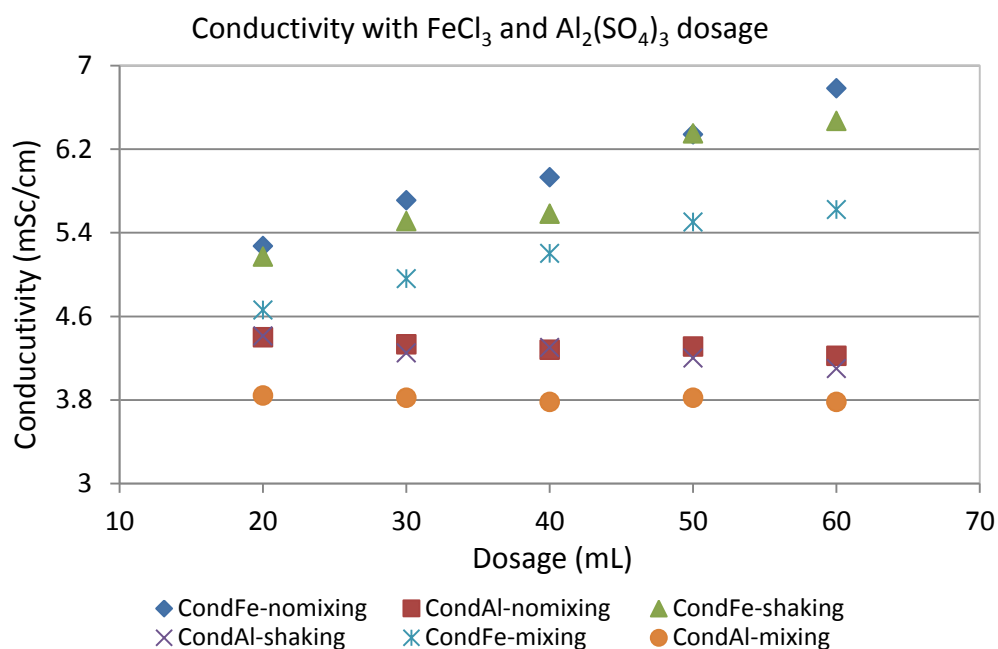


Figure 2.4: Conductivity in AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing.

Figures. 2.5 and 2.6 show the turbidity of AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing, and the pH vs residual turbidity of FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ before mixing and shaking respectively.

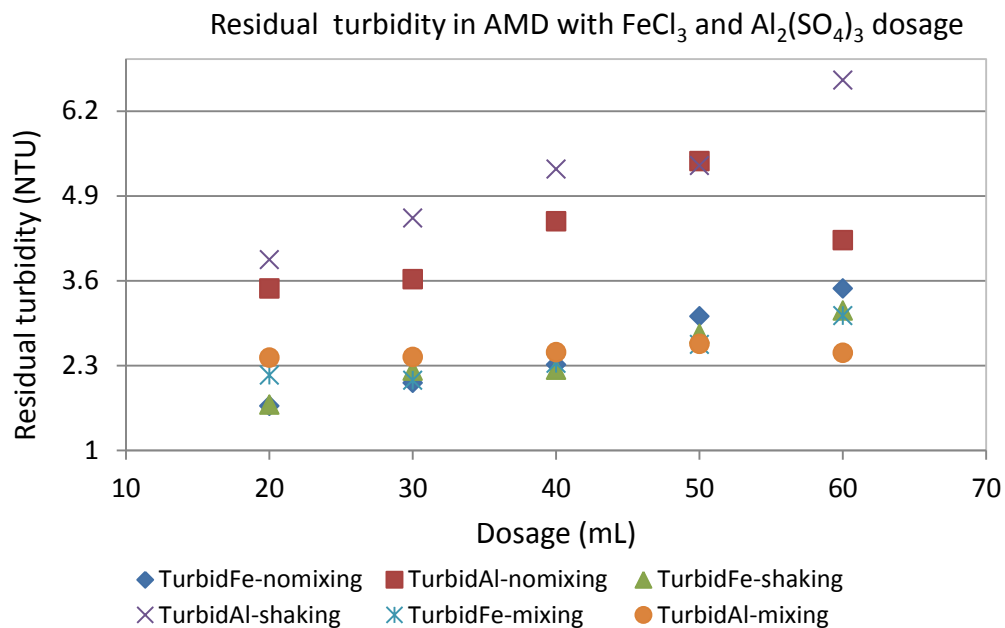


Figure 2.5: Turbidity of AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ with mixing, shaking and without mixing.

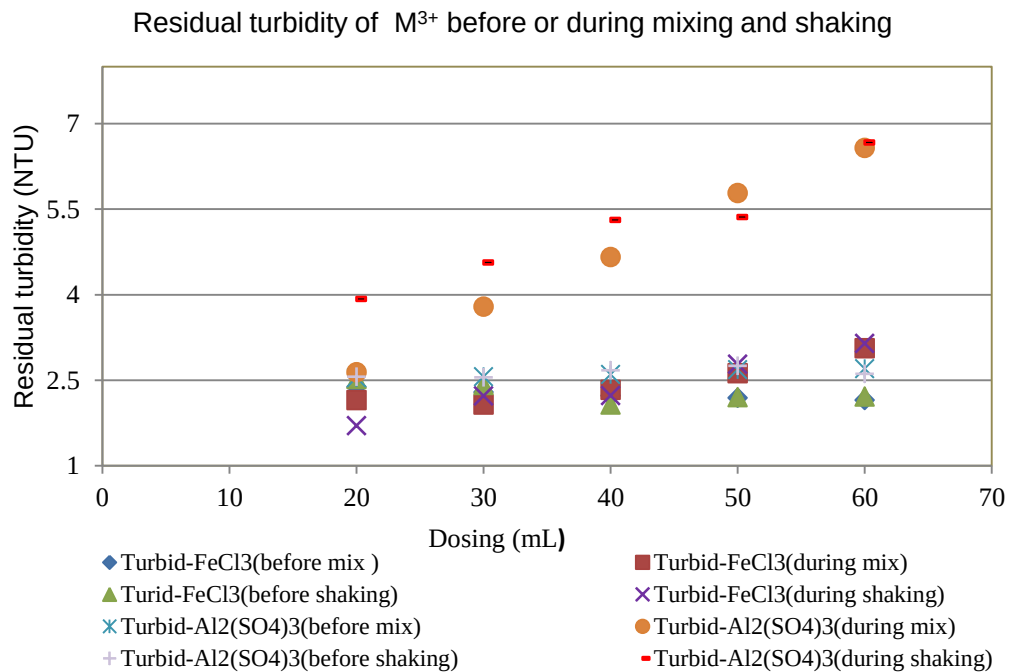


Figure 2.6: pH vs residual turbidity of FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ before mixing and shaking.

Figure 2.7 shows the pH and $E\%$ and mass ratio of Fe^{3+} or Al^{3+} and solid in solution.

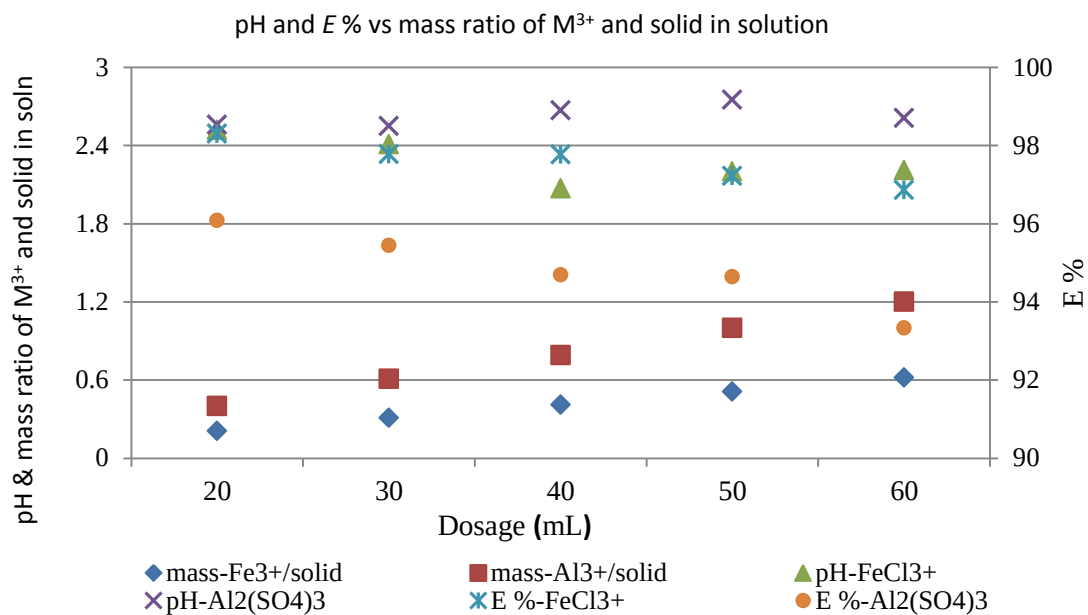


Figure 2.7: pH and E % and concⁿ ratio of Fe³⁺ or Al³⁺ and solid in solution.

Figures 2.8 and 2.9 show the mass of Fe³⁺ in FeCl₃ vs residual turbidity with shaking and the mass of Al³⁺ in Al₂(SO₄)₃ vs residual turbidity with shaking.

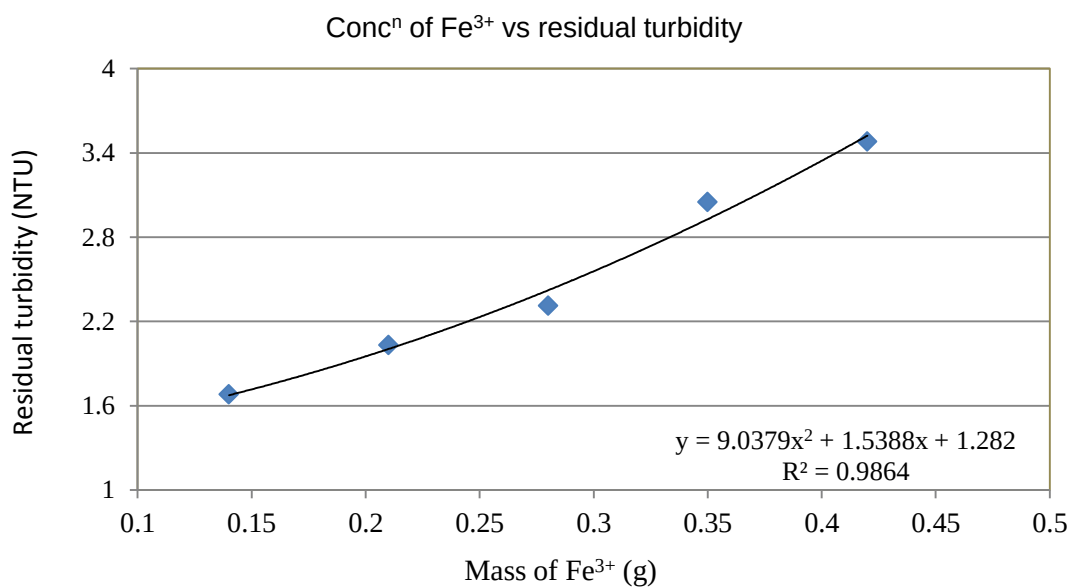


Figure 2.8: Concentration of Fe³⁺ in FeCl₃ vs residual turbidity with shaking.

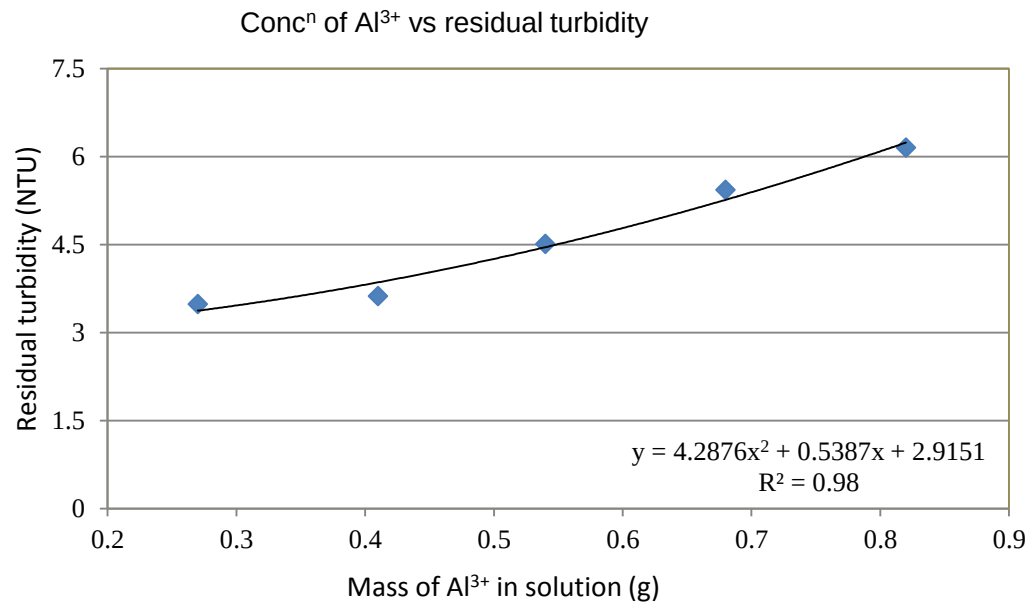


Figure 2.9: Concentration of Al³⁺ in Al₂(SO₄)₃ vs residual turbidity with shaking.

Figures 2.10 and 2.11 show the turbidity removal efficiency vs conductivity with FeCl₃ dosage and the turbidity removal efficiency vs conductivity with Al₂(SO₄)₃ dosage.

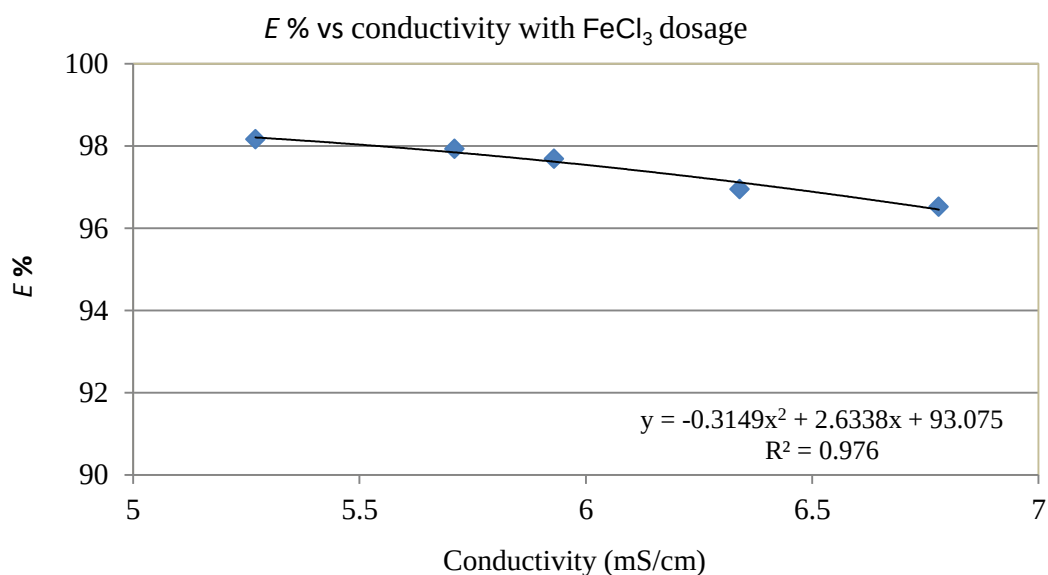


Figure 2.10: Turbidity removal efficiency vs conductivity with FeCl₃ dosage.

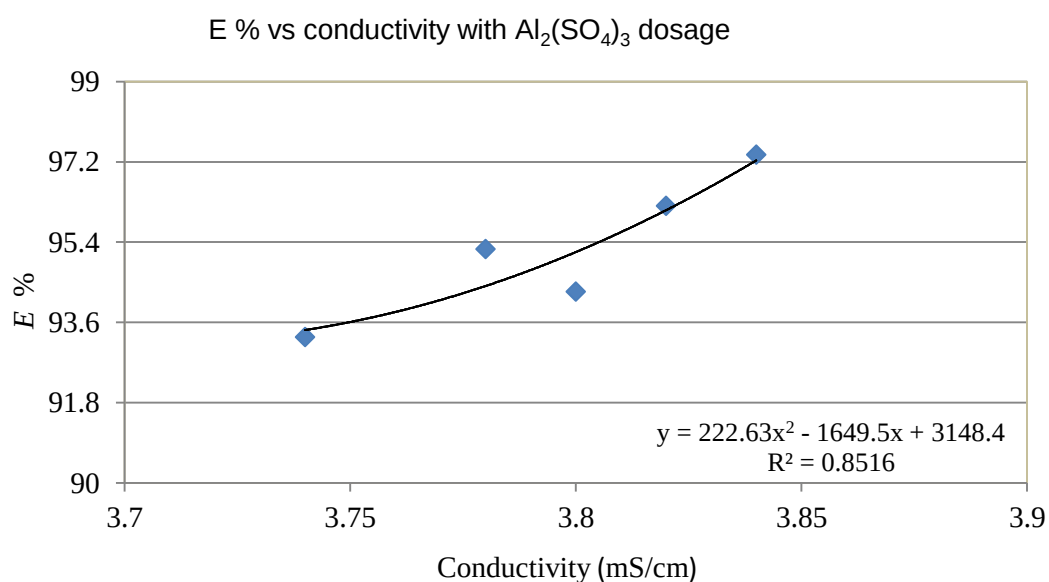


Figure 2.11: Turbidity removal efficiency vs conductivity with Al₂(SO₄)₃ dosage.

Figures 2.12 and 2.13 show the SEM micrographs obtained from the sludge of the AMD samples with FeCl₃ dosage during shaking and mixing, and the SEM micrographs obtained from the sludge of the AMD samples with Al₂(SO₄)₃ dosage during mixing and without mixing (25000x).

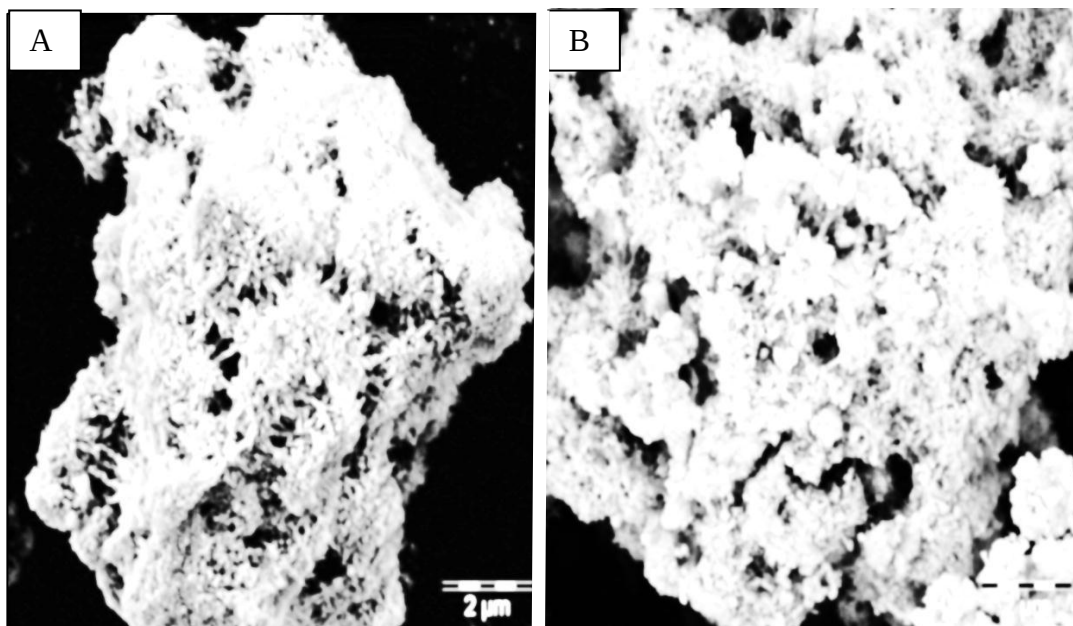


Figure 2.12: SEM micrographs obtained from the sludge of the AMD samples with FeCl_3 dosage, A=shaking and B=mixing (25000x).

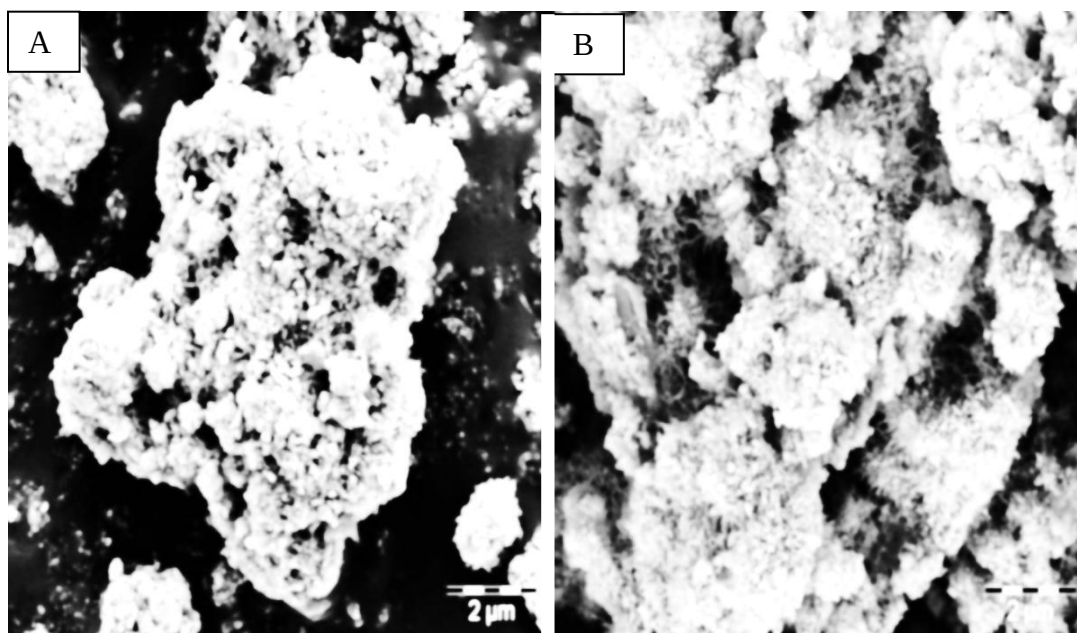


Figure 2.13: SEM micrographs obtained from the sludge of the AMD samples with $\text{Al}_2(\text{SO}_4)_3$ dosage, A=mixing and B=without mixing (25000x).

Figure 2.14 shows X-ray diffractogram of the AMD sludge with FeCl_3 dosage with shaking.

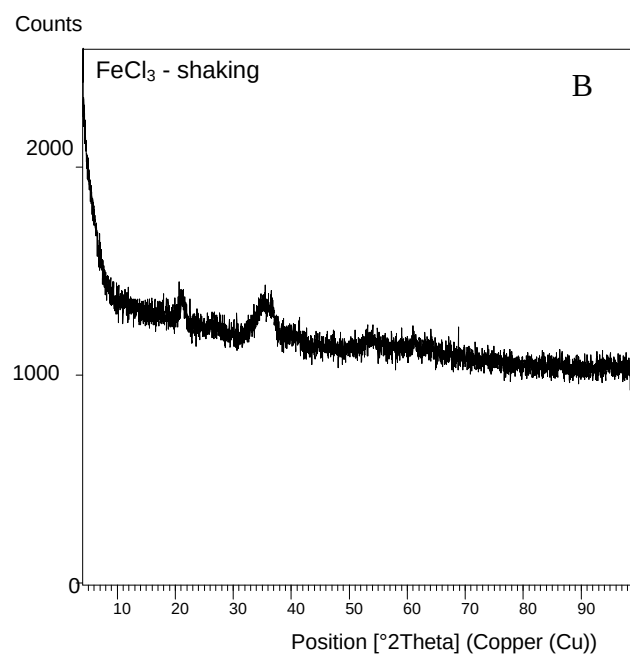
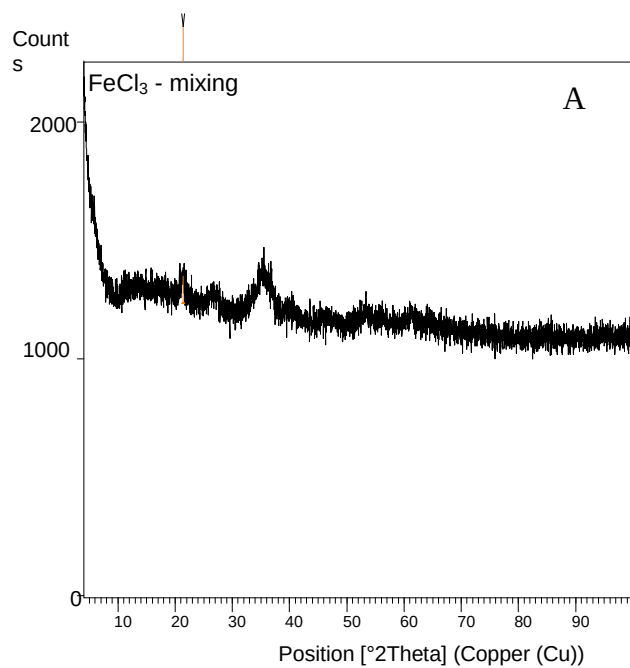


Figure 2.14(A) and (B): Diffractogram of the AMD sludge with FeCl₃ dosage with shaking.

2.5 DISCUSSION

Figure 2.3 shows that the pH in samples with FeCl_3 dosage (rapid mixing) decreases from 2.56 (untreated AMD) to a range of 2.38-2.15 and the trend decreases with increasing dosage. The pH of the samples with shaking shows a decreasing trend and became constant between 20-30 mL and 50-60 mL dosage respectively (2.52-2.41 and 2.20-2.21 respectively). The pH in the sample with 40 mL dosage is the lowest (2.07). The pH in samples without mixing showed a similar changing trend, i.e. decreasing trend between 20 and 30 mL (2.41-2.35), and constant trend between 50 and 60 mL (2.23-2.24) FeCl_3 dosage, while 40 mL dosage also yielded a lowest pH (2.03). The pH in samples with $\text{Al}_2(\text{SO}_4)_3$ dosage (rapid mixing) also decreases in a range of 2.66-2.54, also decreases with increasing dosage. The pH of the samples with shaking showed a constant trend and decreased between 20-30 mL (2.56-2.55) and 50-60 mL (2.75-2.61) dosage respectively. The pH in the sample with 40 mL dosage is the second highest with a value of 2.67.

Figure 2.4 shows that the conductivity in samples with FeCl_3 (rapid mixing) exhibit an increasing trend with increasing dosage in a range of 4.66-5.62 mS/cm, whereas in samples without mixing it is slightly higher in a range of 5.27-6.47 mS/cm; the range in the samples with shaking is 5.17-6.45 mS/cm. Conductivity in samples with $\text{Al}_2(\text{SO}_4)_3$ (rapid mixing) shows an inconsistent changing trend with increasing dosage in a range of 3.78-3.84 mS/cm, without mixing and with shaking is in a range of 4.22-4.40 mS/cm respectively.

Figure 2.5 shows the residual turbidity in the samples with mixing ranges from 2.15-3.06 NTU, whereas in the samples without mixing and with shaking is in a range of 1.68-3.48 and 1.70-3.14 NTU respectively. Turbidity in samples with $\text{Al}_2(\text{SO}_4)_3$ dosage (rapid mixing) is in a range of 2.64-6.73 NTU, whereas in the samples without mixing and with shaking is in a range of 3.48-6.15 and 3.92-6.67 NTU respectively.

Figure 2.6 is a comparison between pH and residual turbidity in AMD with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage between sample dosing between mixing and shaking. The comparison was to determine the changing trend in both pH and turbidity removal between the samples which has been treated in a jar test and shaking.

Figure 2.7 shows the relation between the pH and turbidity removal efficiency in AMD with a mass of solid metal ions (g of Fe^{3+} or Al^{3+}) in 200 mL of solution. The rationale was to determine the amount of metal ions which undergo hydrolysis and adsorption processes with varying dosing rates.

Figures 2.8 and 2.9 show the relation between the mass of the Fe^{3+} in FeCl_3 and Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ in 200 mL of AMD sample which precipitated to form flocs that participated during the adsorption of the colloidal particles in the AMD during shaking. The choice of the samples with shaking was based on the correlating changing trend of both the residual turbidity and the dosage.

Figures 2.10 and 2.11 show the correlation between turbidity removal efficiency and conductivity in AMD with 0.043 M FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage. The rationale was to determine the effect of conductivity in hydrolysis as increasing dosages cause an increase in dissolved ions in the solution, thus increasing the conductivity.

Figures 2.12 and 2.13 show the SEM micrographs of FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage with mixing-shaking and mixing-without mixing respectively; showing the morphological structure of the sludge of treated AMD sample. Figure 2.12 shows SEM micrographs of the samples with FeCl_3 dosage with shaking and mixing using 25000 magnification, whereas Figure 2.13 are samples with $\text{Al}_2(\text{SO}_4)_3$ dosage, with and without mixing respectively using 25000 magnification. Figure 2.14 represents the XRD images of AMD sludge with FeCl_3 dosage with mixing and shaking.

Figure 2.14 (A) and (B) shows XRD results on the residual copper in AMD samples with FeCl_3 in a jar test (mixing) and shaking respectively. Results shown by the sample without mixing are also identical to those with mixing and shaking, including the samples with $\text{Al}_2(\text{SO}_4)_3$ dosage employing similar methods (mixing, shaking and without mixing). The values are identical, which indicates that mixing, without mixing and shaking, has similar minerals reduction potential. Based on the possibility of poor turbidity/TSS reduction due to the rupturing of the flocs during severe rapid mixing due to shear stress/forces, it is recommended that mixing must be replaced by shaking technique.

Table 2.4: pH vs % turbidity removal efficiency in AMD with FeCl₃ and Al₂(SO₄)₃ dosage

Coagulant	R ² -value	Model
FeCl ₃ -mixing	0.9996	$y = -34.658x^2 + 160.93x - 88.836$
Al ₂ (SO ₄) ₃ -mixing	0.9862	$y = 20.533x^2 - 139.21x + 318.33$
FeCl ₃ -no-mixing	0.8898	$y = 35.964x^2 - 157.54x + 269.26$
Al ₂ (SO ₄) ₃ -no-mixing	0.9493	$y = -144.8x^2 + 744.11x - 859.32$
FeCl ₃ -shaking	0.8900	$y = 17.484x^2 - 78.555x + 185.33$
Al ₂ (SO ₄) ₃ -shaking	0.8121	$y = -35.111x^2 + 177.67x - 129.01$

The changing trend of the pH plays a pivotal role as it indicates the formation of the specific hydrolysis species (Flynn, 1984) and also indicates the rate of hydrolysis (Ntwampe *et al.*, 2013a).

Figure 2.3 shows that the pH in samples with 0.043 M Fe³⁺ in FeCl₃ dosage rapid mixing in a range of 2.15-2.38, and fluctuates with increasing dosage; whereas the pH in the samples without mixing and with shaking is in a range of 2.03-2.41 and 2.07-2.52 respectively. The lowest pH is obtained in the samples with 50 and 60 mL (mixing), 40 mL (without mixing) and 40 mL (shaking). According to Flynn (1984), maximum adsorption occurs in a stable metal hydroxide species (M(OH)_{3(s)}), Equations. 11 and 14, and that is corroborated the study conducted by Ntwampe *et al.*, (2013a) which states that the rate of hydrolysis is inversely proportional to the pH (high turbidity removal efficiency). The amorphous ferric hydroxides (am~Fe(OH)_{3(s)}), which are the first species to formed at low solubility (Faust *et al.*, 1983) assists the stable ferric hydroxide species with turbidity removal. Apart from the turbidity removal by those species, other species such as dimer and polymer of both Fe³⁺ and Al³⁺ salts are formed (Flynn, 1984, Faust *et al.*, 1983). It is suggested

that the kinetic aspect during speciation has an impact in the hydrolysis reaction, and that will be elaborated on under the turbidity removal discussion.

Figure 2.3 shows that the pH in samples with 0.043 M Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ dosage (rapid mixing) is in a range of 2.56-2.66, and also fluctuates with increasing dosage, whereas the pH in the samples without mixing and with shaking is in a range of 2.53-2.70 and 2.55-2.75 respectively. Unlike FeCl_3 , all the samples show that the $\text{Al}_2(\text{SO}_4)_3$ has a lower pH suppressing ability compared to FeCl_3 .

This can be explained by the reaction of chloride from FeCl_3 to form HCl , which dissociates completely to form H^+ and Cl^- . It is postulated that the H^+ ions suppress the pH of the solution. In the case of $\text{Al}_2(\text{SO}_4)_3$, the protons (H^+) combine with SO_4^{2-} ions to form H_2SO_4 , which then dissociates to form H^+ and HSO_4^- ions. A further dissociation occurs to form H^+ and SO_4^{2-} which can also shift backwards to H^+ and HSO_4^- , thus behaving as a buffer (Ghaly *et al.*, 2006).

The $\text{Al}_2(\text{SO}_4)_3$ behaves similar to FeCl_3 by forming different species during hydrolysis. However all the species formed with $\text{Al}_2(\text{SO}_4)_3$ exhibit low solubility (Equations 12-14), which also indicate that adsorption is maximal. Aluminium hydroxide species are formed at a pH range of 3-6, which is slightly higher than the values obtained in Figure 2.3. The high turbidity removal shown by $\text{Al}_2(\text{SO}_4)_3$ indicates that most of the turbid material are adsorbed by amorphous aluminium hydroxides ($\text{am}\sim\text{Al}(\text{OH})_{3(s)}$) as in the with FeCl_3 (Flynn, 1984).

The conductivity in this study is an indication of the concentration of the ions which has been added to the solution from 4.43 mS/cm in untreated AMD sample.

According to the previous studies, conductivity has not been considered as a parameter which influences turbidity removal efficiency. In this study, the correlation between pH, conductivity and turbidity was investigated to determine the effect of conductivity during hydrolysis. When the metal salts of FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ are added to an aqueous solution, the Fe^{3+} and Al^{3+} are hydrated/solvated, to form $\text{M}(\text{H}_2\text{O})_6^{3+}$, whereas the conjugated acid component (Cl^- and SO_4^{2-}) dissolve in the solution, and that increases ionic charge in the system (Figure 2.4). The other charged trace elements also add to the conductivity and increase the electric conductance of the solution, contributing to electropositive property in the colloidal suspension. Figure 2.4 shows that the conductivity in the samples without mixing is slightly higher compare to the samples with mixing and shaking. It is inferred that this might be due to the lack of mechanical agitation as occurring in both mixing and shaking, i.e. the equilibrium state is stable. It is suggested that active anions react with some cationic elements in AMD and form precipitates, thus reducing turbidity. The ionic concentration in the samples with FeCl_3 is slightly higher than in the samples with $\text{Al}_2(\text{SO}_4)_3$, in a range of 5.30-6.56 and 3.74-3.83 mS/cm respectively.

As a jar test is a simulation of the water treatment purification plant, the operating parameters should be identical. The most important parameter in mixing is the speed of the impellor, as high speed may break the flocs and reduces the surface area of the flocs (Oldshue, 1983). The liquid which is nearer to the impeller experiences maximum kinetic energy whereas above and below is forced upwards and downwards by shear forces respectively. One of the models relating to collision

which is induced by mixing (Suzuki, 1990) assumes that if two or more particles come close together, they collide and form a larger particle. The closeness that determines the collision of the particles to occur is defined as “zone of influence” and if the zones of two particles overlap, then the particles will agglomerate. It is imperative to calculate the Reynolds number to determine the intensity of mixing during the experiments conducted in a jar test applying Eq. 18. Sarti *et al.* (2004) used 1.13 g/cm and 1 g/cm.s for density and viscosity of the wastewater respectively to calculate the Reynolds number. Diameter of a beaker = 8.5 cm, impellor speed = 250 rpm:

$$Re = \frac{\rho V D}{\mu} \quad (18)$$

$$\begin{aligned} V &= \frac{250 \text{ rpm} \times 2\pi \text{ rad}}{60 \text{ sec} \times 4.25 \text{ cm}} \\ &= 111.3 \text{ cm/s} \\ Re &= \frac{1.13 \frac{\text{g}}{\text{cm}} \times 111.3 \frac{\text{cm}}{\text{s}} \times 8.5 \text{ cm}}{\frac{1 \frac{\text{g}}{\text{cm}}}{\text{s}}} \\ &= 1069.03 \end{aligned}$$

The Reynolds number indicates that the flow of the fluid during mixing is laminar, which indicates that destabilization-hydrolysis in our experimental jar test is not influenced by the intensity of mixing. Since the speed of an impellor in a jar test is set at 250 rpm, this suggests that the energy induced during mixing is a summation of

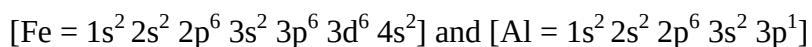
optimal destabilization energy. The low residual turbidity obtained in the AMD samples which were treated in a jar test is influenced by low stirring intensity (no shear forces) as calculated in Eq. 18. This indicates that the laminar condition of the impellor speed of the clarifier can yield a relatively low residual turbidity, a condition which is impossible as is not a design condition of any large-scale clarifier. It is therefore recommendable to replace high speed mixing with high speed shaking to achieve optimal turbidity removal (Figure 2.5).

Since both coagulants (Fe^{3+} and Al^{3+} salts) exhibit a very low residual turbidity (high removal efficiency), but that minute change is elucidated in this study so that a clear understanding about turbidity reduction in a highly acidic AMD sample are stated. The decreasing rate of the pH values with increasing dosage from 2.56 to as low as 2.03 (Figure 2.3) is an indication of an effective turbidity removal (Ntwampe *et al.*, 2013a). The residual turbidity in both Fe^{3+} and Al^{3+} salts, (Figure 2.5) is essential in the determination of the reactivity efficiency between a monoprotic and diprotic metal salt (FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$). They are both trivalent, and van der Waals radii, the radii, and ionization energy, are the three distinct properties which separate them, i.e. 0.126 and 0.143 nm, 0.064 and 0.05 nm and 5268 and 5137 kJ/mol respectively as shown in Table 2.1. The difference in residual turbidity of the AMD samples with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ dosage during mixing, shaking and without mixing is insignificant (Figure 2.5). According to the conductivity of untreated AMD sample (4.43 mS/cm) and the ionic distribution in Figure 2.2, it is evident that the AMD sample has a high ionic charge due to its highly acidic state (high ionic density from

H⁺ ions). The conductivity (4.43 mS/cm) obtained in the AMD sample therefore shows that the colloidal suspension has a remarkable ionic charge, and exhibits spontaneous reaction property, which is confirmed by Jiang *et al.*, (1997), Kurniawan *et al.*, (2006) and Meghzili, (2008) stating that a colloidal suspension with high ionic charge or high charge density is highly reactive. It is therefore reasonable to suggest that the low residual turbidity in the AMD samples without mixing is due to spontaneous destabilization-hydrolysis due to the addition of metal salts (Fe³⁺ and Al³⁺) with a high valence electron (Figure 2.2). That is in agreement with the findings by (Duan *et al.*, 2002 and Ntwampe *et al.*, 2013a) that destabilization-hydrolysis depends on the characteristics of the colloidal suspension and the metal salt. Another confirmatory statement is the high values shown by the combined energies of Fe and Al which released when they react (Equations 6 and 7). This indicates that diffusion which occurs during destabilization (Figure 1) is caused by chemical activation energy stored in the compound/reagents (Rodriguez-Cruz *et al.*, 1999). This energy (enthalpy), which was converted to potential energy and stored in the chemical bonds of the compound, is released during collision of the molecules which is induced by Brownian motion, in cases where there is no mechanical energy (AMD sample without mixing, Figures 2.5 and 2.6). Equation 8 shows the overall energy which is available in a compound during a chemical reaction. Arrhenius theory which states that chemical energy is utilized during the self-exchange system on the vibration of the six water molecules around the metal ions thereby inducing vibration of the nucleus and jumping of electrons during redox, also corroborate the reaction without mixing. It is suggested that the collision frequency and vibration of the charges

(mainly positive) (Arrhenius theory) determine the rate of destabilization. This occurs during a double layer compression due to ionic strength of the metal ions (M^{n+}) added.

Since chemical reaction involves ionization energy during hybridization of the metals (Wulfsberg, 1987), there is likelihood that the electron configuration of both metal ions influences the process (reactivity efficiency):



It has been mentioned that ionization energy plays a role in determining the reactivity between Fe and Al, and that is explained by energy released during hybridization. The Fe atom loses 3 electrons, two occupying 4s-orbital and one occupying 3d-orbital whereas Al loses one electron occupying 3p-orbital and two occupying 3s-orbital. There is less energy used in Fe atom to remove one electron from a pair in 4s-orbital, more energy to remove the second unpaired electron, and less energy to remove a one pair electron from 3d-orbital. There is more energy in Al atom to remove a single electron from 3p-orbital, less energy to remove one electron from a pair in 3s-orbital, and more energy to remove the second electron from 3s-orbital. The Fe atom has one unpaired electron in 3d-orbital (active), whereas there are three paired electron in Al atom (inactive). According to the results of hybridization, Fe exhibits a more active property compared to Al, a suggestion which may be associated with its low residual turbidity values.

Based on the explanation and the values obtained in Table 2.1, it shows that the hydrated Fe^{3+} has more electron affinity than Al^{3+} , which suggests that it is more reactive than Al^{3+} . This collaborates with the turbidity values shown in Figs. 4 and 5, where Fe^{3+} exhibits higher turbidity removal efficiency than Al^{3+} . This is confirmed by a study conducted by Ntwampe *et al.*, (2013a) on paint wastewater with Fe^{3+} and Al^{3+} salts also revealed that turbidity removal with a monoprotic salt (FeCl_3) is slightly higher than the diprotic salt of $\text{Al}_2(\text{SO}_4)_3$. However, this observation is not rigid with the wastewater sample dosed with synthetic polymers prepared with inorganic acid-free metal salts (Ntwampe *et al.*, 2013b). They suggested that a better turbidity removal with diprotic metal salts might be caused by further adoption of residual particles onto the particles during the second dissociation (Chang *et al.*, 2004). Since acidic AMD has a high concentration of protons (H^+), each mole of divalent $(\text{SO}_4)^{2-}$ reacts with two moles of protons which obliterates the formation of secondary flocs during orthokinetic flocculation. Although the reaction still occurs with the monoprotic salt, the buffering property of both FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ does not affect pH changing trend, but turbidity removal as seen in Figures 2.4 and 2.5.

The results in Figure 2.6 show that there is no significant difference in the pH and the turbidity removal in the samples with FeCl_3 or $\text{Al}_2(\text{SO}_4)_3$ dosing before mixing or shaking compared to dosing during mixing or shaking. The overall turbidity removal efficiency with both coagulants is in a range of 94.6-98.3 %. This correlates with our objective to replace jar testing with shaking in order to avoid high shear force which results in the rupturing of the flocs during rapid mixing. Figure 2.6 also confirms that

the mass of Fe^{3+} or Al^{3+} in a 200 mL of solution yielded relatively equal pH and turbidity removal efficiency in the range of 2.51-2.79 or 2.10-2.48 and 94.6-95.3 or 96.7-98.4 % respectively.

Figures 2.8 and 2.9 show the correlation between the concentration of Fe^{3+} and Al^{3+} and turbidity removal efficiency. The mass of hydrated metal ions added to a solution changes the pH of the system, which shows a correlation with turbidity removal efficiency. The R^2 with both Fe^{3+} and Al^{3+} salt is 0.985 and 0.980 (98.5 and 98.5 %) respectively, which indicates that there is a correlation between the pH and turbidity removal efficiency. A study by Ntwampe *et al.*, (2013a) using alkaline paint wastewater with Fe^{3+} and Al^{3+} salts showed that the rate of change of pH determines the rate of hydrolysis. Pratt *et al.*, (2007) and Kosmulski *et al.*, (2004) mentioned that pH is one of the significant parameters that determine the reduction efficiency of minerals in the wastewater, the statement corroborated our experimental results. On the contrary, our results differ with Jiang *et al.*, (1997) and Widderska-Broz *et al.*, (2009) when they stated that addition of Al^{3+} and Fe^{3+} salts at pH of 6-8 fastens the rate of hydrolysis, leading to very rapid precipitation and optimal turbidity removal. This may only be applicable to wastewater treatment with pH adjustment. Pearson correlation coefficient (r) is employed to calculate the relation between pH and residual turbidity.

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (19)$$

According to the correlation coefficient, (0.70 or higher is very strong relationship), (0.40-0.69 is a strong relationship), and (0.30-0.39 is moderate relationship). The data on the pH vs E % using FeCl_3 during mixing and shaking is shown in Table 2.5.

Table 2.5: pH vs E % in samples with FeCl_3 dosage with mixing and shaking.

Dosage	20	30	40	50	60
pH-mixing	4.66	4.96	5.20	5.50	5.62
E %-mixing	97.9	97.9	97.7	97.4	96.9
pH-shaking	2.52	2.41	2.06	2.20	2.21
E %-shaking	98.3	97.8	97.8	97.2	96.9

X_{nm} =pH without mixing, x_{sh} =pH with shaking, y_{nm} =turbidity without mixing and y_{sh} =turbidity with shaking.

$$\Sigma x_{nm} = 11.3, \Sigma x_{nm}^2 = 25.4, \Sigma y_{nm} = 12.3, \Sigma y_{nm}^2 = 33.7 \text{ and } \Sigma xy_{nm} = 28.1$$

$$\Sigma x_{sh} = 11.4, \Sigma x_{sh}^2 = 26.2, \Sigma y_{sh} = 11.8, \Sigma y_{sh}^2 = 30.4 \text{ and } \Sigma xy_{sh} = 27.3$$

The r-values of samples with mixing and shaking obtained from the values in Table 2.5 are 0.68 and 0.60 (68 and 60 %) respectively. The range of the correlation coefficient is from -1 to 1. Our correlation coefficients in samples without mixing and with shaking fall within a range of strong relationship. This is validated by the R^2 of pH converted to concentration of Fe^{3+} and Al^{3+} vs turbidity removal efficiency in samples without mixing, as shown in Figures 2.10 and 2.11, i.e 0.986 and 0.980 respectively.

According to the comparison in residual turbidity between the samples with mixing and shaking in Figure 2.5, FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ exhibit similar turbidity removal values in corresponding dosages. The SEM images shown by Figure 2.12 (A) and (B)

show that the larger floc in the latter (mixing) exhibits demarcations/boundaries which are signals of potential rupturing. This shows that further rapid mixing would result in breakage of the floc, a condition which results in re-stabilization and poor turbidity removal as stated by Freeze *et al.*, (2001), Swartz *et al.*, (2004), Aboulhassan *et al.*, (2006) and Zhang *et al.*, (2007). The floc of the sample (with mixing) shows some round flocs which are attributed to effective adsorption. The image showing a sample which has been shaken almost has a similar morphological matrix, except that it is compact with less rounded flocs. The identical crystal morphology between the samples with shaking and mixing indicates that their adsorption potential is identical. The crystal morphology of the samples with mixing, shaking and without mixing shows that the flocs form a filter-cake structure which is an adsorption substrate.

Similarly, the sample with $\text{Al}_2(\text{SO}_4)_3$ dosage with mixing in Figure 13 (A) shows a large floc with some demarcations, which indicates that rupturing was inevitable in the event of prolonged mixing. There are also some smaller flocs around the larger floc which also indicate that breakage occurred of a larger one. The image of a sample with $\text{Al}_2(\text{SO}_4)_3$ dosage without mixing shows a large floc with smaller round flocs almost of the same quantity to those in a sample with mixing. These four images confirm that destabilization with a multivalent metal ions added to a highly charged colloidal suspension is spontaneous.

2.7 CONCLUSION

Chemical reactivity between hydrated metal salts and colloidal particles is a spontaneous process and it is not influenced by mixing. The ionic concentration and charge density in the system (wastewater) during treatment determines the rate of destabilization-hydrolysis. The turbidity removal in the AMD samples treated with mixing is similarly identical to that in the samples with shaking, indicating that shaking is an ideal replacement technique for mixing. The turbidity removal can still be effective in acidic wastewater using inorganic coagulants without pH adjustment. The similarity shown by the turbidity removal values with FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ and also the SEM micrographs indicate that the flocs which are formed consist of a filter-cake structure which with identical adsorption capacity in samples treated with mixing, shaking and without mixing. Apart from hydrolysis of metal ions to form the flocs ($\text{M}(\text{OH})_{3(s)}$), it is suggested that other precipitates such as CaCO_3 , MgCO_3 and $\text{Mg}(\text{OH})_2$ are inevitable due to the reaction of the Ca^{2+} or Mg^{2+} when exceeding solubility, enhancing polymerization reaction (SEM and turbidity removal values)

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CHAPTER 3 Treatment of acid mine drainage using Fe^{3+} salts and acid-free polyferric chloride polymer of calcium hydroxide without pH adjustment

Abstract

A 200 mL of acid mine drainage sample were poured into 5 glass beakers and dosed with FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and polymers of a mixture of FeCl_3 and $\text{Ca}(\text{OH})_2$ (af-PFCl) respectively. The samples were placed in a flocculator and stirred at 250 rpm for 2 minutes. The samples were allowed to settle for 1 hour after which the pH, conductivity and turbidity were measured. A similar set of experiments was conducted by pouring 200 mL of the sample into five Erlenmeyer flasks with the same dosage and were placed in a shaker using similar timing and measurements. A third similar set of experiments was conducted but without mixing, settled for 1 hour and the same measurement taken. The fourth and fifth sets of experiments were conducted with $\text{Ca}(\text{OH})_2$ and af-PFCl polymer respectively. The results showed that the pH and residual turbidity in the samples with Fe^{3+} salts, $\text{Ca}(\text{OH})_2$ and af-PFCl dosages in corresponding dosages are almost identical. The difference between the pH and residual turbidity in the corresponding sample dosages with mixing, shaking and without mixing exhibit is insignificant.

Keywords: polymer, mixture, settle, turbidity, dosages, mixing.

3.0 INTRODUCTION

Chemical coagulation is commonly used in the raw water and wastewater treatment plants to destabilize the colloidal suspension for the removal of pollutants. FeCl_3 and $\text{Ca}(\text{OH})_2$ are common reagents dosed to wastewater for coagulation and pH adjustment respectively. They are associated with corrosion and scaling related defects respectively when dosed separately. Furthermore, the latter also adds to turbidity in wastewater and combines with bicarbonate to form calcium carbonates. It can be ideal to reduce their volume percentage and mix 50 % molar mass of each to form one reagent which can be used for multi-purposes. Another problem is that separate dosing of these reagents tends to deter the wastewater treatment process compared to a simultaneous dosage as a compound (Nielsen, *et al.*, 2008, Firer, *et al.*, 2008 and Nielsen, *et al.*, 2005)

In this study the focus was on the investigation of the turbidity removal efficiency of the compound ($\text{FeCl}_3\text{-Ca}(\text{OH})_2$) compared to that of FeCl_3 or $\text{Ca}(\text{OH})_2$. Acid mine drainage (AMD) has been identified as the wastewater which can be treated with $\text{FeCl}_3\text{-Ca}(\text{OH})_2$. AMD is generated from both closed and operating mines, where the latter attributes to environmental degradation by discharging untreated wastewater to the water-course. AMD can be generated from the mining activities such as production and beneficiation processes, or accelerated by naturally-occurring bacteria such as *acidobacillus ferrooxidans* (Akci *et al.*, 2006). The problem associated with the AMD is that it is localized around mining areas such as the coalfields and tends to

disrupt the ecology of the surrounding area. Pyrite (FeS_2) is a common mineral found in coal and results in the formation of AMD and it is usually associated with the other sulphides in the coal beds (Maree *et al.*, 2004, Giere *et al.*, 2006 and Huang *et al.*, 2010). High sulphur content in coal in the form of pyrite is the main attribute to environmental degradation.

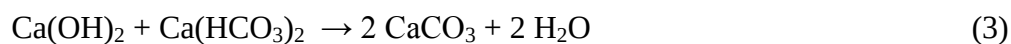
A lot of research which has been conducted on the wastewater treatment explores new technological approach such as distillation, reverse osmosis, carbon nanotubes, Fenton's reagent, wet oxidation, advanced oxidation, coagulation-electro oxidation. These techniques are complex, incur high costs and do not cover a wide range of the wastewater poor quality. Apart from new technology, lime-, dolomite-neutralization, iron oxidation, gypsum crystallization and activated carbon are common treatment techniques. Diversification of research unveils more complicated technologies such as co-treatment of AMD solution with the municipality wastewater using activated sludge (Bratby, 2006 and Santos *et al.*, 2011). Sewage effluent with relatively high concentrations of suspended solids may enhance iron oxyhydroxide precipitation by encouraging iron, which is often present in high concentrations in AMD, to form flocs (Johnson *et al.*, 2006a, Neto *et al.*, 2010 and Winfrey *et al.*, 2010). Phosphate which is present in high concentrations in sewage effluent, can be sorbed onto the iron oxyhydroxide precipitates (Sibrell *et al.*, 2009; Wei *et al.*, 2009 and Wei *et al.*, 2010), or react with Al to form hydroxyl-phosphates (Johnson *et al.*, 2006a and Johnson *et al.*, 2006b).

Lime neutralization is popular and employed in AMD treatment, but the disadvantage is that it cannot remove certain minerals such as arsenic and molybdenum. Their removal requires co-precipitation using metal salts such as iron, Fe^{3+} , (Aubé *et al.*, 2003). Scaling poses another problem occurring during lime neutralization of AMD where the pH is elevated to precipitate certain metals. Controlling the pH to a typical value of 9.5 allows metals such as iron (Fe) and zinc (Zn) to precipitate. Other metals such as nickel (Ni) and cadmium (Cd) require a higher pH (in a range of 10.5 to 11.0) to effectively precipitate as hydroxides Aubé *et al.*, 2003). Lime dosing can be extended to higher density sludge (HDS) processing. The precipitates are formed onto existing particles which are recycled within the process to create larger and denser particles that can settle and compress better than the typical precipitates (Aubé *et al.*, 2003). Lime preparation for the neutralization process is performed through calcium oxide (slake) hydration to form calcium hydroxide and fed into the system as slurry to raise the pH. Hydration of calcium oxide is shown in Equations 1 and 2.



The increased pH then generates hydroxide ions which combine with the dissolved metals to produce precipitates such as Al(OH)_3 , Fe(OH)_3 , Co(OH)_3 , Cu(OH)_3 , Zn(OH)_3 , Ni(OH)_3 and Pb(OH)_3 (Strosnider *et al.*, 2011a and Strosnider *et al.*, 2011b and Strosnider *et al.*, 2011c). Wastewater pH has been identified as one of the parameters which influence effective wastewater treatment (Juttner *et al.*, 2000,

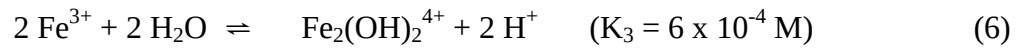
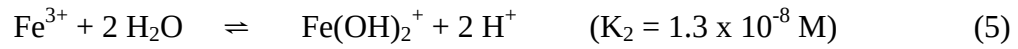
Freeze *et al.*, 2001 and Aboulhassan *et al.*, 2006). It enables the concentration of coagulants to exceed the solubility of their metal hydroxides so that precipitates can be formed (Aguilar *et al.*, 2002, Wang *et al.*, 2004, Tunay *et al.*, 2003 and Shammass *et al.*, 2004). A pH lower than 6 causes adsorption of the hydrolysis products onto the colloidal surfaces to interact with the dissolved components in the colloid, thus resulting in re-stabilization which is caused by charge reversal (Jiang *et al.*, 1997, Goldberg, 2002, Amuda *et al.*, 2006 and Ghaly *et al.*, 2006). A high chemical dosing is required when the wastewater pH is above 6 (Jiang *et al.*, 1997; Gregory *et al.*, 2001, Lee, 2001, Ghaly *et al.*, 2006, Molony, 2005 and Pratt *et al.*, 2007). Sulphuric or hydrochloric acid is dosed for pH adjustment in alkaline colloid, whereas Ca(OH)₂, NaOH or Na₂CO₃ are dosed in acidic colloidal suspension (Water Specialist Technology, 2003). During the lime neutralization process, Ca(OH)₂ can also react with HCO₃⁻ to form CaCO₃ as shown by Equation 3.



The problem with Ca(OH)₂ dosage is its addition to the turbidity of the solution, which in turn requires a lime saturator. This is a process unit used to mix water with the slurry lime from a post lime system to restrict the addition of turbidity (Kurniawan *et al.*, 2006). Parsons *et al.*, (2008) and Edwards *et al.*, (2007) disapproved lime neutralization when Fe³⁺ salts are dosed to the AMD solution.

In the present study, lime is dosed in a form of a polymer which will eliminate all the disadvantages afore-mentioned. Its reaction with the other component of a synthesised polymer (FeCl₃) to form acid free polyferric chloride (af-PFCl) is dosed

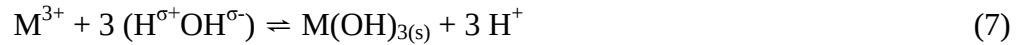
in the AMD solution to destabilize the colloidal suspension; thereby causing hydrolysis of the coagulants as shown by Equation 4-6



According to the solubility constants of the hydrolysis species (Equations 4-6), all the three hydrolysis species can be observed at their specific solubility constant.

Turbidity removal efficiency of the acid-free polymers which is prepared with FeCl_3 and $\text{Ca}(\text{OH})_2$ to produce af-PFCl used in this study will be compared with that of Fe^{3+} salts of FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$. This polymer was earlier used in a study by Ntwampe *et al.*, (2013b) on paint wastewater treatment. The results showed that the polymer reacted relatively well with alkaline paint wastewater, but there was no direct correlation between the pH and turbidity. The novelty in this study is that the experiments are conducted using highly acidic AMD without the addition of metal hydroxide for pH adjustment, using an acid-free polymer. Polymers which have been used before were prepared by partial hydrolysis of acidic AlCl_3 or FeCl_3 solution in a special reactor (Jiang *et al.*, 1997). Instrumental techniques employed for mineralogical characterization are scanning electron microscopy (SEM) and X-ray diffraction (XRD). In the present study the turbidity removability potential when wastewater treatment is conducted without pH correction is also investigated.

A study by Ali *et al.* (2002) on surface electrical phenomena reported that raw water contains microscopically visible colloidal particles that possess high electrophoretic mobility or a high zeta potential which has to be reduced by the chemical treatment. This occurs during destabilization when the equilibrium between the electrostatic forces of repulsion and van der Waals forces of attraction are disturbed; a shift towards van der Waals forces of attraction reduces the diameter of the neighbouring particles and the distance between them (Swartz *et al.*, 2004 and Freeze *et al.*, (2001). The particles collide with one another to form flocs, whereas the M^{3+} ions hydrolyse by forming a bond with OH^- as a result of a cleavage of the polar water molecules ($H^{\sigma+}OH^{\sigma-}$) to form metal hydroxide species as shown by Equations 7 and 8.



Equation 8 depicts the hydrolysis reaction when metal ion reacts with hydroxyl ions, whereas Equation 9 represents the different species which are formed during hydrolysis, where the pH of a solution decreases during the hydrolysis process. The first solid species formed is an unstable am $\sim M(OH)_{3(s)}$. It is formed due to a very low solubility product of the metal hydroxide. Ageing causes the conversion of an unstable amorphous metal hydroxide to a stable $\alpha\sim MO(OH)_{(s)}$, which is formed at the lowest M^{3+} concentration. Some other species such as beta ferric hydroxide ($\beta\sim MO(OH)_{(s)}$) are also possible depending on the compound which is used in the wastewater treatment process (O'Melia, 2001). Equation 8 shows that hydrogen (H^+)

ions are released during hydrolysis, thus lowering the pH of the solution. Table 3.1 shows the pH range in which different hydrolysis species can exist:

Table 3.1: pH range favourable for Fe^{3+} hydrolysis species

Species	pH range
$\text{Fe}(\text{OH})^{2+}$	1-5
$\text{Fe}(\text{OH})_2^+$	2-7
$\text{Fe}(\text{OH})_{3(\text{aq})}$	4-8
$\text{Fe}(\text{OH})_4^-$	4-14

All the reactions which occur during wastewater treatment involve thermodynamic and kinetic dynamics. They are influenced by the type and electron configuration of solvated colloids, valence of metal ion, type and rate of destabilization and dispersion technique of coagulant. All these factors form part in the physico-chemical properties of both the colloids and the reagents. Other factors which play a pivotal role but are always omitted in the studies include the type and ionic strength of the colloidal suspension, particle size and the type of the colloids, namely being either hydrophilic or hydrophobic. For best results, effective turbidity removal can only be achieved when all these factors are integrated. Identification of the colloids, hydrophilic and hydrophobic is essential because it enables the water Chemist to choose an appropriate reagent (metal salts, polymers or coagulant-aid) to be dosed. Hydrophilic colloids are not easy to treat because they are under polarity due to the dipolarity of water molecules, which impair any interaction such as destabilization. Agglomeration of hydrophilic colloids typically involves the addition of significant amounts of ions which compete with the colloids for water molecules, thus resulting in the

dehydration of the colloidal particles ("salting out" of the colloid) (Weber, 1972). Apart from the nature of colloids, other factors such as stability of colloids, mineral/salts content and pH play a pivotal role. The physico-chemical reactions which are involved during wastewater treatment interact with the electron configuration. The electron matrix and arrangement of the ions determine stability of the colloidal suspension, electrical double layer and the size of the aqua-colloids. A double layer is formed by diffuse layer which is concentrated with the positive and negative charges, and the layer of positive charges around the central colloid. A stern layer separates diffuse and those positive charges around the central colloid, which is surrounded by negative charges. The double layer is the part which determines destabilization of the colloidal suspension to form flocs. According to the Gouy-Chapman model, the potential distribution is a flat double layer as described by Equation 9:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \quad (9)$$

ψ = potential at a point in the diffuse layer versus infinity at the bulk solution, ρ = charge density at the same point and ϵ is permittivity. In Equation 9 the charge density at the potential ψ is described by Equation 10. The number of positive and negative ions in the diffuse layer is distributed according to the Maxwell-Boltzmann distribution (Equation 11 for cations and Equation 12 for anions):

$$\rho = ze(n_+ - n_-) \quad (10)$$

$$n_+ - n_- \cdot \exp\left(\frac{ze\psi}{kT}\right) \quad (11)$$

$$n_+ - n_- \cdot \exp\left(-\frac{ze\psi}{kT}\right) \quad (12)$$

n_+ and n_- are the respective numbers of positive and negative ions per unit volume at the point where potential is ψ . n_0 is the concentration of ions at the infinity (bulk solution). z is the valence of the ions, e is the charge of electron, k is Boltzmann's constant and T is temperature. The potential of the particle surface versus bulk solution is called Nernst potential (ψ_0). Between the inner layer and the outer layer is the Outer Helmholtz plane (OHP), which has potential of the particle surface versus bulk solution. However, this potential cannot be directly measured and therefore a common parameter, which depicts the surface charge of the colloid, is ζ -potential (ψ_ζ), which is the electrical potential between the plane of shear and the bulk solution. The diffuse part of the double layer is analogous to the plate condenser. Even though in reality the double layer extends to infinity, the Debye-Hückel length, K^{-1} , is used to describe the thickness of the double layer (Field *et al.*, 1988).

In coagulation and flocculation technologies, the particles are destabilised by the addition of inorganic or organic chemicals which have an effect on the properties of the EDL where the coagulants reduce the repulsive energy between the particles (energy barrier). The particles can therefore easily agglomerate at the primary minimum potential energy. Flocculation, a subsequent process occurs when these agglomerated particles attach to each other with a weak bond (the secondary

minimum potential energy). Sometimes flocculation aids are added to improve floc properties, such as settleability and filterability. Mechanisms which can destabilise colloidal particles in water as stated by (Pokhrel *et al.*, 2004 and Bajpai, 2010) are:

(1) Compression of electrical double layer: The increase of the concentration of ions in bulk solution compresses the EDL and particles come together more easily as the length of the EDL decreases. This mechanism is not employed in water treatment because very high salt concentrations are required for destabilisation. (2) Adsorption destabilisation: This occurs when oppositely charged ions or polymers are adsorbed on the surfaces of particles. They reduce surface charge and thus repulsive force between the particles. Unlike the double layer compression, over-dosing of a coagulant can lead to the restabilisation of the particles because the charge is reversed. (3) Inter-particle bridging: Polymerised metal coagulants or organic chemicals can form bridges between the particles. Polymer can adsorb on the particle surface by charge-charge interactions, dipole interactions, hydrogen bonding or van der Waals interaction. When one polymer chain adsorbs on multiple particles, bridging occurs and molecular weight increases. (4) Precipitation and enmeshment mechanism: This occurs with the high concentrations of metal salts in near neutral pH. In this the pH, metal salts, such as $\text{Al}_2(\text{SO}_4)_3$ or $\text{Fe}_2(\text{SO}_4)_3$, form insoluble hydrolysis products and polymerise. Colloidal particles can then be enmeshed into these sweep flocs. The reactivity of the coagulant is determined by its strength to compress an electrical double layer (EDL) during the destabilization process. The EDL is formed by a layer of positive ions which surround the central negative ions, and the mixture of positive and negative ions bound together by coulomb forces in a

diffuse layer (Lee, 2001, Haselberg, 2009, Kosmulski, 2004, Cosgrove, 2005, Crittenden *et al.*, 2005, Ananikov *et al.*, 2005, Bratby, 2006 and Scholtz, 2010). The complexity of the electron configuration in both the diffuse layer and around the central particle determines the efficiency of the coagulant (Kostamo *et al.*, 2004 and Bratby, 2006).

Many researchers such as Jiang *et al.* (1997), Binnie *et al.* (2003), Kemmer (1988) and Aysegul *et al.* (2002) indicated that mixing is one of the processes which enhances the effectiveness of destabilization. On the contrary, some researchers such as Peavy *et al.* (1985) and Jiang *et al.* (1997) stated that mixing is required when the distance between each particle in the colloidal system is greater than the van der Waals forces of attraction which will deter the destabilization. It induces Brownian motion in the colloidal system such that it should exceed the electrostatic potential of the system in order to achieve the destabilization (Peavy *et al.*, 1985, Jiang *et al.*, 1997, Gregory *et al.*, 2001 and Pratt *et al.*, 2007). This is confirmed by our experimental results showing that turbidity removal efficiency with af-PFCl polymer during mixing, shaking or without mixing shows insignificant difference to that with Fe^{3+} salts (removal between 88.4 and 96.4 %).

3.1 MATERIALS AND METHODS

In this study, coagulation-flocculation treatment has been applied to AMD solution using 0.043 M Fe^{3+} in FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ respectively, 0.043 M Ca^{2+} in $\text{Ca}(\text{OH})_2$

and 0.043 M acid free polymer (af-PFCl) using 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 stirring 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 third batch of experiments was conducted using the same sample and the coagulants and dosages without mixing, they were allowed to settle for 1 hour and thereafter the pH, conductivity and turbidity were measured.

3.1.1 Acid mine water sample

The samples were collected from a mine near Klerksdorp in 25 litre plastic drums. The samples were sealed air-tied and stored at room temperature. The pH, conductivity and turbidity of the AMD solution were 2.56, 4.43 mS/cm and 100 NTU respectively. The solid content of the sample was 6.8 g in a 200 mL sample aliquot.

3.1.2 Coagulants

Inorganic coagulants of 0.043 M of Fe^{3+} in FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ ions (a concentration obtained from the literature) were dosed during flocculation of the acid mine water

and yielded a wide range of results showing effective flocculation. The concentrations of the coagulants in this study were chosen as per a study conducted by Fasemore (2004) on paint wastewater treatment.

The calculation of the mass of metal salt to obtain 0.043 M of M^{3+} ($M^{3+} = Fe \text{ or } Al$) is as follows:

Monoprotic metal salts (MCl_3)

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6H_2O \quad (M^* = Fe) \quad (13)$$

Diprotic metal salts ($M_2(SO_4)_3$)

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*_2(SO_4)_3 \cdot 18H_2O / 2 \quad (M^* = Fe) \quad (14)$$

Acid free- $FeCl_3$ - $Ca(OH)_2$

$$0.043 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6M(OH)_2 \quad (M^* = Fe \text{ or } Ca) \quad (15)$$

Table 3.2 shows monoprotic, diprotic metal salts and Metal hydroxide dosed into the AMD.

Table 3.2: Monoprotic, diprotic metal salts and metal hydroxide dosed into AMD.

Salt	Mass of salt (g)	Conc. (mol/L)	M^{3+} conc. (mol/L)
$FeCl_3 \cdot 6H_2O$	11.4	0.043	0.043
$Fe_2(SO_4)_3 \cdot 18H_2O$	17.2	0.0215	0.043
$Ca(OH)_2$	3.18	0.043	0.043

3.2 EXPERIMENTS

3.2.1 Procedure of a jar test

The equipment used for the jar tests was a *BIBBY Stuart Scientific Flocculator (SW1 model)*, which has six adjustable paddles with the 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^{3+} in FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ were added to the AMD samples. The experiments were conducted employing rapid mixing (250 rpm for 2 mins.), without mixing and with shaking (250 rpm for 2 mins.). The rationale to carry out these experiments was to determine a correlation between the pH changing trend and turbidity removal. The experiments were conducted in the following order:

In the first set of experiments, each 200 mL sample of the five present in the 500 mL glass beakers was dosed with varying dosages of FeCl_3 and treated in three different methods, i.e. mixing in a jar test, without mixing and with shaking. A second similar set of experiments was carried out by replacing FeCl_3 with $\text{Fe}_2(\text{SO}_4)_3$. A third similar set of experiments were carried out by replacing FeCl_3 with acid free $\text{FeCl}_3\text{-Ca(OH)}_2$ polymer (af-PFCl). The samples in all sets of experiments were allowed to settle for 1 hour and thereafter the pH, conductivity and turbidity were measured.

3.3 PERFORMANCE AND 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 measured to determine the removal efficiency of colloidal particles from the samples.

3.3.1 pH measurement

A MettlerToledo Seven Multimetric (*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 as in section 2.3.1.

3.3.2 Conductivity

A EDT instrument FE 280 conductivity-meter (*made in Japan*) was used and calibrated as in section 2.3.2.

3.3.3 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 measure. It was calibrated as in section 2.3.3. The turbidity values were converted to TSS by multiplication with 2.35.

3.4 EXPERIMENTAL RESULTS

Figure 3.1 shows the pH of AMD sample with 20-60 mL FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl dosage with mixing and shaking respectively.

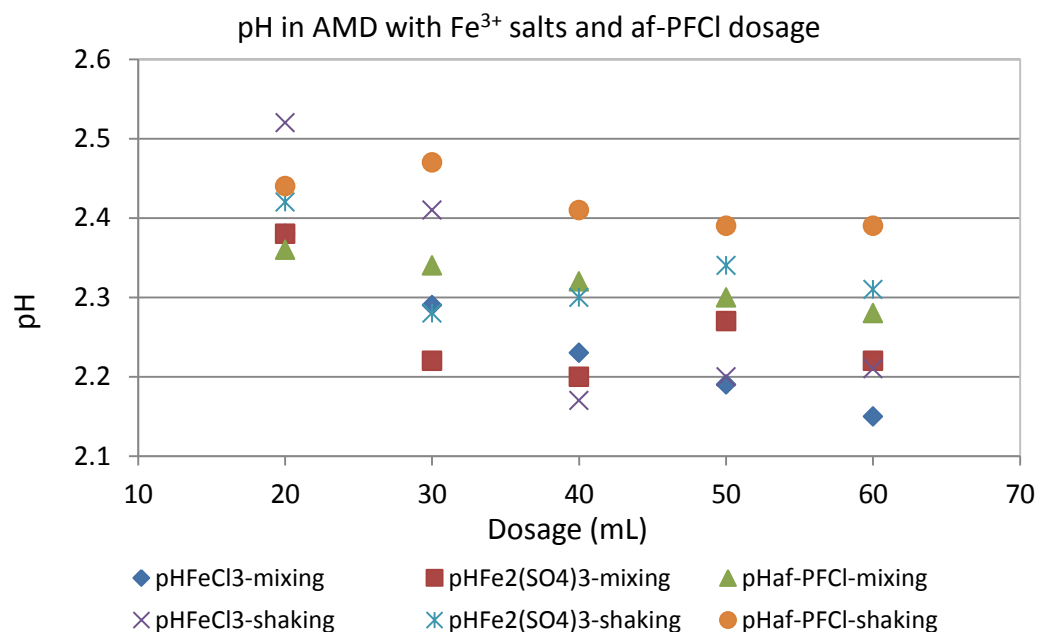


Figure 3.1 pH in AMD with FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl of $\text{Ca}(\text{OH})_2$ with mixing and shaking.

Figure 3.2 shows the conductivity of AMD sample with 20-60 mL of FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl polymer of $\text{Ca}(\text{OH})_2$ dosage with mixing and shaking respectively.

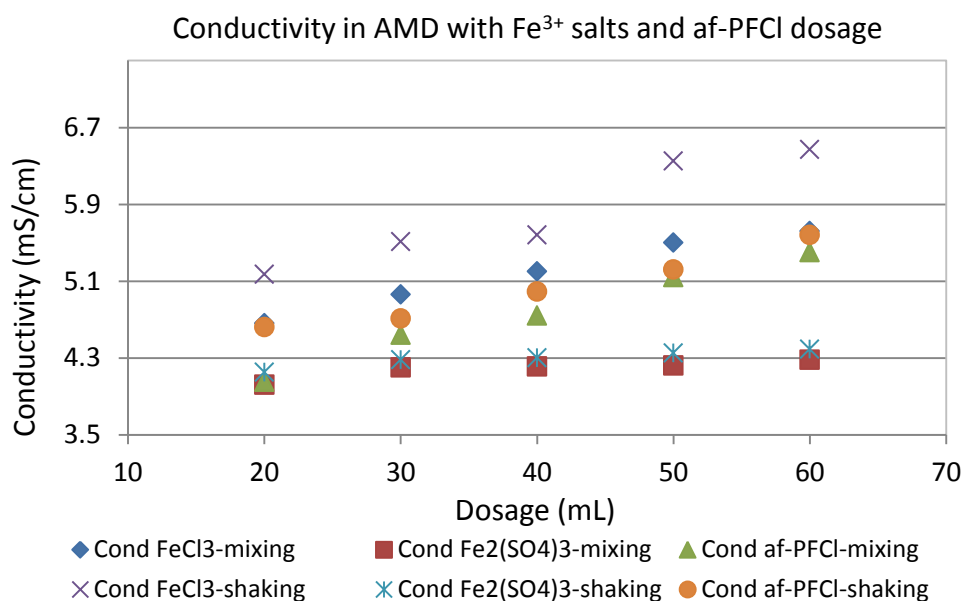


Figure 3.2: Conductivity in AMD with FeCl₃, Fe₂(SO₄)₃ and af-PFCl polymer of Ca(OH)₂ with mixing and shaking.

Figure 3.3 shows the residual turbidity of the AMD sample with 20-60 mL of FeCl₃, Fe₂(SO₄)₃ and af-PFCl polymer of Ca(OH)₂ dosage with mixing and shaking

Figure 3.4 shows the pH vs residual turbidity in AMD sample with Ca(OH)₂ and af-PFCl polymer of Ca(OH)₂ with mixing and shaking.

Figure 3.5 shows the relation between pH and residual turbidity in the AMD sample with af-PFCl polymer of Ca(OH)₂ dosage with mixing, shaking and without mixing respectively.

Figures 3.7 and 3.8 show the residual TSS in AMD samples using varying concentrations and mass of Fe³⁺ and Ca²⁺ in FeCl₃-Ca(OH)₂ and Ca²⁺ in Ca(OH)₂ from 0.043 and 0.086 M standard solutions respectively.

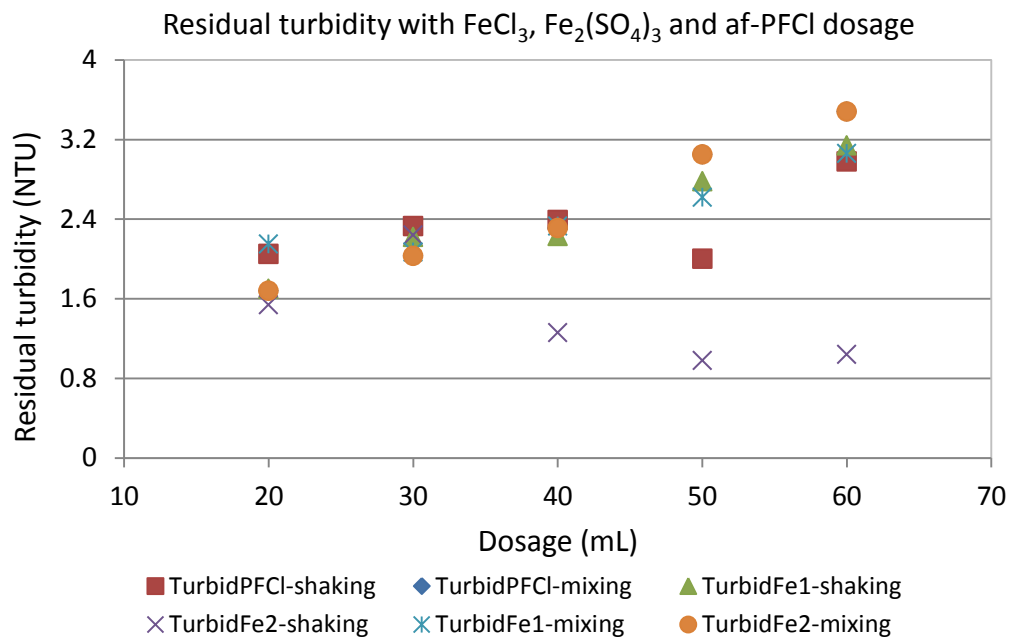


Figure 3.3: Residual turbidity in AMD with FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl polymer of $\text{Ca}(\text{OH})_2$ with mixing and shaking. (Fe1 = FeCl_3 and Fe2 = $\text{Fe}_2(\text{SO}_4)_3$).

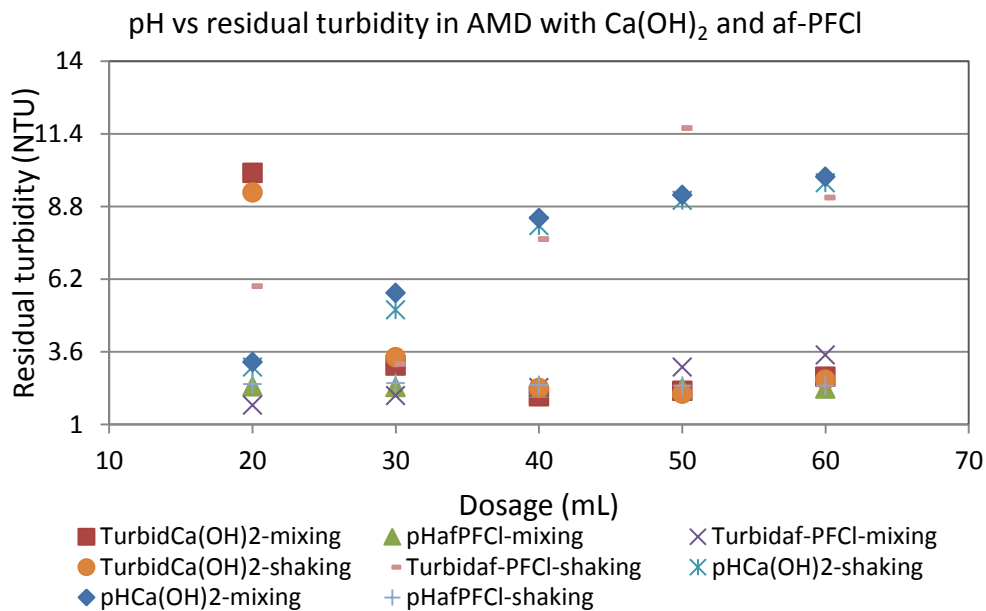


Figure 3.4: pH vs residual turbidity in AMD with $\text{Ca}(\text{OH})_2$ and af-PFCl polymer of $\text{Ca}(\text{OH})_2$ with mixing and shaking.

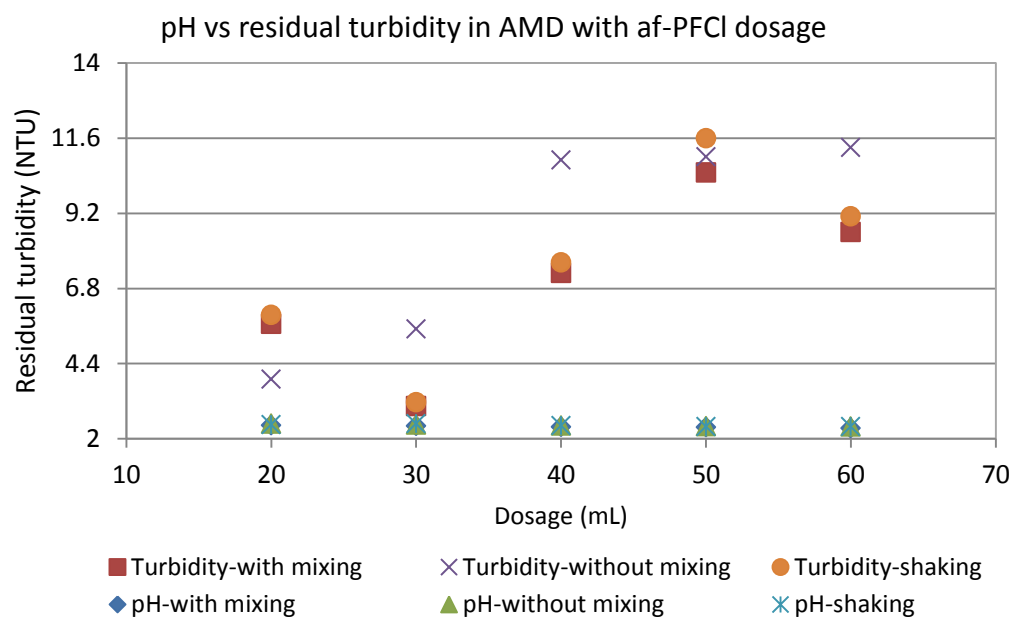


Figure 3.5: pH vs residual turbidity with af-PFCl polymer of $\text{Ca}(\text{OH})_2$ mixing, shaking and without mixing.

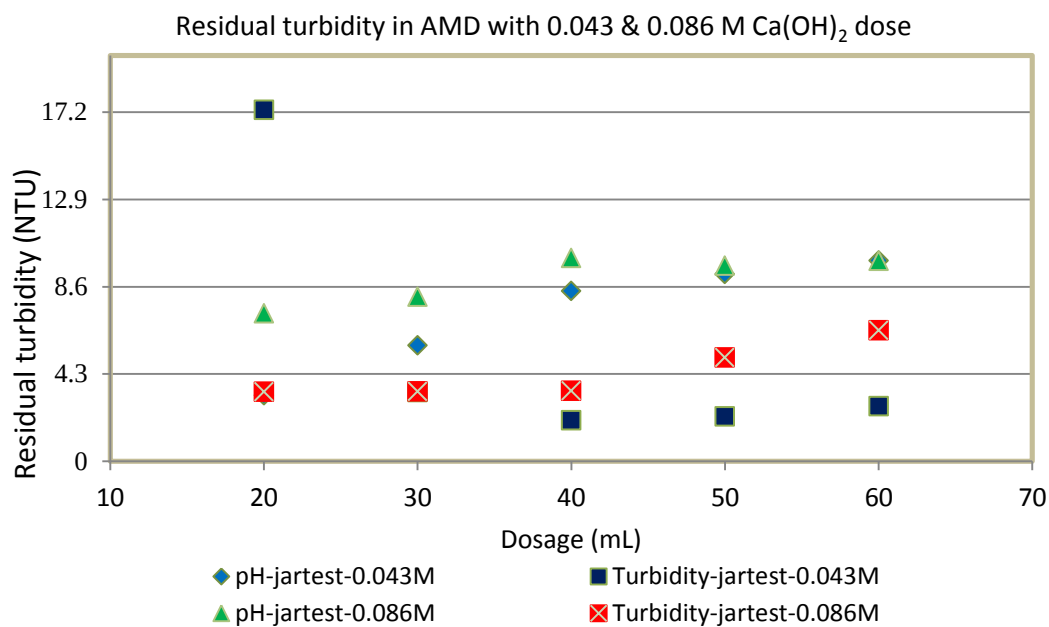


Figure 3.6: Residual turbidity in AMD with 0.043 and 0.086 M $\text{Ca}(\text{OH})_2$.

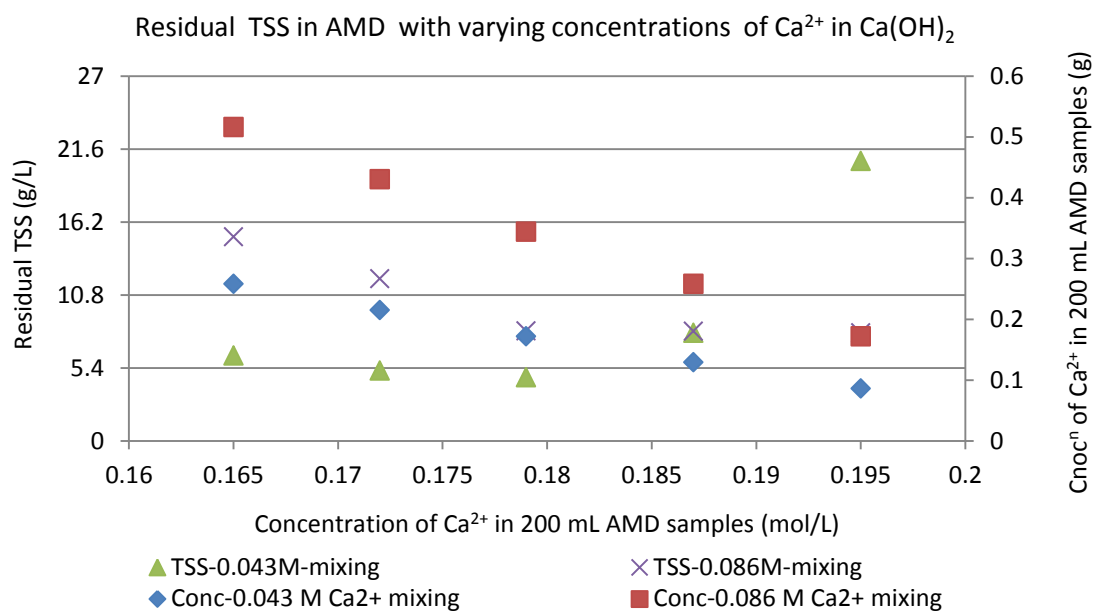


Figure 3.7: Residual TSS in AMD with varying concentrations of Ca^{2+} from 0.043 and 0.086 M standard solution.

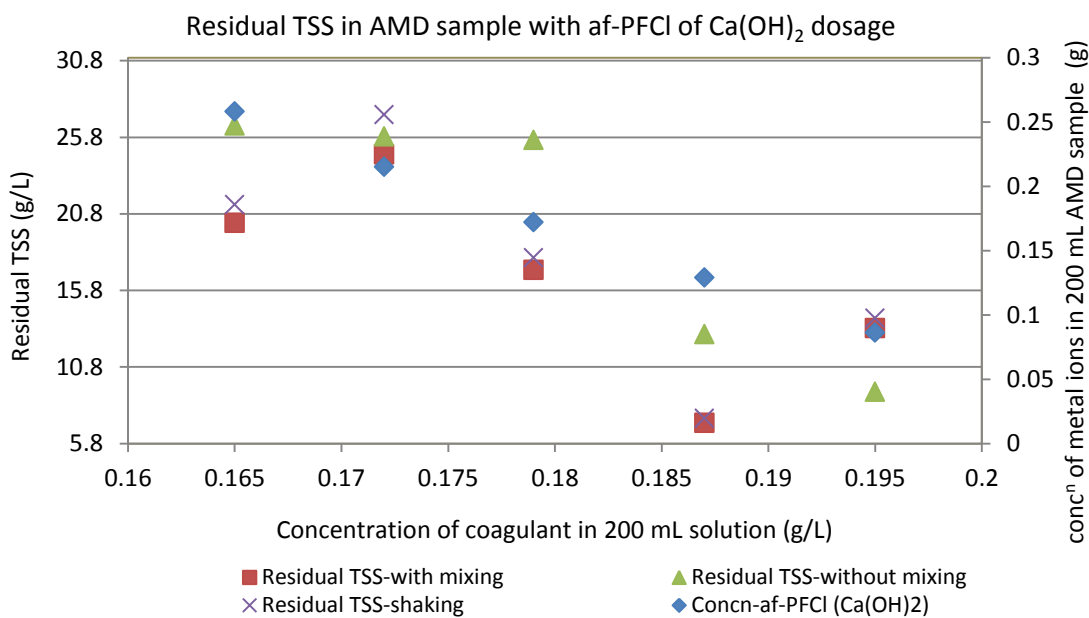


Figure 3.8: Residual TSS in AMD with varying concentrations of Fe^{3+} and Ca^{2+} in af-PFCl polymer of $\text{Ca}(\text{OH})_2$ from a 0.043 M standard solution.

Figure 3.9 shows the relation between the mass of the metal ions (Fe^{3+} or Ca^{2+}) in varying dosages (20-60 mL) which hydrolyzed to form adsorption substrate (flocs) and the residual turbidity of the AMD with FeCl_3 and af-PFCl dosage with shaking and without mixing.

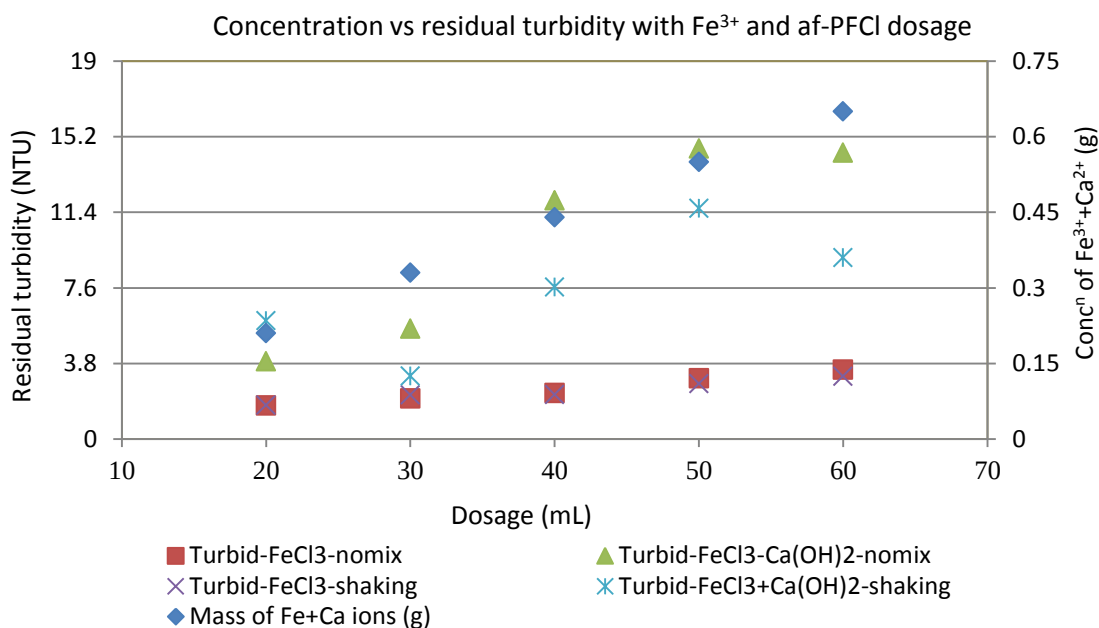


Figure 3.9: Concentration of metal ions in solution vs residual turbidity with shaking and without mixing.

Figures 3.10 and 3.11 show the relation between the pH and total suspended solids (TSS) in the AMD sample with af-PFCl of $\text{Ca}(\text{OH})_2$ dosage with and without mixing. The TSS is calculated applying Equation 39 (Smoluchowski equation) using conversion factor of 2.35 ($\text{TSS} = \text{Turbidity} \times 2.35$). Figure 3.12 shows a correlation between the pH and residual TSS in AMD sample with af-PFCl polymer of $\text{Ca}(\text{OH})_2$ without mixing.

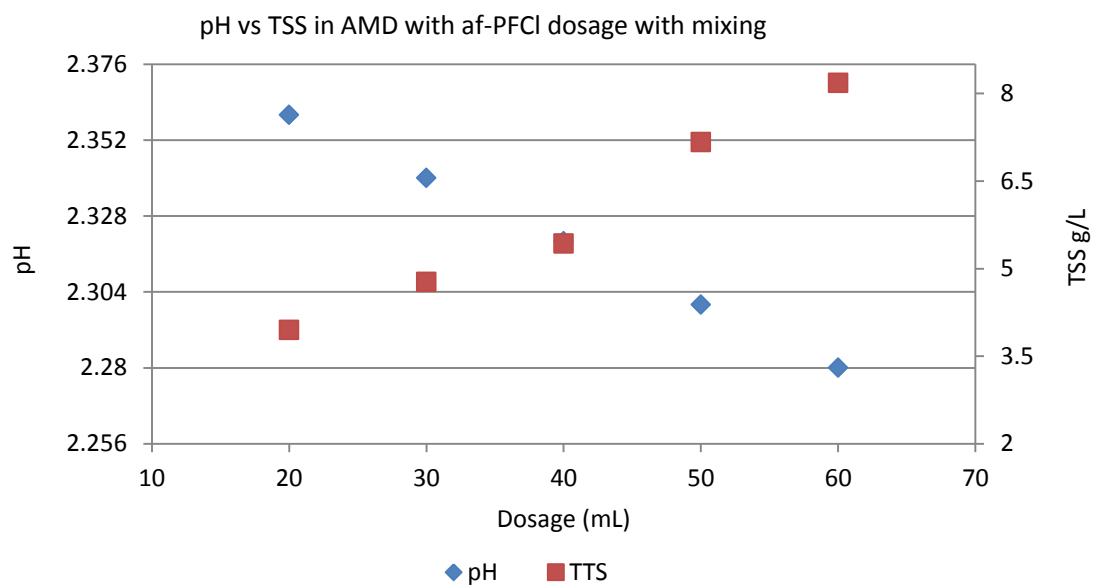


Figure 3.10: pH vs TSS in AMD with aFPFCl of $\text{Ca}(\text{OH})_2$ dosage with mixing.

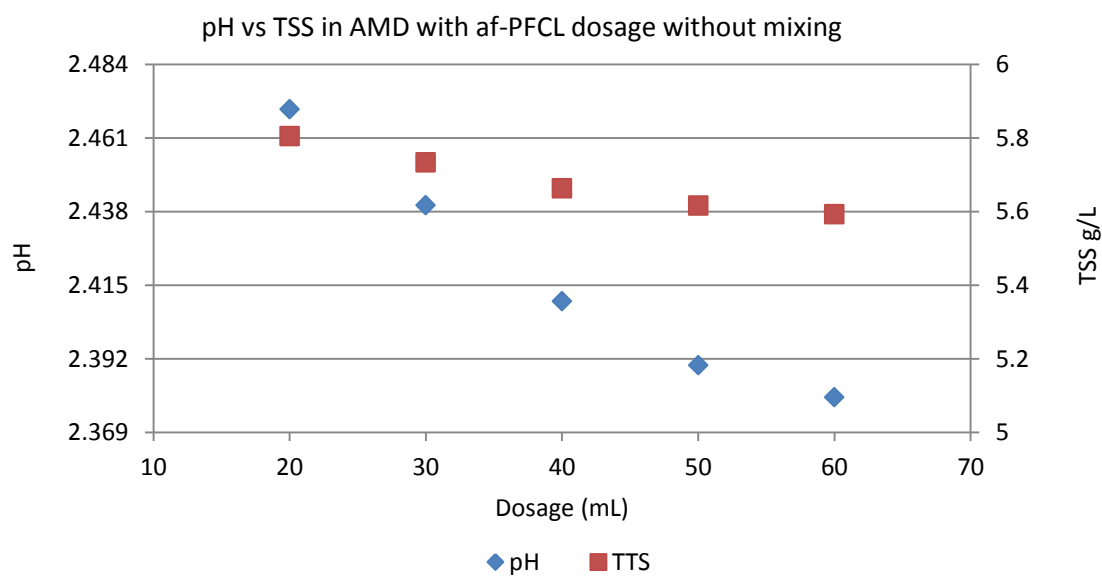


Figure 3.11: pH vs TSS in AMD with af-FPFCl of $\text{Ca}(\text{OH})_2$ dosage without mixing.

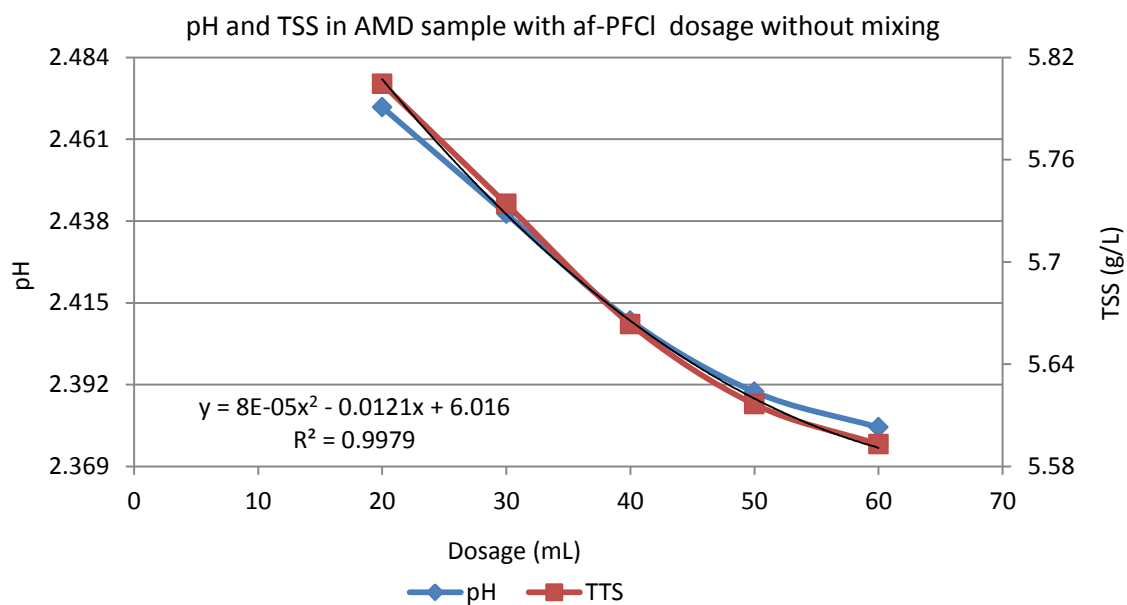


Figure 3.12: Correlation between pH and TSS in AMD with af-PFCl of $\text{Ca}(\text{OH})_2$ dosage without mixing.

Figure 3.13 is the correlation and the R^2 between the turbidity removal efficiency and the pH of the AMD sample with af-PFCl polymer of $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ dosage without mixing. The rationale was to determine the relation between those two parameters.

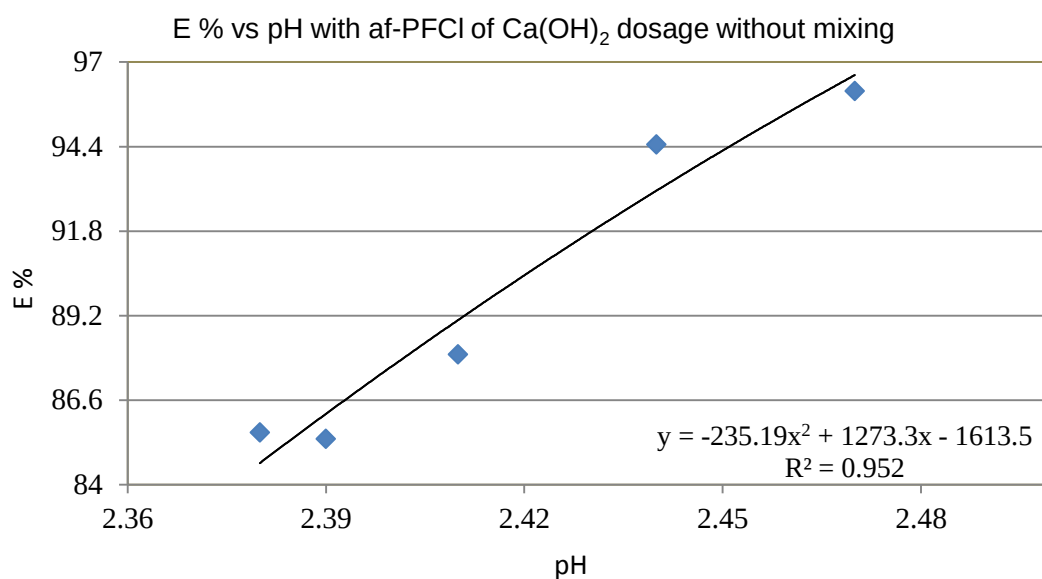


Figure 3.13: pH vs E % of 0.043 M af-PFCl of Ca(OH)_2 without mixing.

Figure 3.14 is the correlation and the R^2 between the turbidity removal efficiency and the pH of the AMD sample with af-PFCl and Ca(OH)_2 dosage with shaking. The rationale was to determine the relation between those two parameters.

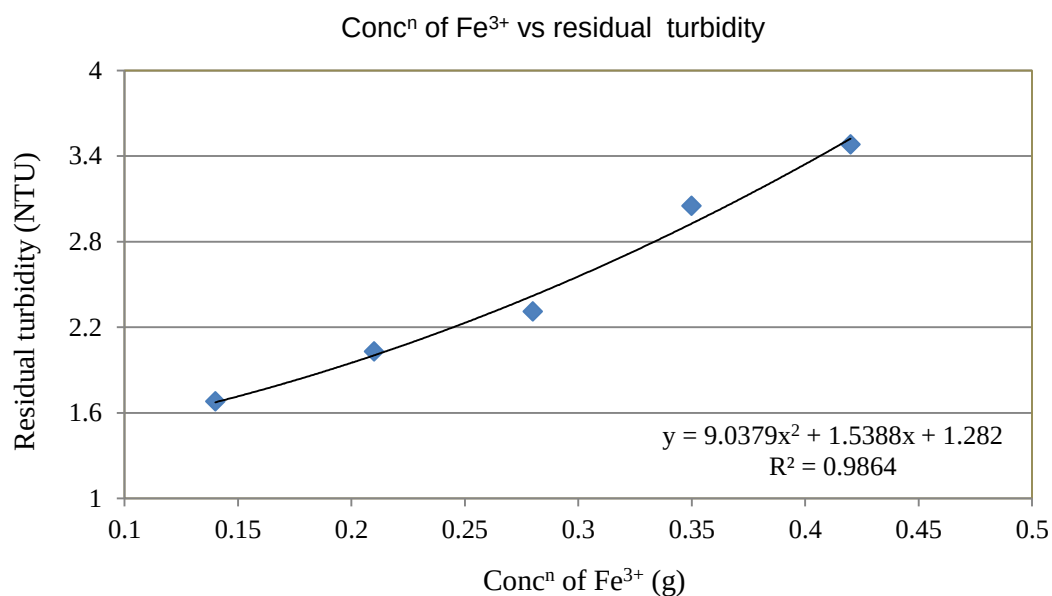


Figure 3.14: pH vs E % of 0.043 M af-PFCl of Ca(OH)₂ with shaking.

Figure 3.15 shows the correlation between the turbidity removal efficiency and the conductivity of the AMD with 20-60 mL af-PFCl and Ca(OH)₂ dosage with shaking.

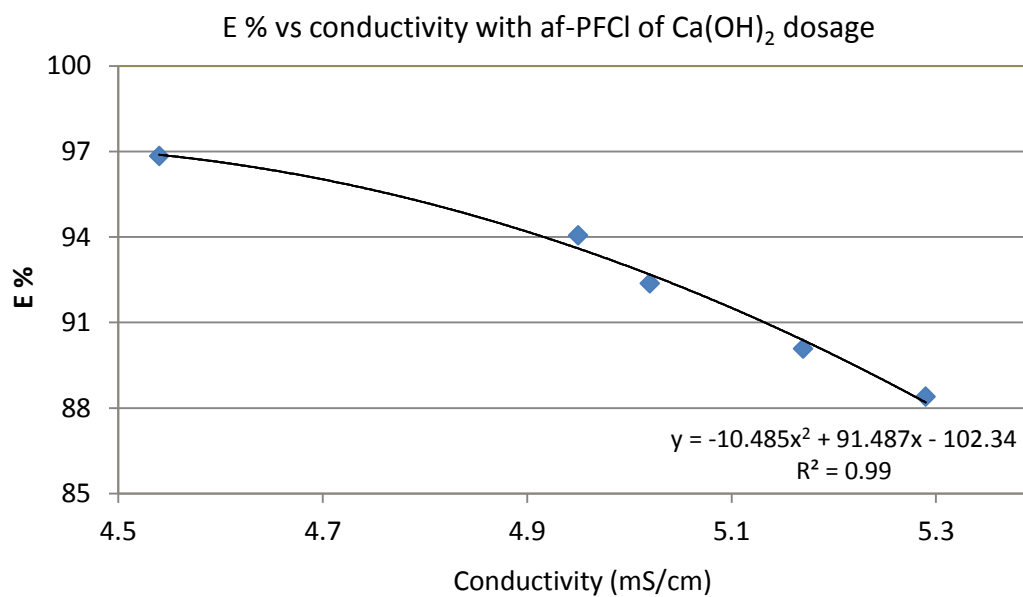


Figure 3.15: Conductivity vs E % of af-PFCl of Ca(OH)₂ dosage with shaking.

Figures 3.16 and 3.17 show the SEM images of the sludge of the AMD samples with FeCl_3 and af-PFCl dosage with mixing.

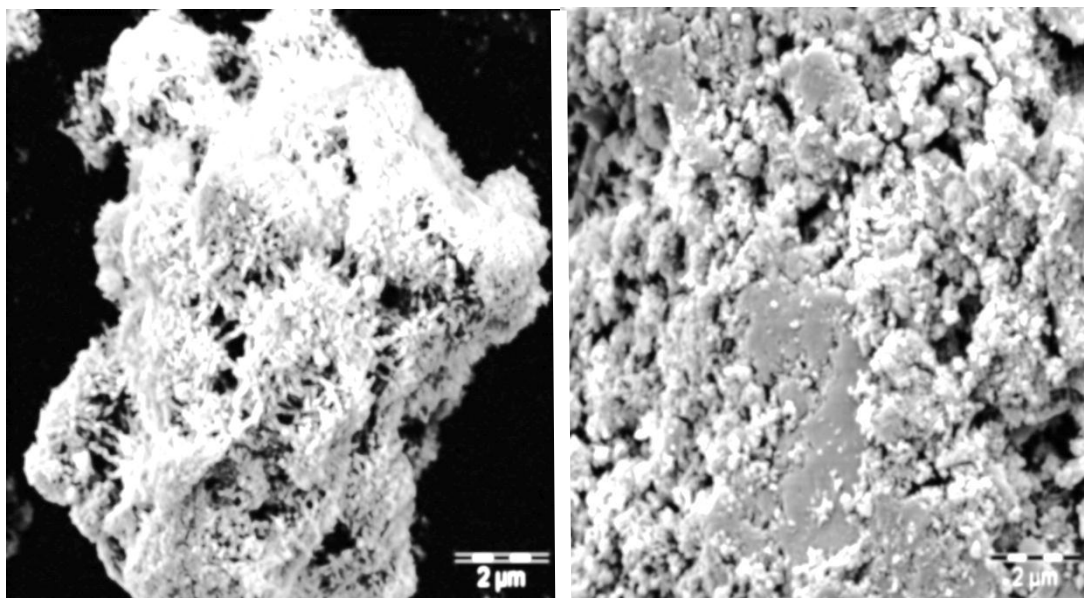


Figure 3.16: SEM images of the sludge of the AMD with FeCl_3 and af-PFCl of Ca(OH)_2 dosage with mixing (25000x).

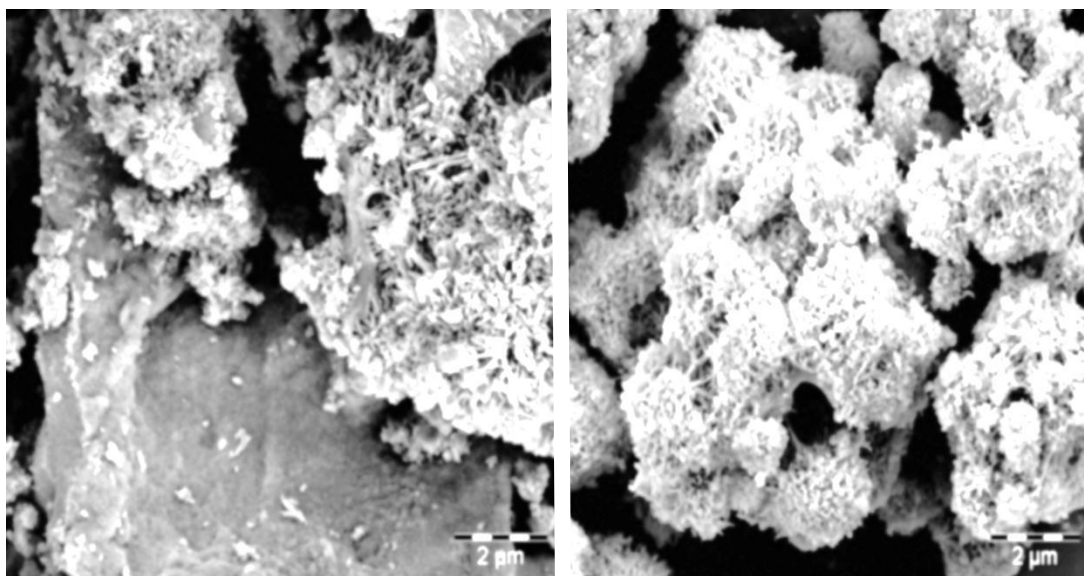


Figure 3.17: SEM images of the sludge of the AMD with FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ dosage with shaking (25000x).

Figure 3.18 A shows the XRD results of the AMD sludge of the samples which have been dosed with $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl without mixing and with shaking. The objective of choosing different coagulants with varying coagulation techniques was to determine their adsorption efficiency on heavy metals.

Figure 3.18 B shows the XRD results of the residual copper present in the AMD samples containing FeCl_3 and af-PFCl with $\text{Ca}(\text{OH})_2$ in a jar test (mixing) and with shaking.

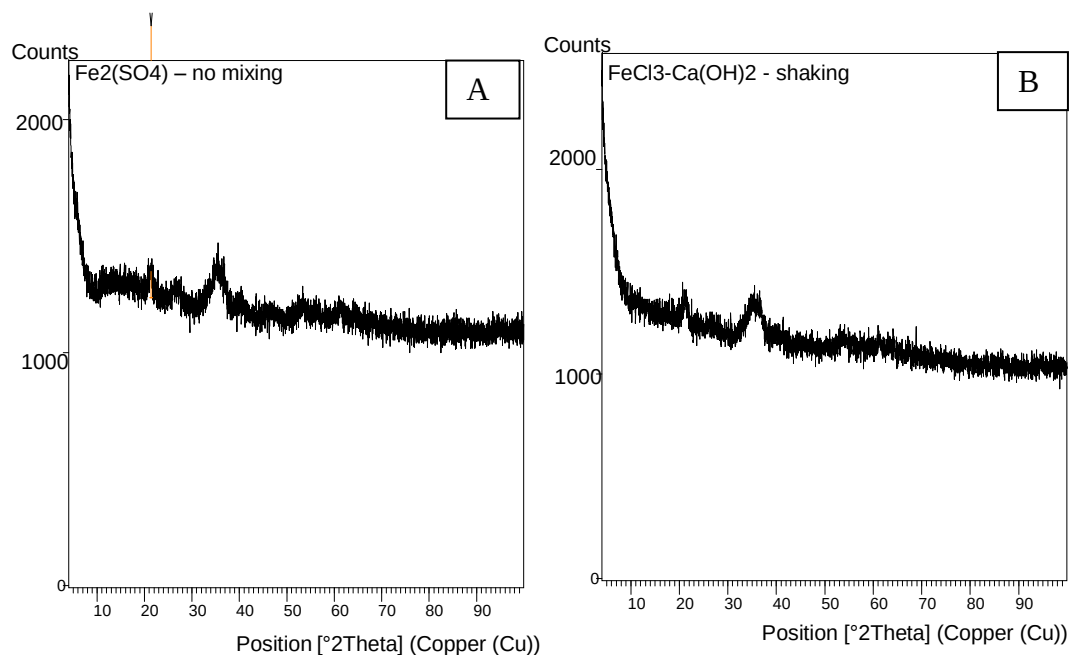


Figure 3.18: Residual copper in AMD sludge with $\text{Fe}_2(\text{SO}_4)_3$ and af-PFCl of $\text{Ca}(\text{OH})_2$ dosage without mixing and shaking.

3.5 DISCUSSION

The pH range of the samples with FeCl_3 dosage and with mixing (Figure 3.1) is slightly lower than in the samples with shaking, 2.38-2.15 and 2.52-2.28 respectively. In the samples with $\text{Fe}_2(\text{SO}_4)_3$ and mixing, the pH decreases in the range of 2.38-2.20, whereas in the samples with shaking, the pH decreases in a range of 2.42-2.23. The pH in the samples with af-PFCl dosage with mixing decreases in a range of 2.36-2.28, whereas in the samples with shaking the pH range was 2.44-2.39.

Conductivity in the samples with FeCl_3 dosage with mixing in Figure 3.2 (4.66-5.62 mS/cm) is lower than in the samples with shaking (5.17-6.47 mS/cm) and the samples with $\text{Fe}_2(\text{SO}_4)_3$ mixing and shaking is in the ranges of 4.02-4.28 and 4.15-4.39 mS/cm respectively; and it is in a range of 4.05-5.40 and 4.62-5.58 mS/cm respectively in mixing and shaking respectively with af-PFCl. The samples with FeCl_3 shaking exhibits the highest mixing intensity as indicated by higher conductivity (high ionic density). The correlation between conductivity and residual turbidity indicates that the former influences the removal of turbidity by increasing electrical conductance in the solution. The pH changing trend with FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ dosage does not ideally exhibit a direct relation with conductivity. This is more likely due to the valence electrons of their anionic components (Cl^- and SO_4^{2-}). The charged complexes dissolve in the solution (AMD) and add to charge density, thus acting as inhibitor during the destabilization. This is shown in Figure 3.2, i.e. that an increase in conductivity deters the turbidity removal.

Residual turbidity in the samples with FeCl_3 dosage with mixing (Figure 3.3) increases in a range of 2.15-3.06 NTU, whereas in the samples with shaking it ranged between 1.70-3.14 NTU. Residual turbidity in the samples with $\text{Fe}_2(\text{SO}_4)_3$ and mixing is in a range of 1.68-3.48 NTU, whereas in the sample with shaking is was 1.54-1.04 NTU. Residual turbidity in the samples with af-PFCl dosage with mixing is in a range of 1.68-3.48 NTU, whereas the experiments incorporating shaking exhibits an inconsistent changing trend in a range of 2.05-2.98 NTU.

The pH changing rate of the AMD samples with FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ dosages from 2.56 to a range of 2.15-2.52 in both mixing and shaking experiments shows that the metal salt reacted as a buffer. The difference is insignificant, but hydrolysis occurred because the values of the residual turbidity are less. Similarly, the pH in the samples with af-PFCl dosage in both mixing and shaking cases the pH ranged between 2.28-2.44. Comparison of the pH between the samples dosed with Fe^{3+} salts differed insignificantly compared to the samples dosed with af-PFCl (0.08-0.13). This indicates that both the Fe^{3+} salts and af-PFCl have the same destabilization potential, which is due to the fact that destabilization is directly proportional to the rate of hydrolysis, hence all the metal salts dosed to the AMD yielded similarly equal residual turbidity. This study introduces destabilization effect of the metal hydroxide during the AMD treatment, a concept which is only associated with the metal salts and polymers only. It is obvious that the metal ions of the metal hydroxides, namely Ca^{2+} and Mg^{2+} undergo hydrolysis reaction in a similar manner to the Fe^{3+} and Al^{3+} ions in salts. The difference between the metal ions in the hydroxides and metal ions

in the salts is that the former are depicted to have less electronegativity compared to the latter (valence electrons). This was also confirmed in the study conducted by Rabiee *et al.*, (2005) on the continuous process for the polymerization of acrylamide and hydrolysis of functional groups in alkaline condition. It was found that acrylamide may be polymerized and hydrolyzed in a single consequential step, whereby, both degrees of polymerization and hydrolysis are controllable. Since the type of the polymeric flocculants (cationic, anionic or non-ionic) is determined by their molecular weight, their chemical reactivity is similar, i.e. destabilization, hydrolysis, agglomeration and sedimentation. These polymeric flocculants can destabilize the suspension particles merely through two different mechanisms; charge neutralization and polymer bridging or both of them simultaneously (Finch, 1996). In polymer bridging, the molecular weight, and in case of charge neutralization, the charge density plays an important role. Also the presence of charged segments along a polymer chain could have a significant effect on bridging flocculation, which results in optimal adsorption of the turbid materials (Figure 3.3).

A more extensive elucidation of the chemical reactions in the AMD sample with the metal hydroxide dosage is stated under the discussion of the residual turbidity. Although the studies carried out by Feng *et al.* (2000), Geldenhuys *et al.* (2001), Naicker *et al.* (2003), Maree (2004), Semerjian *et al.* (2003), Watten *et al.* (2005), Akcil *et al.* (2006), Kurniawan *et al.* (2006), Herrera *et al.* (2007) and Sibrell *et al.* (2009) stated that the addition of the metal hydroxide to acidic wastewater (AMD) is

for the OH^- ions to neutralize the solution and to form precipitates of metal hydroxide with the heavy metals. This study explains the effect of metal hydroxides to the wastewater as of destabilizing the colloidal suspension and form hydrolysis species.

Figure 3.4 shows the pH and residual turbidity in the AMD samples with 0.043 M Ca^{+} in $\text{Ca}(\text{OH})_2$ and af-PFCl with mixing and shaking. It can be observed that the pH increases with increasing dosage in all the samples in a range of 2.23-9.88. All the samples with $\text{Ca}(\text{OH})_2$ mixing and shaking have higher pH values than those with af-PFCl dosage. Comparison of the residual turbidity between mixing and shaking in the samples with $\text{Ca}(\text{OH})_2$ dosage is relatively identical (range of 2.0-10.0 NTU) whereas in the samples with af-PFCl dosage with mixing it is slightly lower than shaking (range of 1.68-3.48 and 3.16-11.6 NTU respectively). The samples containing 20 mL $\text{Ca}(\text{OH})_2$ dosage is higher than the rest of the samples by 59.4 %. The increasing pH trend observed in Figure 3.4 indicates that the OH^- released by the metal hydroxide was not active during hydrolysis, shown by the increasing pH.

The pH in the samples with af-PFCl dosage with mixing as shown in Figure 3.5 decreases in a range of 2.42-2.33, whereas in the samples without mixing the pH is 2.47-2.38, and in the samples with shaking is was 2.44-2.38. Turbidity in the samples with mixing exhibit an inconsistent changing trend in a range of 3.04-10.5 NTU, whereas the samples without mixing increases in a range of 3.9-11.3 NTU, and in the samples with shaking to 3.16-11.6 NTU.

The corresponding residual turbidity in both the mixing and shaking experiments in Figure 3.5 is below 3.4 NTU, which is above 96.6 %. The residual turbidity values in the AMD samples with af-PFCl dosage with mixing are similarly equal to those in the AMD samples with $\text{Ca}(\text{OH})_2$, but slightly higher in the samples with shaking, above 88.4 %. Residual turbidity in the samples with 20 mL dosage is slightly higher than that in the other samples, in a range of 9.3-10.1 NTU, whereas residual turbidity in the samples with 20 mL Fe^{3+} salts and af-PFCl is in a range of 1.54-5.95 NTU. This can be caused by the deficiency of OH^- released by $\text{Ca}(\text{OH})_2$ which are essential during hydrolysis, a situation that varies with that of Fe^{3+} salts and af-PFCl dosages; where each Fe^{3+} releases three OH^- whereas Ca^{2+} releases only two.

Hydrolysis process plays a pivotal role during coagulation-flocculation with metal salt dosage, which also occurs with polymers. Although polymers, commonly termed polyelectrolytes are depicted to be involved in physical reaction during wastewater treatment as an adsorption substrates (Zhu *et al*, 2003, Zhou *et al.*, 2004, Liu *et al.*, 2004, Rodriguez-Cruz *et al.*, 2005, Sanchez-Martin *et al.*, 2008 and Muherei, 2009). However, it is also mentioned that they destabilize the colloidal suspension by either neutralization or bridging, and can also include both (Finch, 1996). This study revealed that polymers also form part during destabilization-hydrolysis-adsorption employing similar chemical reactions compared to metal salts.

The varying trend of turbidity removal (Figures 3.4 and 3.5) is influenced by the nature of the polymer based on the charge density and molecular weight. The former plays a pivotal role during charge neutralization whereas the latter in polymer bridging. The presence of charged segments along a polymer chain has a significant

effect on bridging flocculation (Finch, 1996). Adsorption is influenced by the presence of specific affinity which outweighs the electrical repulsion which would operate between a negative surface and anionic segment of the polymers' chain. Again, ionic strength is prone to play an important role, since the dissolved salt can effectively reduce that repulsion and promote adsorption (Rabiee, *et al.*, 2005).

Adsorption of a polymer onto the surface of dispersed particles may have either of two effects: stabilization and flocculation (Finch, 1996). During the stabilization process, association and settling of the particles are inhibited and the particles remain in a dispersed state for a long period of time. Application of this phenomenon appears in most of wastewaters with organic and inorganic content. During the flocculation process, the particles interact so as to be easily separated from the surrounding medium and form aggregates. Application of this phenomenon is covered by AMD sample because it appears in water treatment, paper manufacturing, mineral enrichment and recovery from mining.

Residual turbidity results show that the effectiveness of the destabilization potential with af-PFCl is comparable to that with Ca(OH)_2 . The former can then be used in AMD treatment to reduce scaling which is caused by the latter, as stated by Coulson *et al.* (1999). The results show that af-PFCl has the same destabilization efficiency for both Fe^{3+} salts and Ca(OH)_2 , the reagents which have long been used in wastewater treatment. This further shows that af-PFCl polymer utilizes the same chemical energy during EDL compression to counteract electrostatic repulsive and

van Der Waals attractive forces (Gregory *et al.*, 2001 and Peavy, 1985). The inclusion of the experiments where coagulants were dosed without mixing and with shaking was to determine the rate at which the reagents react with the AMD solution. The trivalent property of Fe^{3+} salts is an attribute to the spontaneous destabilization-hydrolysis process. A study by Vilg -Ritter (1999) on the chemistry and structure of aggregates with Fe^{3+} salts dosage to turbid materials revealed that the pH and the nature of the turbid materials were not effective during speciation or the level of complexation, but played a major role in the structuring of the flocs, an approach followed in this study. Although FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ exhibit similarly equal turbidity removal efficiency to af-PFCl, hydrolysis in the former differs from that of af-PFCl because it occurs in a complex acidic medium, and it is limited to the oligomeric form due to the rate of the protonation reaction which results in monomeric, dimeric and trimeric species. It is suggested that in af-PFCl, nucleation is likely to be predominant because the polymer consists of hydrolysis species which already exit from polymerization. It also acceptable that the products of hydrolysis of the Fe^{3+} salts are hydroxo-ferric-complexes which are involved in adsorption; whereas there exist primary and secondary flocs in the case of af-PFCl. The flocs in the former are formed during metal ions-solution interaction, whereas in the latter were formed during floc-floc interaction (nucleation).

Figure 3.6 shows the relation between residual turbidity, dosage and the concentration (g/L) of Fe^{3+} and Ca^{2+} with shaking and without mixing. The mass of Fe^{3+} in FeCl_3 only together with that of Fe^{3+} and Ca^{2+} in af-PFCl polymer (Figure 3.6)

is in a range of 0.21-0.65 g in 20-60 mL of the dosage. Residual turbidity in the samples with FeCl_3 dosage without mixing increases in a range of 1.68-3.48 NTU, whereas in the samples with shaking is in a range of 1.70-3.14 NTU. Residual turbidity in the samples with af-PFCl dosage without mixing is in a range of 3.9-14.6 NTU, whereas in the samples with shaking exhibits an inconsistent changing trend in a range of 3.16-11.6 NTU. The samples with 20 and 30 mL af-PFCl dosage yielded low residual turbidity below 4 NTU whereas dosage above 30 mL yielded residual turbidity between 8 and 12 NTU. This residual turbidity range is relatively low because it yielded turbidity removal efficiency between 88-92 %.

The mechanism of turbidity removal with FeCl_3 is often described as a complexation of Fe with pH values around 5, and adsorption of organic molecules onto Fe hydroxides at a pH of around 7 (Dempsey *et al.*, 1984). In this study, turbidity removal values showed that speciation is only slightly affected by the pH, as the difference between the raw and treated AMD is so insignificant. In our experimental conditions, complexation appears to be the main mechanism which affects turbidity removal at any pH within the range of 2.33-2.47.

The results of the comparison of the TSS removal between the AMD samples dosed with 0.043 and 0.086 M Ca^{2+} in $\text{Ca}(\text{OH})_2$ in Figure 3.7 show that the former molar concentration yielded a better removal performance than the latter, except in the first sample with 20 mL dosage (0.086 M Ca^{2+}). It can also be observed that the 20 mL of 0.043 M contains 0.086 M Ca^{2+} which is lower ($< 7 \text{ g/mL}$) than all the concentrations of Ca^{2+} in 0.086 M of Ca^{2+} in $\text{Ca}(\text{OH})_2$. The best TSS removal occurred in the AMD

samples with 0.179, 0.172 and 0.165 M of Ca^{2+} in $\text{Ca}(\text{OH})_2$ (0.043 M), the values which are lower than those of 0.086 M Ca^{2+} in $\text{Ca}(\text{OH})_2$. The TSS removal of varying concentrations of 0.086 M Ca^{2+} in $\text{Ca}(\text{OH})_2$ are slightly lower than those of varying concentration of 0.043 M Ca^{2+} in $\text{Ca}(\text{OH})_2$. Notwithstanding the influence of other microscopic phenomena, this is probably caused by equilibrium disturbance as a result of excessive metal ions (Ca^{2+}) to reverse speciation reaction and cause re-stabilization (Freeze *et al.*, 2001, Swartz *et al.*, 2004, Aboulhassan *et al.*, 2006)

The results shown by the residual TSS in AMD samples with af-PFCl polymer of $\text{Ca}(\text{OH})_2$ indicate that a combined concentration (mol/mL) of Fe^{3+} and Ca^{3+} of 0.129 M in af-PFCl polymer (30 mL) with mixing and shaking in Figure 3.8 is an optimum dosage to achieve maximum removal. A 20 mL dosage (0.086 M of Fe^{3+} and Ca^{3+} in af-PFCl polymer) without mixing also yielded a similarly equal residual TSS to those yielded by the samples with mixing and shaking. The poor residual TSS removal ($10 > \text{TSS} < 27 \text{ g/mL}$) in the rest of the samples can be as result of re-stabilization. The optimum TSS removal shown by 30 mL dosage (0.129 M of Fe^{3+} and Ca^{2+} in af-PFCl polymer) with mixing and shaking indicate that destabilization-hydrolysis is controlled by both micro- and macroscopic approach. This inference is based on the fact that the 30 mL lies between 20 and 40-60 mL, hence it is suggested that there are some complex reactions involved which make 30 mL dosage distinctive. Another factor which has not been deliberated in the formation of polymers is the reactivity of metal ions of one compound (FeCl_3) with the metal ions of another compound ($\text{Ca}(\text{OH})_2$), i.e. Fe^{3+} (FeCl_3) with Ca^{2+} ($\text{Ca}(\text{OH})_2$) to form polymer (af-PFCl). Another factor which might impair effective removal of the TSS is the solubility conditions of

the coagulant (polymer) after it has been added to a colloidal suspension. It should be borne in mind that atomic radii and energy levels of the metal ions play a pivotal role during their interfacial reaction. The metal ion with a relatively smaller radius will attract the other metal ion closer to its nucleus and form a “screening effect”. That condition changes the original ionic strength of the central metal ion, hence TSS removal efficiency of Ca(OH)_2 in Figure 3.7 is better than with af-PFCl polymer of Ca(OH)_2 in Figure 3.8.

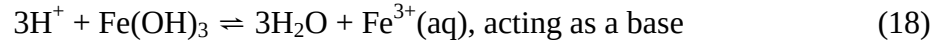
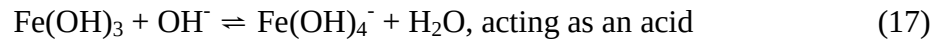
The results of the experiments using shaking and without mixing interpreted kinetics of the reaction, i.e. the spontaneity of the reactions which took place between coagulant/flocculent and the AMD sample (Figures 3.9, 3.10 and 3.11). The impact of the poly-ionic property of the polymers (af-PFCl) on the turbidity removal efficiency, a condition which is similarly identical to that obtained in the commonly used Fe^{3+} salts. The experimental results suggested that the cationic component of the polymer increases the charge density of the positive charges whereas the anionic charges increase the charge density of the negative charges, causing optimal destabilization-hydrolysis reaction. Furthermore, the former is actively involved in the adsorption of the negatively charged colloidal particles whereas the latter in the adsorption of positively charged colloidal particles. The turbidity removal trend (Figures 3.9, 3.10 and 3.11) indicates that the properties of the polymers are influenced by the repulsion between charged segments, which tend to give more extended configuration (Rabiee *et al.*, 2005). Since more extended chain is inevitable and likely to give an enhanced bridging possibility, it is predicted that the flocculation

would be enhanced at low ionic strength. It also revealed that at low ionic strength, there is a likelihood of a greater repulsive distance between the chains, and that needs to be spanned. In order for adsorption to occur some specific affinity have to be present to outweigh the electrical repulsion which operate between a negative surface and anionic segment of the chain. Furthermore, ionic strength plays an important role, since the dissolved salt would effectively reduce this repulsion and promote adsorption.

The poor TSS removal in AMD samples (Figures 3.7 and 3.8) with alkaline pH values is due to the fact that coagulation and sedimentation of iron compounds is slower than in acidic sample around pH less than 4.5. These compounds tend to remain suspended in the colloidal suspension/treated effluent and lead to increased turbidity as stated by Lefebvre *et al.* (1990). Although temperature is not regarded as a major role player in wastewater treatment in a larger scale, it is suggested that the interaction between the polymer(s) and the solvated colloids is temperature-dependent. However, has not been elaborated in this study due to thermodynamics factor.

The AMD samples with higher dosages of af-PFCl of $\text{Ca}(\text{OH})_2$ (Figure 3.9) showed relatively higher residual turbidity values compared to their corresponding samples with FeCl_3 dosage. It is suggested that the OH/Fe mole ratio of the af-PFCl exceeded the concentration of the colloidal particles in AMD sample, reversing equilibrium of the hydrolysis reaction (Figs. 7 and 8). Another inference could be the slow rate of Fe^{2+} conversion to Fe^{3+} during oxidation to form insoluble metal hydroxide, a

condition which resulted in poor turbidity removal. The study by Kuyucak (2002) revealed that the AMD samples with high concentration of ferrous irons at high pH values are passed through an aeration tank, where the ferrous hydroxide precipitates are converted to insoluble ferric hydroxide. It is essential to employ stoichiometric quantities when dosing coagulants, because over-or under-dosing can result in poor turbidity removal. The amphoteric nature of the water molecules as discovered by Brønsted–Lowry theory, is prone to attribute to the pH conditions of the solution as shown by Equations 16-18.



It is thus suggested that the inconsistency in the pH changing pattern is influenced by the interference of water molecules during the destabilization-hydrolysis process. Another suggestion is that Eqs. 16 and 17 show that the Fe^{3+} ions which react with H_2O molecules during hydrolysis reaction reach equilibrium point with the $\text{Fe}(\text{OH})_3$ precipitates (Eq. 16). Beyond the equilibrium point, the reaction entails the reaction between the precipitates and the residual OH^- ions from the metal hydroxide (Eq. 17). This shows that the effect of the concentration of the metal ions of a metal hydroxide ($\text{M}(\text{OH})_2$) in a polymer on the pH is insignificant (Figure 3.5).

Figures 3.10 and 3.11 show the relationship between the pH and the residual TSS at specific af-PFCl dosages. The rationale is to determine the turbidity removal as TSS,

a parameter which is more representative than indicative. The results (Figure 3.8) show that the rate of TSS removal is inversely proportional to the pH and directly proportional to af-PFCl of $\text{Ca}(\text{OH})_2$ dosage. The residual TSS in AMD samples without mixing (Figure 3.11) is directly proportional to the pH and inversely proportional to af-PFCl of $\text{Ca}(\text{OH})_2$ dosage. The pH values are slightly higher than in the AMD samples with mixing (Figure 3.8), in a range of 2.38-2.47 and 2.28-2.36 respectively. The results (Figures 3.10 and 3.11) show that destabilization process, precursor to hydrolysis-adsorption is a spontaneous phenomenon, which is in agreement with the findings of the study by Ntwampe *et al.* (2013). The TSS reduction efficiency of the af-PFCl polymers dosage with mixing reduced the turbid materials from 123.5 g/L in raw AMD to a range of 3.95-8.18 g/L (Figure 3.8). On the other side, the reduction efficiency of the af-PFCl polymer dosage without mixing reduced turbid materials to a range of 5.59-5.80 g/L. The higher removal efficiency in the AMD sample without mixing (Figure 3.11) is due to the destabilization-hydrolysis due to a lack of from shear forces which causes rupturing of flocs that are prone to cause restabilization or deflocculation (Swartz *et al.*, 2004, Aboulhassan *et al.*, 2006). This is also supported by the decreasing trend of the TSS removal with increasing dosage indicating that the rate of hydrolysis (speciation) exhibited a linear characteristic. That has been supported by the correlation between the pH and residual TSS with R^2 of 0.998 (99.8 %) as shown in Figure 3.10. However, this observation (no-mixing) does not necessarily imply that mechanical agitation is not required during wastewater treatment because the spontaneity of the reaction in this study is mainly due to the highly acidic AMD sample, a condition which is

uncommon in water treatment works. Instead, shaking is recommended as a replacement of rapid mixing as confirmed by the results obtained in the AMD samples treated with a shaker.

The correlation between the turbidity removal efficiency and the pH of the AMD sample with af-PFCl and Ca(OH)_2 dosage without mixing in Figure 3.13 is 0.952 ($R^2 = 0.952$). The correlation between the turbidity removal efficiency and the pH of the AMD sample with af-PFCl and Ca(OH)_2 dosage with shaking in Figure 3.14 is 0.986 ($R^2 = 0.986$). The correlation between the turbidity removal efficiency and the conductivity of the AMD with af-PFCl and Ca(OH)_2 dosage with shaking in Figure 3.15 is 0.99 ($R^2 = 0.99$). The r-values of samples with mixing and shaking obtained from the values in Table 3.5 are 0.68 and 0.60 (68 and 60 %) respectively. The range of the correlation coefficient is from -1 to 1. Our correlation coefficients in samples without mixing and with shaking fall within a range of strong relationship. This is validated by the R^2 of pH converted to mass of Fe^{3+} and Al^{3+} vs turbidity removal efficiency in samples without mixing, as shown in Figures 3.13 and 3.14, i.e. 0.986 and 0.980 respectively.

According to optimal turbidity removal in the sample with af-PFCl dosage (Figure 3.3), it indicates that the destabilization-adsorption occurs in multi-stages. That can involve more than one destabilization and adsorption process, a situation where very little amount of turbid materials is left in the solution. It is suggested that charge neutralization (negatively charged colloids by cationic products) and the

incorporation of impurities in an amorphous hydroxide precipitate are predominant types of the destabilization with af-PFCl polymers as stated by Duan *et al.* (2002). In addition, this could also include charge neutralization and inter-particle bridging due to the primary hydrolysis species and polymers respectively. The comparison of the adsorption efficiency between Fe^{3+} salts and acid-free polymers as shown by SEM in Figure 3.16 during mixing, confirming that the latter (an image on the right) forms a large “cake-like” polymeric structure which enhances adsorption efficiency, whereas the former (image on the left) forms a cluster of structures which could be diversified as mono-, di- and tri-meric agglomerates. These images corroborate the objective of our study which is to investigate the turbidity removal efficiency of af-PFCl for the replacement of separate dosages of FeCl_3 and $\text{Ca}(\text{OH})_2$.

According to the comparison of the residual turbidity between the samples with mixing and shaking (Figure 3.3), FeCl_3 and af-PFCl exhibit similarly equal turbidity removal values in corresponding dosages. The SEM images of the sludge of the AMD samples with FeCl_3 dosage with mixing (Figure 3.17) show a large floc covering almost 70 % of the total area with small cavities. This indicates that the flocs formed by FeCl_3 are susceptible to rupture during rapid mixing, hence there is 30 % of unoccupied area. This also shows that further rapid mixing would result in more breakage of the floc, a condition which results in re-stabilization and poor turbidity removal as stated by Freeze *et al.*, (2001), Swartz *et al.*, (2004) and Aboulhassan *et al.*, (2006). The image with FeCl_3 dosage confirms the statement by Rose *et al.*, (1998) when indicating that Fe^{3+} has a tendency of becoming weakly

hydrolysed and appears as monomeric, dimeric or trimeric species within the colloids.

The image of the sludge of the AMD sample with af-PFCl dosage (Figure 3.18) on the right formed a large “cake-like” structure with the tiny and larger flocs spreading throughout the area. The SEM images of the sludge of the AMD with FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ dosage with shaking in Figure 3.15 show almost similar crystal morphological structure with identical turbidity removal efficiency exhibited by both Fe^{3+} salts.

Under experimental conditions, the reaction of FeCl_3 with $\text{Ca}(\text{OH})_2$ to form a polymer yielded the best turbidity removal as shown in Figure 3.5. This might be caused by the aggregation of the flocs due to their hydrophobic or hydrophilic nature. This happens when the concentration of dispersant/coagulant increases, causing the monomers that are adsorbed by a solid surface to begin to aggregate and form micelle-like structures that are called admicelles or hemimicelles (depending on whether the aggregated monomers have one or two dispersant layers, respectively). After these structures form on a solid surface, the adsorption of additional dispersants can rapidly increase until a complete bilayer of dispersant covers the solid surface (Muherei *et al.*, 2009). It can be suggested 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. We therefore conclude that optimal turbidity

removal in AMD solution is of a physical nature. Equation 19 is applied to calculate the ionic strength of ionic species.

$$I = 0.5 \times \sum C_j Z_j^2 \quad (19)$$

C = concentration of ionic species and Z = charge of ionic species.

Table 3.3: Ionic strength of Fe^{3+} , Ca^{2+} and combined Fe^{3+} and Ca^{2+}

Species	Ionic strength
Fe^{3+}	0.193
Ca^{2+}	0.086
$\text{Fe}^{3+} + \text{Ca}^{2+}$	0.323

The calculations show that af-PFCl has the ability to perform better than Fe^{3+} salts and $\text{Ca}(\text{OH})_2$.

Experimental results of the pH and residual turbidity indicate that the correlation between these two parameters is not based upon the pH range as stated by Peavy (1985), but the correlation between the ratio of the concentration of the metal ion and the mass of particles on the solution ($M^{n+}_{\text{conc}}/\text{TSS}_{\text{mass}}$) as shown in Figures 3.6 and 3.7. Although the dosage has an impact on the pH changing rate, the constituents might also influence its changing rate to deviate from that stated by Peavy (1985). We suggest that effective adsorption is determined by the reaction efficiency of the metal ions (concentration) added to destabilize the EDL. The pH depends on the dosage, and that has been confirmed by the models and the square of the correlations above 95 % in the sample with af-PFCl dosage without mixing and with shaking (R^2)

in Figures 3.13 and 3.14 respectively. The best turbidity removal 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. We used Pearson correlation coefficient (r) to calculate the relation between pH and residual turbidity using Equation 3.20.

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (20)$$

According to the correlation coefficient, 0.70 or higher is a very strong relationship, 0.40-0.69 a strong relationship, and 0.30-0.39 to a moderate relationship.

X_{nm} =pH without mixing, x_{sh} =pH with shaking, y_{nm} =turbidity without mixing and y_{sh} =turbidity with shaking.

$$\sum x_{nm} = 12.09, \sum x_{nm}^2 = 29.23, \sum y_{nm} = 50.4, \sum y_{nm}^2 = 610 \text{ and } \sum xy_{nm} = 121.23$$

$$\sum x_{sh} = 12.08, \sum x_{sh}^2 = 29.18, \sum y_{sh} = 37.7, \sum y_{sh}^2 = 323 \text{ and } \sum xy_{sh} = 90.5$$

Using the results of the pH and turbidity removal efficiency of the AMD with af-PFCl and $Ca(OH)_2$ dosage without mixing and with shaking yields the r -values of 0.995 and 0.62 (99.5 and 62 %) respectively. The range of the correlation coefficient is from -1 to 1. The correlation coefficients in samples without mixing and with shaking fall within a range of strong relationship. This is validated by R^2 of the mass of Fe^{3+} and Ca^{2+} vs turbidity removal efficiency in samples with shaking and without mixing as shown in Figures 3.7, 3.8 and 3.9 of 0.952, 968 and 0.990 respectively.

3.6 CONCLUSION

A synthetic af-PFCl polymer of $\text{Ca}(\text{OH})_2$ yielded a better turbidity removal which is comparable to that of FeCl_3 or $\text{Ca}(\text{OH})_2$, indicating that all three coagulants have the same destabilization potential. The pH and residual turbidity in the corresponding sample with mixing, shaking and without mixing exhibit an insignificant difference. The af-PFCl polymer of $\text{Ca}(\text{OH})_2$ is an ideal replacement of both reagents due to their corrosive and environmental degradation implications. The af-PFCl polymers of $\text{Ca}(\text{OH})_2$ also show a high spontaneous reactivity as it yielded a better turbidity removal in the samples without mixing and with shaking.

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CHAPTER 4: Destabilization potential of Fe^{3+} and Al^{3+} chloride salts and acid free- polyferric chloride polymer of magnesium hydroxide in AMD sample without pH adjustment

Abstract

A 200 mL of AMD was poured into 5 glass beakers and thereafter dosed with Fe^{3+} and Al^{3+} salts and a synthetic polymer of FeCl_3 and $\text{Mg}(\text{OH})_2$. The samples were treated in a jar test at 250 rpm for 2 minutes, settled for 1 hour after which the pH, conductivity, turbidity, dissolved oxygen (DO) and oxidation reduction potential (ORP) were measured. A similar batch experiments was conducted by placing the samples on a shaker using the same timing and measurements. A similar third batch of experiment was conducted with samples without mixing and employed similar settling time and measurements, and the fourth similar set of experiments was conducted dosing AMD sample with 0.1 M af-PFCl of $\text{Mg}(\text{OH})_2$ in mixing and shaking. The turbidity removal in the samples in the samples with FeCl_3 , AlCl_3 and af-PFCl dosage was effective and comparable, whereas FeCl_3 yielded better performance. The SEM images show that the sludge in the samples with af-PFCl of $\text{Mg}(\text{OH})_2$ dosage consists of a large cake-like structure, with the likelihood of optimal adsorption. The turbidity removal in the AMD sample with 0.1 M af-PFCl polymer of

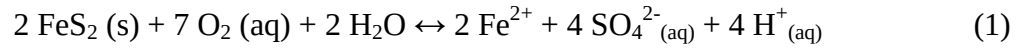
Mg(OH)₂ with mixing and shaking is similarly identical, and also ORP results showed that redox reaction is predominant during destabilization-hydrolysis.

Key words: AMD, wastewater, neutralization, coagulant, mixing, shaking

4.0 Introduction

Acid mine drainage (AMD) that is generated from various mining activities has become a global major environmental concern. AMD is sulphide-rich and results from minerals when rocks are exposed to oxidizing conditions in coal and other mining activities. Coal mining is a source of acid mine drainage where coal is a commodity which is found in abundance worldwide and is used as a cheap source of energy world-wide (Finkelman, 2007). Large volumes of AMD is generated during mining and cleaning, thus posing a detrimental impact to the environment and human health from, for example hazardous inorganic trace elements emerging from coal mining and combustion (Gupta, 2007; Huang *et al.*, 2008; Hower *et al.*, 2008; Cravotta *et al.*, 2008; Silva *et al.*, 2009; Galatto *et al.*, 2009; Silva *et al.*, 2010). Sulphide minerals are other constituents in the coal which play an enormous role in environmental degradation through the sulphide oxidation process (Giere *et al.*, 2006 and Huang *et al.*, 2008). AMD is characterized by a low pH (2-3), high salinity levels, broad range of heavy metal ions and high concentrations of sulphate, iron, aluminium and manganese. Pyrite (FeS₂) and pyrrhotite (FeS) are sulphide species commonly found in coal (Sasowsky *et al.*, 2000, Kuyucak, 2005 and Kuyucak, *et al.*, 2006). Upon exposure to water and oxygen, pyritic minerals oxidize to form acidic,

iron complexes and sulphate-rich drainage, where sulphuric acid is catalysed by sulphur oxidizing bacteria (Sawyer *et al.*, 1994). Pyrite oxidizes in the following reaction:



Traditionally, metal hydroxides have been used for neutralization of AMD (Herrera *et al.*, 2007; Sibrell *et al.*, 2005, Watten *et al.*, 2005; Feng *et al.*, 2000; Semerjian *et al.*, 2003). It is used to raise the pH of AMD and supplies AMD with hydroxide (OH^-) so that dissolved metals in the water will form insoluble metal hydroxides and settle out of water. In some other instances, the addition of metal hydroxide to AMD is used to oxidize Fe^{2+} in FeS_2 shown in Equation 1 to Fe^{3+} so that ferric hydroxide hydrolysis species ($\text{Fe}(\text{OH})_3$) can be formed for adsorption of colloidal particles as shown by Equation 2 and 3.



The optimal pH suitable to precipitate most metals from water ranges from 6 to 9, where ferric irons precipitate at about pH 3.5. Several new processes have been developed, based upon the use of precipitated calcium carbonate or lime pre-treatment for neutralization of AMD and partial desalination (Maree *et al.*, 2004). The disadvantage of using lime or limestone is that metal hydroxides are precipitated

together with gypsum. An attractive, alternative alkali for neutralization of AMD is magnesium hydroxide. This is because magnesium sulphate (260 g/L) has a high solubility, and only metal hydroxides form precipitates (Bologo *et al.*, 2009). Mg(OH)_2 also has the ability of raising the pH to 10, which is sufficient for the removal of metals such as manganese and zinc, a high pH level which cannot be achieved with limestone. Kuyucak *et al.* (2005) stated that Mg(OH)_2 can form low volume and dense metal hydroxide sludge when it is properly applied in a neutralized system. It is more soluble than CaSO_4 which can also remove metals through surface adsorption. However, the rate of neutralization is slow, and the buffering capability of Mg(OH)_2 prevents the pH from reaching the maximum depending on the pH requirements, and therefore recommended that it should be used in combination with NaOH. It is normally used in treatment plants where sludge generated is high in order to reduce disposal costs (Kuyucak *et al.*, 1999 and Kuyucak *et al.*, 2002). Maree *et al.* (2004) used Mg(OH)_2 and Ba(OH)_2 in AMD treatment in their study, where the former is used for pH adjustment and acid neutralization. The problem they encountered was that Ba(OH)_2 requires Ca(OH)_2 as coagulant-aid to effectively remove some of heavy metals. Another problem was to separate BaSO_4 and CaCO_3 as they tend to co-precipitate.

There are two mechanisms in operation when AMD containing metals is neutralized with Mg(OH)_2 . The first mechanism includes the precipitation of metals as metal hydroxides and the second mechanism is the absorption of metals onto the surface of magnesium hydroxide particles (Weast, 1971). Teringo (1987) found that metals can

be removed from a solution at one pH unit with magnesium hydroxide; lower than with sodium hydroxide. $\text{Mg}(\text{OH})_2$ produces a faster settling rate for metal hydroxide flocs, as well as a denser sludge than other neutralizing agents such as $\text{Ca}(\text{OH})_2$ and NaOH (Marshall *et al.*, 1992). This is attributed to the its lower solubility, which results in a slower release of the OH^- ions into the solution that causes a more gradual increase in pH. The formation of larger metal hydroxide particles and a more compact or denser sludge occurs under such conditions.

The studies which have been conducted with $\text{Mg}(\text{OH})_2$ were mainly acid neutralization and pH adjustment, whereas its ability to form polymers when reacting with metal salts to form $\text{FeCl}_3\text{-Mg}(\text{OH})_2$ polymers has not been researched, the approach which is also adopted in this study. This study also investigate the chemical reactivity in monoprotic behaviour associated with FeCl_3 and AlCl_3 , and compare with af-PFCl of $\text{Mg}(\text{OH})_2$. Many authors such as Freeze *et al.* (2001), Aboulhassan *et al.* (2006), Water Specialist Technology (2003) and Pratt *et al.* (2007) stated that pH plays a pivotal role in wastewater treatment. Iron hydroxide shows a minimum solubility in a wide pH range of 7–10, while the values outside this range increase the solubility of iron than aluminium hydroxide (Binnie *et al.*, 2003). Crozes *et al.* (1995) reported that aluminium ions form acidic medium in water and exhibit less solubility than ferric ions. Ghaly *et al.* (2006) and Aysegul *et al.* (2002) discovered that the addition of Fe^{3+} and Al^{3+} salts at a pH 6–8 causes an uncontrollable rise in the rate of hydrolysis which leads to very rapid precipitation. On the contrary to all these statements, Flynn (1984) and Peavy (1985) stated that hydrolysis species formed during coagulation have a pH range of dominance, each with some overlap. They

exist in an order as Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_{3(s)}$ and $\text{Fe}(\text{OH})_4^-$ covering an area in the pH range 1-5, 2-7, 4-8 and 4-14 respectively.

In the present study, AMD is treated with synthetic af-PFCl prepared by FeCl_3 and $\text{Mg}(\text{OH})_2$. Previous studies by Jiang *et al.* (1987) used partially acidified FeCl_3 or AlCl_3 to form PFCl prepared by partial hydrolysis of acidic solution in a special reactor. The dosing of af-PFCl polymer in this study is to determine the reactivity potential of combined FeCl_3 and $\text{Mg}(\text{OH})_2$ in a polymeric state with AMD. A lot of research on AMD treatment has been intensively studied over a range of conditions utilizing a wide array of techniques and theory such as SAVMIN, Aqua-K, Reverse Osmosis and Electrodialysis. Conventional techniques which have been conducted mostly involve metal hydroxide (lime, dolomite, limestone) neutralization, iron oxidation and gypsum crystallization (Maree *et al.*, 2004).

A conventional method of wastewater treatment using inorganic coagulants is employed in this study, focusing on electrochemistry and double layer compression on the effect of aqua-metal ions (M^{3+}) on the colloids (solvation). The study is complemented by the use of synthetic af-PFCl polymers $\text{Mg}(\text{OH})_2$ as conducted in the study by Ntwampe *et al.* (2013) using paint wastewater. The pH of the paint wastewater was 8.09 and there was no adjustment before treatment, an approach adopted also in this study. The study focuses more on destabilization and hydrolysis kinetics using the correlation between the pH, conductivity, turbidity and metal ionic ($\text{Fe}^{3+}/\text{Mg}^{2+}$) mobilization. A jar test is employed to coagulate-flocculate the AMD

sample. Two instrumental techniques are employed for mineralogical characterization such as scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The complexity of wastewater due to a varying mineral content causes a perpetual uncertainty which results in the exploration of different treatment technologies. These technologies are controlled by the quality of wastewater and particle type and size. It is very significant to know the minerals content in wastewater so that the right choice of coagulant and dosages can be prepared. In conventional wastewater treatment, physico-chemical properties of both hydrated metal ions and colloids play a pivotal role to effect destabilization and hydrolysis as shown in Table 4.1.

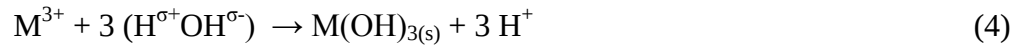
Table 4.1: Chemical and physical properties of iron and aluminium atoms

Description	Iron	Aluminium
Electronegativity	1.8	1.5
van der Waals radius	0.126 nm	0.143 nm
Ionic radius	0.076 nm (2+)	0.05 nm (3+)
Ionic radius	0.064 nm (3+)	0.05 nm (3+)
Electronic shell	[Ar] 3d ⁶ 4s ²	1s ² 2s ² 2p ⁶ 3s ² 3p ¹
Density	7800 kg/m ³	2700 kg/m ³
1 st ionization energy	761 kJ/mol	577.4 kJ/mol
2 nd ionization energy	1556 kJ/mol	1816.1 kJ/mol
3 rd ionization energy	2951 kJ/mol	2744.1 kJ/mol

Subsequent reactions/processes such as nucleation, crystal growth and aggregation will then be optimal to maximize turbidity removal. These processes are also determined by the rate of destabilization-hydrolysis (Wu *et al.*, 2001; Tan *et al.*, 2000), hence in the present study the focused is more on the double layer compression. An identification of the type of colloids in the colloidal suspension is

significant in order to be able to choose an appropriate coagulant. The types of colloids include hydrophobic colloids (water-hating) and hydrophilic (water-loving), not easily interactive. The latter is not easy to destabilize because of dipolar water molecules surrounding the colloids, adding to existing charge density from electrostatic charge and van der Waals forces in the double layers of the neighbouring aqua-particles (Cheng, 2002, Sincero *et al.*, 2003 and Widderska-Broz *et al.*, 2009). Effective destabilization occurs due to high ionic charge, high electronegativity and charge per surface area (Z^2/r) (Cheng, 2002, Swartz *et al.*, 2004, Spellman 2009 and Widderska-Broz *et al.*, 2009). The presence of a high concentration of hydroxyl ions combined with more Fe^{3+} or Al^{3+} ions reduce the charge on the hydroxoferric complex (Barnes *et al.*, 1983 and Pratt *et al.*, 2007).

Ali *et al.* (2002) reported in their study that raw water contains microscopically visible colloidal particles that possess high electrophoretic mobility or high zeta potential. Addition of coagulants causes collision of the particles with one another to form flocs, whereas the M^{3+} ions hydrolyse by forming a bond with OH^- as a result of a cleavage of the polar water molecules ($\text{H}^{\sigma+}\text{OH}^{\sigma-}$) to form metal hydroxide species as shown by Equations 4 and 5



Equation 4 shows the hydrolysis reaction when metal ion reacts with hydroxyl ions, whereas Equation 5 represents the different species which are formed during

hydrolysis, where the pH of a solution decreases during the hydrolysis process. The first solid species formed is an unstable amorphous metal hydroxide ($\text{am-M}(\text{OH})_{3(s)}$). It is formed due to a very low solubility product of the metal hydroxide. Ageing causes the conversion of an unstable amorphous metal hydroxide to a stable $\alpha\text{-MO}(\text{OH})_{(s)}$, which is formed at the lowest M^{3+} concentration. Some other species such as beta ferric hydroxide ($\beta\text{-MO}(\text{OH})_{(s)}$) are also possible depending on the compound which is used in the wastewater treatment process (O'Melia, 2001). Equation 2 shows that hydrogen (H^+) ions are released during hydrolysis, thus lowering the pH of the solution. A study by Ntwampe *et al.* (2013) on paint wastewater treatment using inorganic coagulants revealed that the release of hydrogen ions into the solution influences the hydrolyzing potential of the coagulant(s) added to a solution. This work indicated that the coagulant(s) which have a high deprotonation potential have high turbidity removal efficiency.

Mechanical energy input such as mixing has been recommended as another factor which influences effective wastewater treatment (Binnie *et al.*, 2003, Kemmer, 1988, Heath *et al.*, 2002, Clark *et al.*, 1993, Aguilar *et al.*, 2002, Aguilar *et al.*, 2005 and Sincero *et al.*, 2003). Mixing induces a velocity gradient ($\Delta v/\Delta d$), which is also regarded to be playing a pivotal role in wastewater treatment, and it has been stated that the best results with Fe^{3+} and Al^{3+} salts are possible when the velocity gradient is between 20 and 70 s^{-1} (Swartz *et al.*, 2004). O'Melia (2001) reported that slow mixing is important after rapid mixing since it is a stage where relative motion induces a velocity gradient of the particles which causes a high shear rate in a liquid

phase. On the contrary, some researchers such as Oldshue (1983), Swartz *et al.* (2004) and Sincero *et al.* (2003) stated that intensive extensive mixing for a longer period is an attribute to poor effluent quality as it causes rupturing of the flocs (high shear rate) at high speed. Our study conducts experiments involving chemical addition without mixing and with shaking to compare turbidity removal efficiency with samples from a jar test. Another prediction is to attenuate the rupturing of the flocs during mixing by the use of shaking, which could be an ideal mechanical approach for the dispersion of coagulants throughout the colloidal suspension.

4.1 MATERIALS AND METHODS

In this study, coagulation-flocculation treatment has been conducted by pouring 200 mL of AMD into five 500 mL glass beakers and dosed with 0.043 M Fe^{3+} and Al^{3+} in FeCl_3 and AlCl_3 respectively, combined with 0.043 M of Fe^{3+} in FeCl_3 and Mg^{2+} in $\text{Mg}(\text{OH})_2$ dosage to prepare a polymer (af-PFCl) and were treated in a jar test at 250 rpm for 2 minutes. The samples were allowed to settle for 1 hour and then the pH, conductivity and turbidity were measured. A similar set of experiments was conducted and the samples were treated in a shaker at 250 rpm for 2 minutes, settled for 1 hour and the same measurements were conducted. A third similar set of experiments was conducted including coagulation without mixing with 0.021 and 0.043 M of af-PFCl dosage respectively, settled for 1 hour and then similar measurements were conducted. A fourth set of experiments was conducted on AMD sample with a polymer of 0.1 M FeCl_3 and 0.1 M $\text{Mg}(\text{OH})_2$ in a jar test and a shaker

respectively (250 and 100 rpm for 2 and 10 minutes respectively), settled for 1 hour, after which the pH, turbidity, DO and ORP were measured. The molarity was increased to 0.1 M in order to determine the possibility and/or extent of oxidation-reduction reaction in the destabilization-hydrolysis reaction.

4.1.1 Acid mine water sample

The AMD sample was collected from Western Decant in Krugerdorp, in a 25 litre plastic drum. The sample was stored in an air-tied container at room temperature. The pH, conductivity, turbidity, DO and ORP of the AMD were measured to be 2.56, 4.43 mS/cm, 100 NTU, 4.94 mg/L and 232 mV respectively. The solid content of the AMD sample was 6.8 g in a 200 mL volume.

4.1.2 Coagulants

Inorganic coagulants of 0.043 and 0.021 M of Fe^{3+} in FeCl_3 , Al^{3+} in AlCl_3 and Mg^{2+} in $\text{Mg}(\text{OH})_2$ (typical concentration found in literature) were dosed during flocculation of the AMD and yielded a wide range of results showing effective flocculation. The concentrations were chosen as per a study conducted by Fasemore (2004) on paint wastewater treatment, whereas the concentration of 0.1 M of Fe^{3+} or Mg^{2+} in af-PFCl polymer in this study was to increase the molarity in order to determine the possibility and/or extent of oxidation-reduction during destabilization-hydrolysis.

The calculation of the mass of metal salt to obtain 0.10, 0.084, 0.043 and 0.021 M of M^{3+} ($M^{3+} = Fe \text{ or } Al$) was as follows:

Monoprotic metal salts (MCl_3)

$$0.10, 0.086, 0.043 \text{ or } 0.021 \text{ M of } M^{3+} \times \text{mass of } M^*Cl_3 \cdot 6H_2O \text{ (} M^* = \text{cation)} \quad (6)$$

$$0.10 \text{ M of } M^{2+} \times \text{mass of } M^*(OH)_2 \text{ (} M^* = Mg) \quad (7)$$

In Table 4.2 the metal salts and metal hydroxide dosed into the acid mine water samples are shown.

Table 4.2: Metal salt and metal hydroxide dosed into AMD samples.

Salt	Mass of salt (g)	Conc. (mol/L)	M^{3+} conc. (mol/L)
FeCl ₃	3.5	0.021	0.021
AlCl ₃	5.1	0.021	0.021
FeCl ₃	7.0	0.043	0.043
AlCl ₃ ·6H ₂ O	10.1	0.043	0.043
Mg(OH) ₂	2.49	0.043	0.043
FeCl ₃	14.0	0.086	0.086
AlCl ₃	20.2	0.086	0.086
Mg(OH) ₂	5.79	0.10	0.10

4.2 EXPERIMENTAL PROCEDURE

The different procedures used during the present experiment are listed in the following sections.

4.2.1 Jar test Procedure of a jar test

The equipment used for the 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 0.10, 0.086, 0.043 and 0.021 M Fe^{3+} or Al^{3+} in FeCl_3 and AlCl_3 or af-PFCl polymer were added to AMD samples respectively. The experiments were conducted employing rapid mixing (250 rpm for 2 minutes. and/or 100 rpm for 10 minutes), and also chemical reaction in AMD sample without mixing. The rationale was to determine a correlation between the pH changing trend with turbidity removal. The experiments were conducted in the following order:

4.2.2 Sample shaking in a shaker

A Labotec shaker (*model 261*) made in South Africa was used. The samples were poured into five 500 mL Erlenmeyer flasks, placed and tightened in the shaker, after which the coagulants/flocculants mentioned under subsection 4.2.1 were added, using similar timing and rpm, settling and measurements (sub-section 4.2.1).

4.3 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 measured to determine the removal of colloidal particles from the samples.

4.3.1 pH measurement

A MettlerToledo Seven Multimetric (*made in Germany*) pH meter with an electrode filled with silver chloride solution, and the outer glass casing fitted with a small membrane covering at the tip was used. The equipment was calibrated as in section 2.3.1.

4.3.2 Conductivity

An EDT instrument FE 280 conductivity-meter (*made in Japan*) was used and calibrated as in section 2.3.2.

4.3.3 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 measure. It was calibrated as in section 2.3.3.

4.3.4 DO measurement

A SensoDirect Multimetric (*made in South Africa*) pH/ORP/DO/CD/TSS 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 pH of 4.0 and 7.0 before use. A DO measurement was selected and the measurements were conducted.

4.3.5 ORP measurement

A similar equipment as in sub-section 4.3.5 was used and ORP measurement was selected and thereafter measurements were conducted.

4.4 RESULTS

Figures 4.1-4.3 show the pH, conductivity and residual turbidity in the samples which have been dosed with FeCl_3 , AlCl_3 and af-PFCl with shaking. The choice for shaking is due to consistency of the pH and turbidity changing trend in all the three methods.

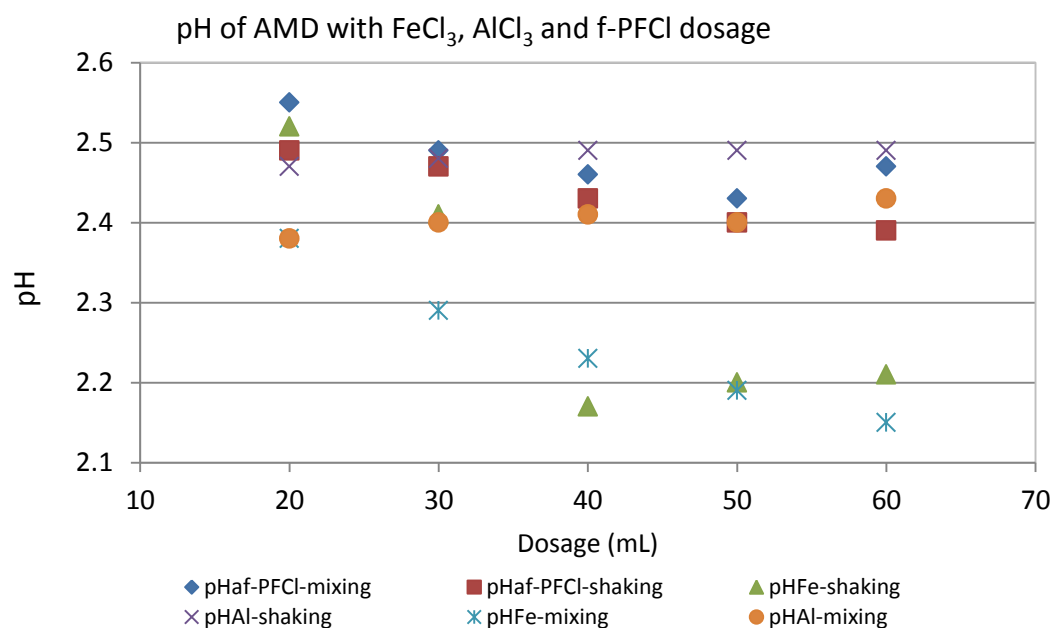


Figure 4.1: pH of AMD with FeCl_3 , AlCl_3 and af-PFCl dosage with mixing and shaking.

The pH of the AMD samples (Figure 4.1) which were dosed with FeCl_3 , AlCl_3 and af-PFCl with mixing was in a range 2.15-2.38, 2.38-2.43 and 2.43-2.55 respectively, whereas in the samples with shaking the Ph was in a range of 2.17-2.52, 2.47-2.49 and 2.39-2.49 respectively

The conductivity in the AMD samples (Figure 4.2) which were dosed with FeCl_3 , AlCl_3 and af-PFCl with mixing, changes inconsistently in a range 4.66-5.62, 4.63-5.33 and 4.57-5.29 respectively, whereas in the samples with shaking show similar changing trend in a range of 5.17-6.43, 4.48-5.19 and 4.60-5.21 respectively.

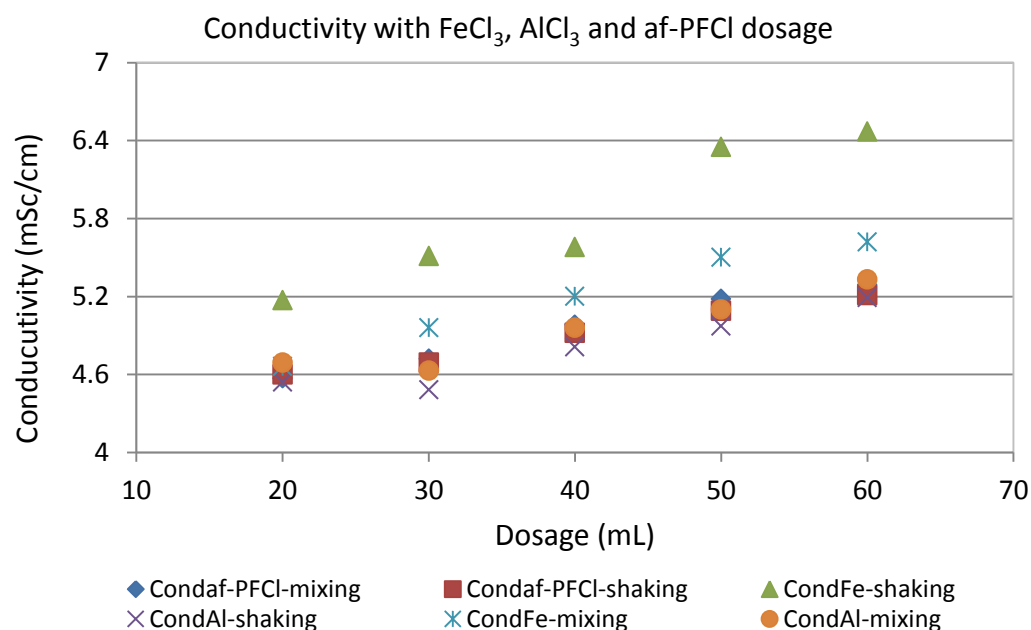


Figure 4.2: Conductivity in AMD with FeCl_3 , AlCl_3 and af-PFCl dosage with mixing and shaking.

The residual turbidity in the AMD samples (Figure 3) with FeCl_3 , AlCl_3 and af-PFCl dosage with mixing was in a range of 2.7-3.06, 1.0-1.49 and 3.0-5.7 NTU respectively, in the samples with shaking was in the range of 1.70-3.14, 0.72-1.44 and 2.5-4.9 NTU respectively.

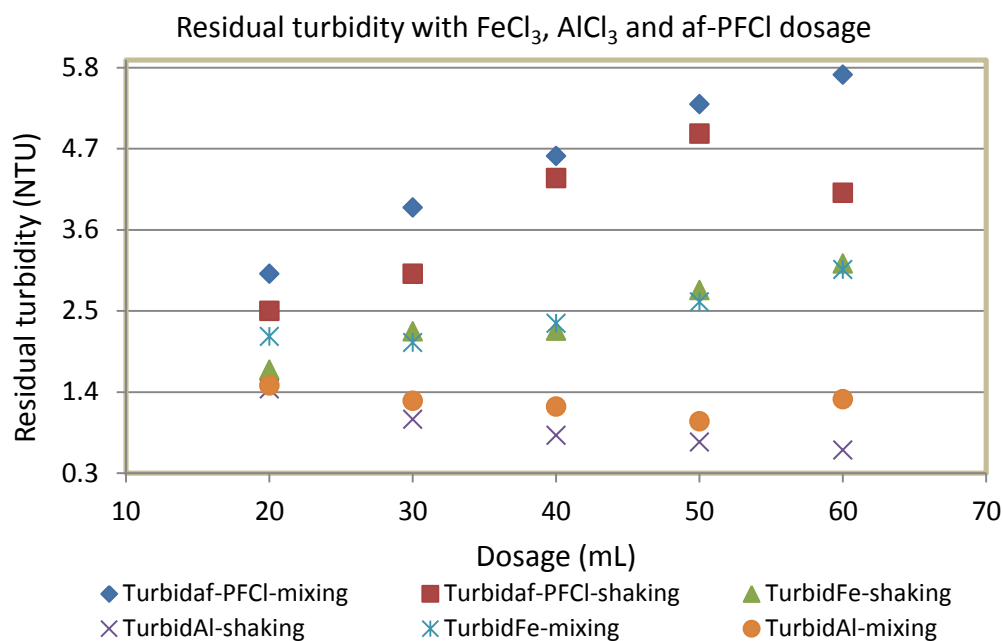


Figure 4.3: Turbidity of AMD with FeCl_3 , AlCl_3 and af-PFCl with mixing and shaking.

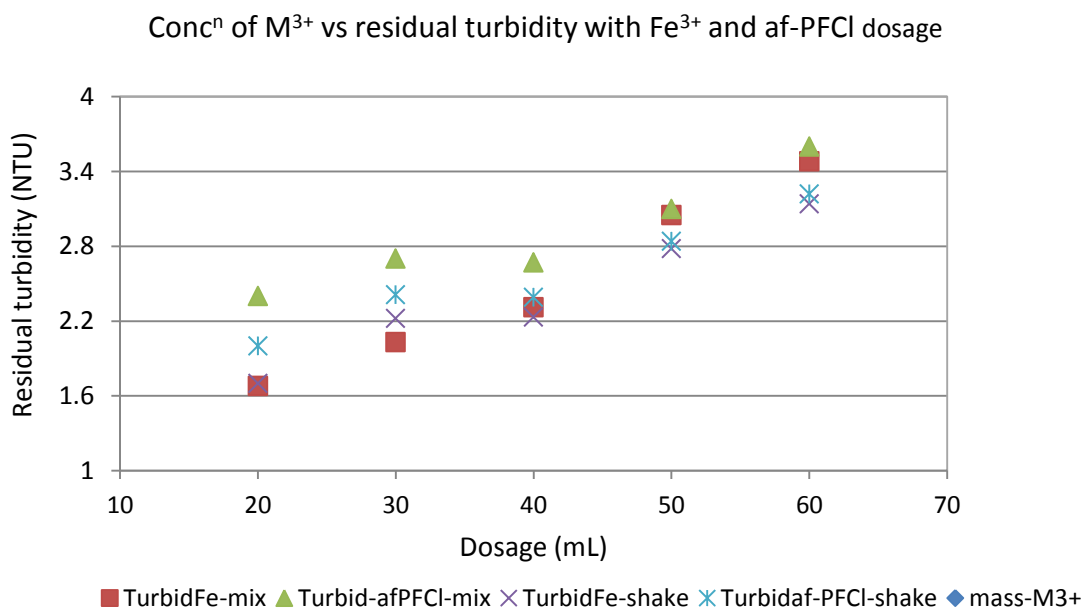


Figure 4.4: Concⁿ of 0.043 M Fe^{3+} vs residual turbidity of Fe^{3+} and af-PFCl with shaking and without mixing.

Figure 4.4 shows the mass of Fe or a combination of Fe^{3+} and Mg^{2+} in a solution (coagulant) which flocculated aqua-colloids in 200 mL of AMD to yield residual turbidity values as shown by the graph. Residual turbidity values in the AMD samples with mass of Fe^{3+} and a combination of solvated Fe^{3+} and Mg^{2+} in the solution with mixing is in a range of 1.68-3.48 NTU, whereas in the samples with shaking the residual turbidity is 1.70-3.14 NTU. Residual turbidity in the AMD samples with a combined mass of Fe^{3+} and Mg^{2+} (polymer) conducted with mixing and shaking is in a range 2.1-3.6 and 2.0-3.22 NTU respectively. The identical residual turbidity values between both the Fe^{3+} salt and polymer indicate that their reactivity to the AMD samples is similar.

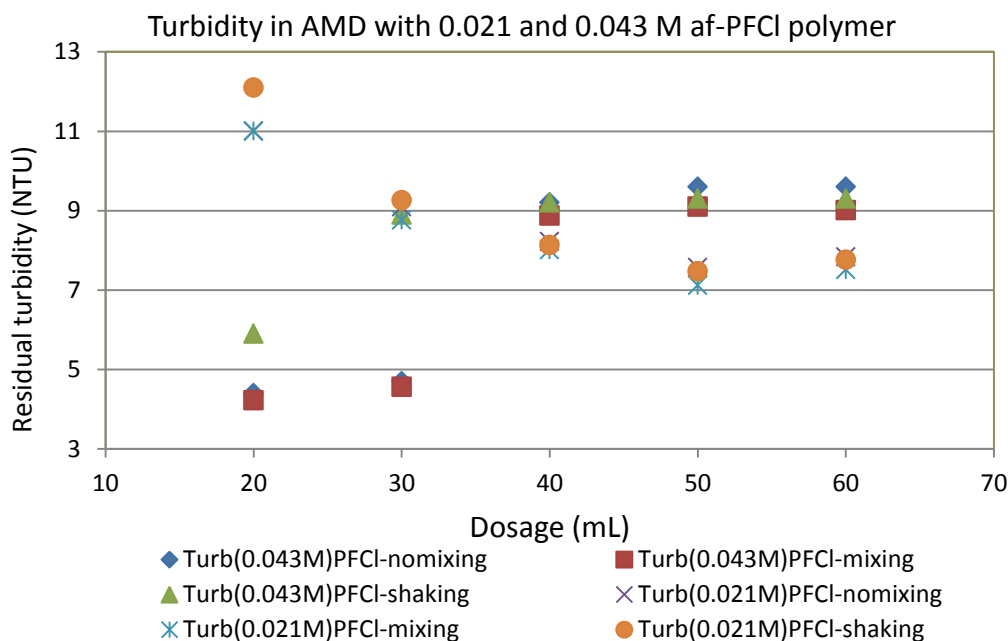


Figure 4.5: pH in AMD with 0.021 and 0.043 M af-PFCl with $\text{Mg}(\text{OH})_2$ with mixing, shaking and without mixing.

Residual turbidity in the AMD samples with 0.043 M af-PFCl dosage mixing (Figure 4.5) increases in a range 4.22-9.01 NTU, whereas a decreases in a range 11.0-7.51 NTU is observed in the samples with 0.021 M af-PFCl dosage. The residual turbidity increases in a range of 4.40-9.60 NTU for the samples with 0.043 M af-PFCl dosage without mixing and decreases in a range of 11.0-7.83 NTU in samples with 0.021 M af-PFCl. It then increases in the samples with 0.043 M af-PFCl (shaking) in a range of 5.90-9.30 NTU, and also increases in a range of 12.1-7.76 NTU in samples with 0.021 M af-PFCl dosage.

Figures 4.6 and 4.7 shows the pH, DO, ORP and turbidity in the AMD sample with 0.1 M FeCl_3 alone and 0.1 M af-PFCl polymer of $\text{Mg}(\text{OH})_2$ with mixing and shaking respectively.

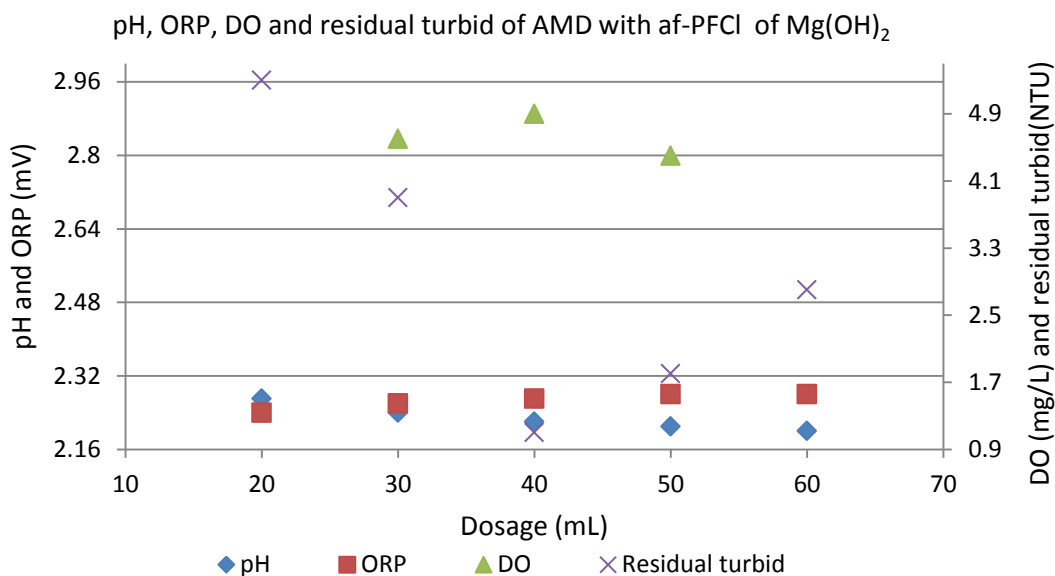


Figure 4.6: pH, DO, ORP and residual turbidity in AMD sample with 0.1 M af-PFCl polymer of $\text{Mg}(\text{OH})_2$ with mixing.

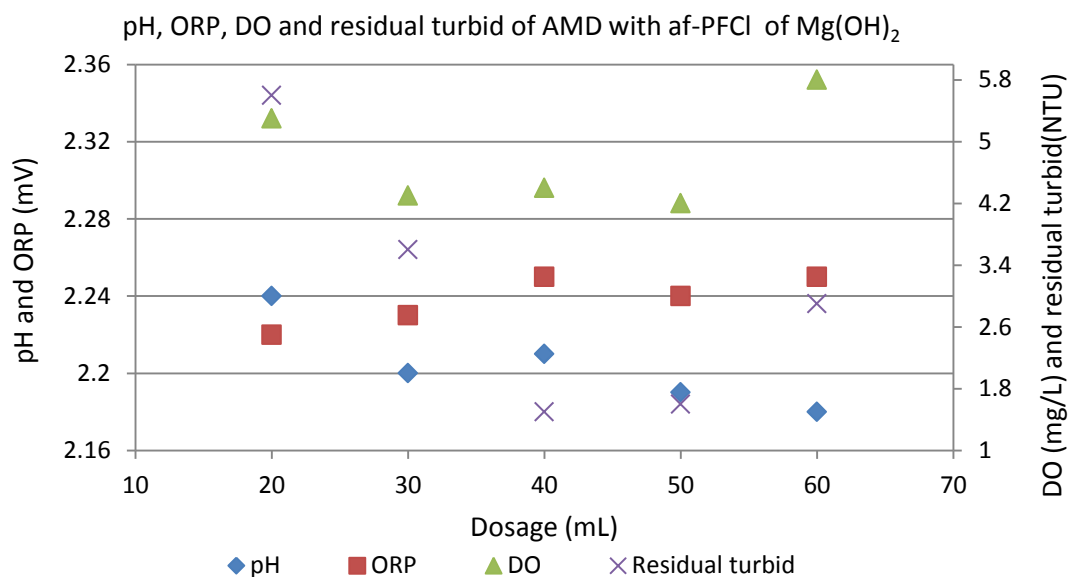


Figure 4.7: pH, DO, ORP and residual turbidity in AMD sample with 0.1 M af-PFCl polymer of $\text{Mg}(\text{OH})_2$ with shaking.

Figures 4.8 and 4.9 are derived from the pH and residual turbidity efficiency of AMD with 0.043 M af-PFCl dosage without mixing and with shaking to calculate the equations and the R^2 as shown in Figure 4.8.

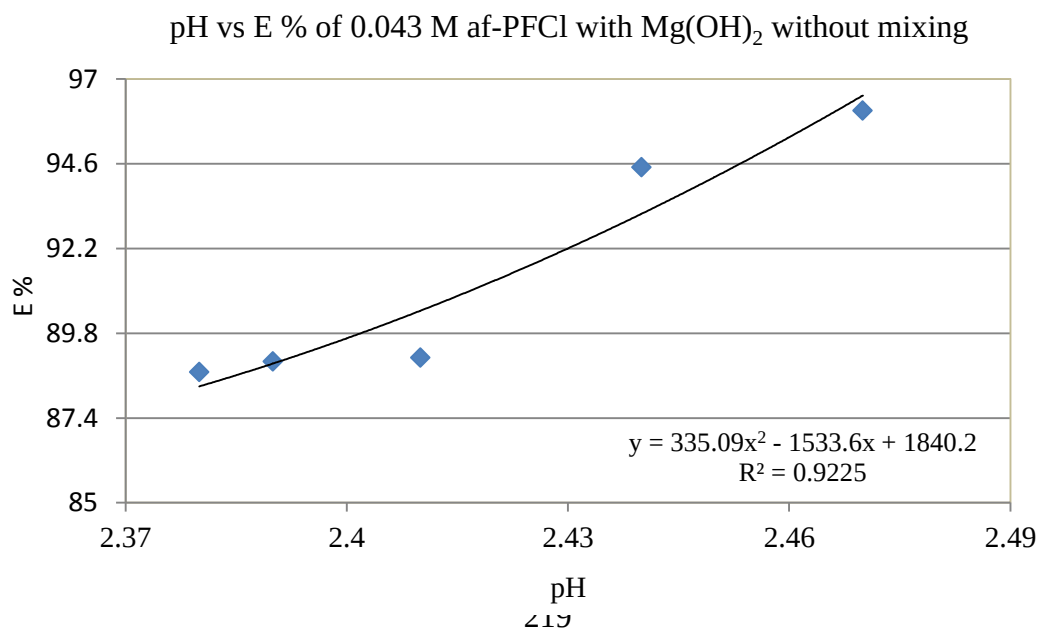


Figure 4.8: pH vs E % of 0.043 M af-PFCl of Mg(OH)₂ without mixing.

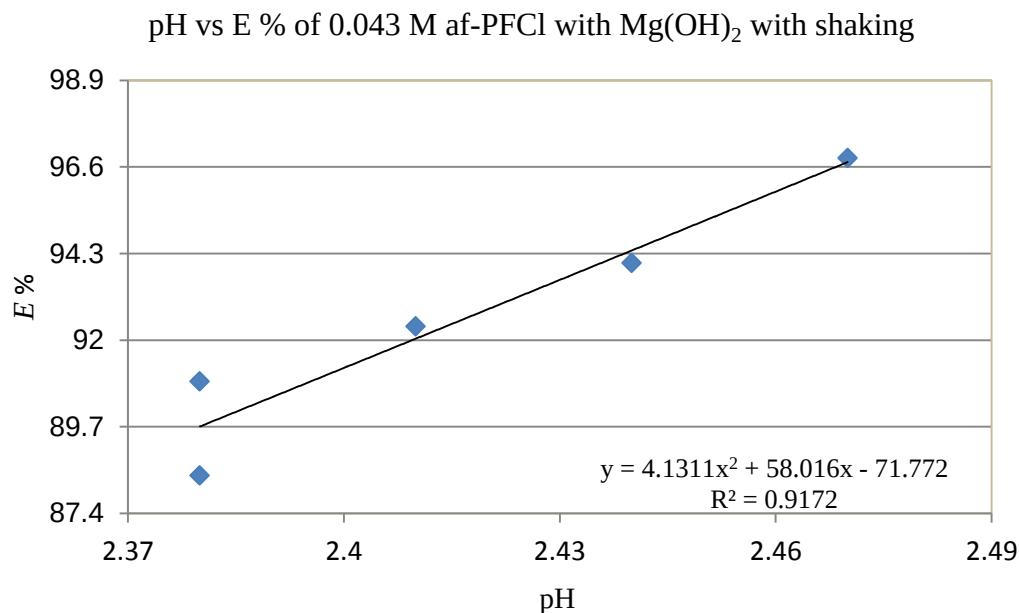


Figure 4.9: pH vs E % of 0.043 M af-PFCl of Mg(OH)₂ with shaking.

Figure 4.10 shows XRD results of the residual copper present in the AMD samples with AlCl₃ in a jar test (mixing) and with shaking. Results shown for the sample without mixing are also identical to those with mixing and shaking, including the three methods with FeCl₃ dosage. The values are identical, which indicates that the experiments with mixing, shaking and without mixing yield similarly equal minerals reduction potentials.

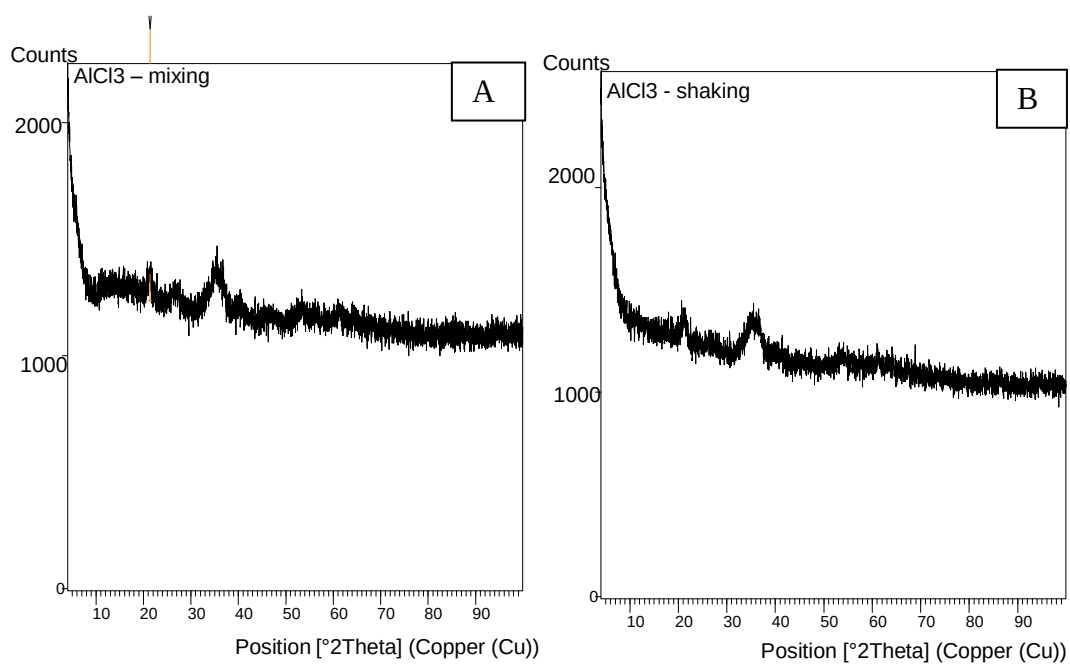


Figure 4.10: Residual copper in AMD sludge with AlCl_3 dosage with mixing and shaking.

Figures 4.11 and 4.12 show the SEM images of AMD samples sludge with FeCl_3 and af-PFCl dosage with shaking at 25000 x magnification.

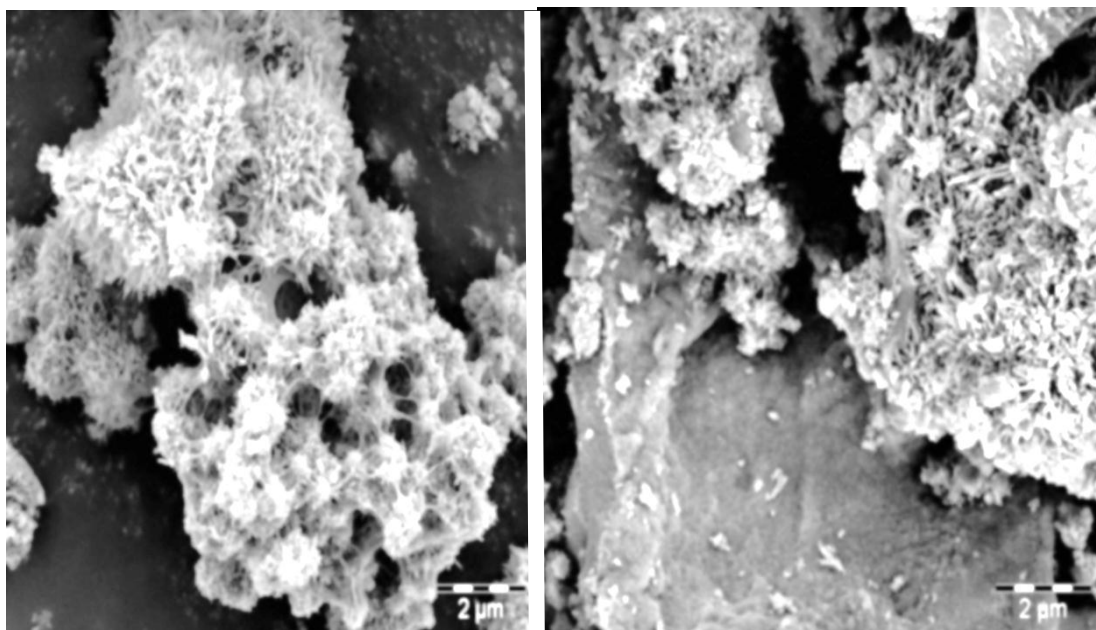


Figure 4.11: SEM of AMD sludge with FeCl_3 and af-PFCl with shaking (25000x).

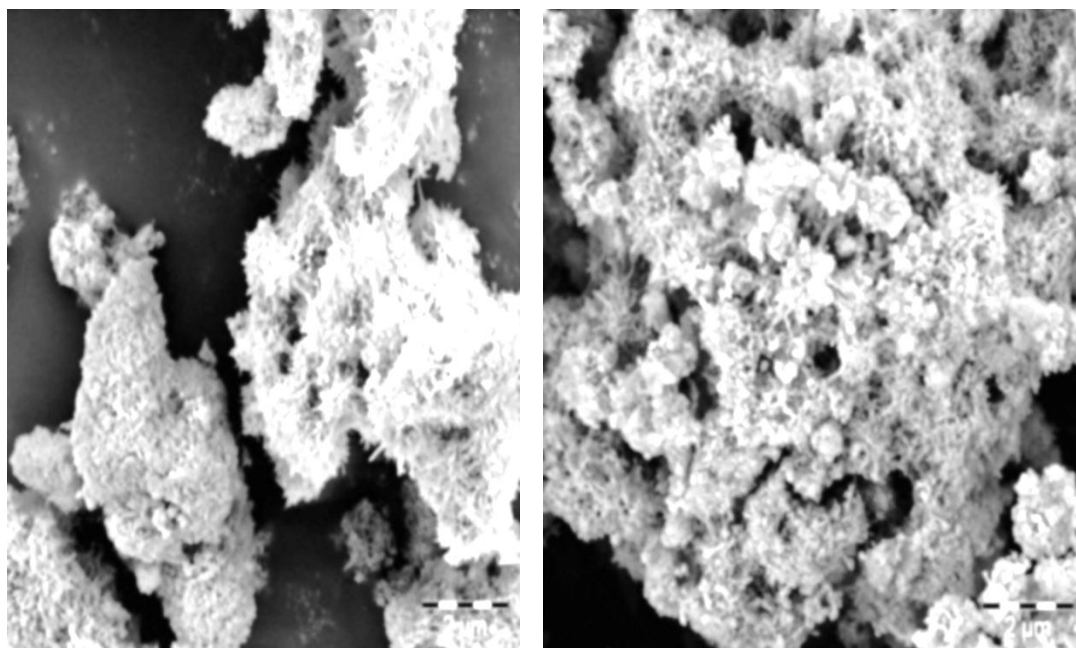


Figure 4.12: SEM of AMD sludge with FeCl_3 and AlCl_3 mixing (25000x).

4.5 DISCUSSION

The discussion is based upon the effect of the ionic strength of the metal salts on the destabilization of the AMD solution. Destabilization is a nonlinear function of the concentration of the coagulant. The minimum concentration of a coagulant to cause effective destabilization is termed critical coagulation concentration (CCC) (Mark *et al.*, 2013). Apart from the concentration of a coagulant, ionic strength plays a role in the destabilization. Ionic strength reduces the thickness of the diffuse layer by reducing the energy barrier that has to be overcome to allow the particles to collide resulting in decreasing stability of the colloidal suspension. At some ionic strength the net interactive energy is attractive at all separation distance. Based upon that, it can be inferred that the ionic strength is a function of both the molar concentration and valence of a metal ion. A negative charge patch on one particle is attracted to the positive charge patch of another, resulting in effective destabilization at any dosage (low or above) that requires charge neutralization. In addition, the valence of the ions also affects the thickness of the diffuse layer, an area where counter-ions are concentrated. Temmink *et al.* (1989) stated that destabilization is caused by two minimum energies derived from the summation of attraction and repulsion forces between the particles having similar charges. The primary minimum is energy on a minimum distance that the particle-particle resides after coagulation, whereas secondary minimum is at longer distance, and this is energy minimum of flocculation. Potential energy at the primary minimum is significantly smaller than at the secondary minimum, and hence the particles at the primary minimum are more

tightly attached. Between the primary and secondary potential energy minimums, an energy barrier exists which the particles have to overcome with their kinetic energy before coagulation can take place (Temminck *et al.* 1989). It is reasonable to affirm that destabilization and hydrolysis co-exist, a concept which has never been mentioned in all the studies. Their co-existence is derived from the fact that after the addition of hexagonally hydrated metal ion to an ionic solution, so that the metal ion weakens the equilibrium existing due to the electrostatic, van der Waals and hydrodynamic forces (destabilization), whilst deprotonation is taking place on the metal ion (hydrolysis).

The ionic species which attributes to a change in conductivity are Cl^- and unreacted Mg^{2+} from FeCl_3 (metal salt and polymer) and $\text{Ca}(\text{OH})_2$ respectively. The samples with mixing (Figure 4.2) yielded higher conductivity values than in the samples with shaking.

Although the samples with AlCl_3 dosage with mixing and shaking (Figure 4.3) show the lowest residual turbidity than in the samples with FeCl_3 and af-PFCl, all the values are low and reflect effective turbidity removal of more than 95.6 %. The most essential point is that FeCl_3 and AlCl_3 dosages are prone to corrosion and Alzheimer respectively; hence an investigation of an alternative equivalent coagulant was imperative. Turbidity removal exhibited in Figure 4.3 indicates speciation occurs at specific pH values as stated by Peavy (1985). The pH range obtained in our experimental results shows that the batch samples falls within a range 2.17-2.55,

which is suitable for the development of various hydrolysis species. Each species has an area of dominance with some overlap as elucidated by Peavy (1985). The $\text{Fe}(\text{OH})^{2+}$ is the first species covering an area in the pH range 1-5, $\text{Fe}(\text{OH})_2^+$ which falls within the pH range 2.0-7.0, and follows $\text{Fe}(\text{OH})_{3(s)}$ which covers a pH range of 4.0-8.0. The pH range of 4.0-8.0 does not imply that precipitation did not occur, but indicates that neutralization by $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})^+$ was predominant to form conglomerates, which resulted in adsorption by sweep flocculation and particles entrapment during orthokinetic flocculation.

Settling time also plays a role in effective turbidity removal. It enhances adsorption in a process where small and larger flocs collide due to the velocity gradient and differential velocity induced by Brownian motion and electrostatic forces (Metcalf *et al.* (2003). According to turbidity removal of more acidic AMD and highly electronegative metal ions, it indicates that turbidity removal occurs through adsorption charge neutralization. This occurs when a highly charged solution (acidic or basic) reacts with a multivalent metal salt with counter-ions. The settling duration also allows further nucleation which results in “sweep flocculation” and “particles entrapment” as both reactions depend on retention time and rate of collision. The low residual turbidity results in the samples which coagulated without mixing (Figure 4.3) show that destabilization under this condition was spontaneous. That occurs when Brownian motion in AMD exceeds the electrostatic potential in the system as stated by Peavy *et al.* (1985). Mixing is also essential, but mostly when the distance between each particle is high and the van der Waals forces of attraction are low. The

mechanical agitation then increases the collision rate of the particles to form agglomerates; which settle out of the system (Peavy *et al.*, 1985). Figure 4.4 shows the residual turbidity in the AMD samples flocculated with the mass of Fe^{3+} and a combination of Fe^{3+} and Mg^{2+} (polymer) in solution as relatively low in a range of 1.6-3.5 NTU. The use of the mass is because particle destabilization is accomplished through adsorption and charge neutralization by coagulant dosage, which correlates with the particle concentration. Stoichiometric effect of particle charge is usually assumed to be proportional to the total surface area concentration of particles in water. Similarly equal residual turbidity between the two coagulants (Figure 4.4) indicates that the adsorption mechanism between the two is homologous. Our inference is that the large flocs which are formed during hydrolysis condense to form dense cake-like, spongy polymers that settle spontaneously due to high settling velocity. These polymers act as a filter and trap the residual colloidal particles, causing further turbidity reduction.

The rate of turbidity removal from the wastewater depends on the ratio of the hydroxide in the metal hydroxide and the metal ion in the metal salt $[\text{OH}]/[\text{Al}]$ or $[\text{OH}/\text{Fe}]$. The polymeric species which are formed are developed into agglomerates which adsorb or are adsorbed onto the colloidal particles. We suggest that the adsorption onto the colloidal particles is a complex phenomenon because of the highly concentrated central particle with neighbouring particles. The flocs are polarized because of dipolarity on the water molecules and ions throughout the colloidal suspension, thus enhancing the rate of adsorption. Jiang *et al.* (1997) stated

that the most predominant parameters which govern the nature of species which are formed are basic ratio, temperature and time. The objective of the experiments with the addition of 0.021 and 0.043 M af-PFCl polymers to AMD (Figure 4.5) was to determine the optimal dosage between the two concentrations. The same as for the Fe^{3+} and Al^{3+} salt dosage, the $\text{Mg}(\text{OH})_2$ component in the polymer played an insignificant role in the pH, in a range of 2.43-2.49. Residual turbidity in the samples with 0.043 M af-PFCl in all three methods is better than in the corresponding samples with 0.021 M af-PFCl which yielded turbidity removal efficiency in a range 90.4-95.6 %.

Figures 4.6 and 4.7 showed the changing pH, turbidity with the ORP and DO in AMD sample dosed with 0.1 M af-PFCl polymer of $\text{Mg}(\text{OH})_2$ with mixing and shaking respectively, to determine the rate of chemical reactions in a system. The ORP is an indication of the potential at which metallic compounds can be oxidized, whereas the DO is for the residual oxygen in the system after oxidation. According to their values (Figures 4.6 and 4.7) from 234 mV and 4.5 mg/L (untreated AMD sample) to the ranges of 224-228 mV and 4.4-6.3 mS/cm respectively, it shows that oxidation-reduction occurred during the treatment (destabilization-hydrolysis). It is suggested that there is a likelihood that the fraction of oxygen content in both ORP and DO was utilized to reduce the Fe^{2+} to Fe^{3+} (Equations 1-3), thereby causing the formation of $\text{Fe}(\text{OH})_3$ precipitates. The pH values in the sample treated with mixing are relatively identical to those of their corresponding samples treated with shaking (range of 2.2-.2.9), indicating that the rate of hydrolysis is similarly identical

(Ntwampe *et al.*, 2013). In general, both DO and ORP values in the AMD samples which have been treated in a jar test (mixing) and a shaker (shaking) showed insignificant difference, with the latter showing a slightly lower pH and residual turbidity values than in the samples with mixing. Based on the fact that the residual turbidity values are so low (1.1-5.3 NTU), this indicates that shaking is a possible replacement of mixing technique to avoid re-stabilization effect due to high shear forces (Swartz *et al.*, 2004, Aboulhassan *et al.*, 2006).

The residual turbidity removal in the AMD sample with both mixing and shaking (Figures 4.6 and 4.7) are reduced from 105 NTU (untreated AMD) to a range of 1.1-5.3 NTU (94.7-98.9 %). This is the best removal efficiency, which indicates that 0.1 M 20, 30, 40, 50 and 60 mL dosage of the polymer of 0.1 M FeCl_3 with 0.1 M $\text{Mg}(\text{OH})_2$ has the best destabilization-hydrolysis effect, which resulted in high turbidity removal. As it has been stated that the effectiveness of coagulation depends on the change in ionic concentration which increases exponentially as the charge of the ions increases (Swartz *et al.*, 2004 and Dey *et al.*, 2004, Edwards *et al.*, 2007, Niesel *et al.*, 2005, Niesel *et al.*, 2008, Firer, 2008 and Sinha *et al.*, 2013), the concentration of 0.1 M af-PFCl of $\text{Mg}(\text{OH})_2$ is therefore ideal for the treatment of highly acidic wastewater (AMD). This can further be explained by the strong ionic strength of the af-PFCl polymer to destabilizes the electrical double layer which (combination of positive and negative ions), weakens repulsive forces and allows destabilization-hydrolysis (Haselberg, 2009, Cosgrove, 2005, Crittenden *et al.*, 2005, Ananikov *et al.*, 2005, Bratby, 2006, Meghzilli, 2008 and Scholtz, 2010).

Figures 4.8 and 4.9 showed the correlation between the pH and turbidity removal efficiency in AMD sample dosed with af-PFCl of $\text{Mg}(\text{OH})_2$ without mixing and with shaking of 92.2 and 91.7 % respectively. Figure 4.10 is the ATG results of the same sample with mixing and shaking showing similarly equal Cu metal count at 2000 and some unspecified metals around 1000 counts. The similarity in Cu counts (Figure 4.10) indicates that the reaction dynamics of the chemicals in the AMD samples of both experiments (mixing and shaking) are similarly identical, a condition which still supports that shaking is an ideal dispersion technique.

Figures 4.11 and 4.12 show the SEM images where the former (FeCl_3 -shaking method) showed large “sponge-like” flocs which are separated from smaller flocs with cavities and filaments. The latter (af-PFCl-shaking) showed a cake-like structure with small and large cake-like porous and non-porous sites. Figure 4.12 showed the AMD samples with FeCl_3 and af-PFCl dosage with shaking, where the former (FeCl_3 -mixing) showed large “sponge-like” flocs which are more separated as a signal of rupture with less cavities and filaments. The latter (af-PFCl-mixing) showed a cake-like structure with large sponge-like porous and non-porous sites. The sample with AlCl_3 and af-PFCl dosage with shaking and mixing respectively, showed almost a similar matrix. An inference from the images of both AlCl_3 and af-PFCl is that the particles joined together and formed large particles due to interfacial and interparticles attractive forces.

The samples with the FeCl₃ dosage with mixing and shaking yielded more attractive turbidity removal efficiency; its pH and turbidity values were used to calculate the Pearson correlation coefficient. The Pearson correlation coefficient (r) to calculate the relation between pH and residual turbidity, by using Equation 8

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \quad (8)$$

According to the correlation coefficient, 0.70 or higher is indicative of a very strong relationship, 0.40-0.69 represents a strong relationship, and 0.30-0.39 is considered as only a moderate relationship. The results from the following data:

X_{nm}=pH without mixing, x_{sh}=pH with shaking, y_{nm}=turbidity without mixing and y_{sh}=turbidity with shaking gives the following values:

$$\sum x_{nm} = 45.3, \sum x_{sh}^2 = 108.6, \sum y_{sh} = 11.9, \sum y_{sh}^2 = 28.5 \text{ and } \sum xy_{sh} = 108.6$$

$$\sum x_{sh} = 12.09, \sum x_{sh}^2 = 29.67, \sum y_{sh} = 42.6, \sum y_{sh}^2 = 371.61 \text{ and } \sum xy_{sh} = 103.58$$

Using the results obtained for the samples with af-PFCl dosage without mixing and with shaking, yielded r-values of 0.46 and 0.836 (46 and 84.6 %) respectively. The correlation coefficients in the samples without mixing and with shaking (Figures 4.8 and 9) fall within a range of strong a relationship (-1 to 1), which is validated by the R² of pH (concentration conversion to mass of Fe³⁺ and Mg²⁺) vs turbidity removal efficiency of af-PFCl shown in Figures 4.8 and 4.9 of 0.923 and 0.917 (92.3 and 91.7 %) respectively, which is very high.

4.6 CONCLUSION

AlCl_3 and af-PFCl polymer of $\text{Mg}(\text{OH})_2$ yield high turbidity removal in the AMD samples treated without pH adjustment, with FeCl_3 showing slightly lower values. The formation of the precipitates does not depend on the pH but the ionic strength of the metal ion to destabilize the colloidal suspension. The turbidity removal efficiency in af-PFCl polymer of $\text{Mg}(\text{OH})_2$ shows that it can be used as a replacement coagulant for metal salts. The SEM images show that the sludge in the samples with af-PFCl polymer of $\text{Mg}(\text{OH})_2$ dosage consists of a large cake-like structure which is symbolic of optimal adsorption. The formation of the precipitates was found to be influenced by the ionic strength of the metal ion rather than by the pH of the solution.

The experimental results showed that there is a correlation between the ORP and pH or turbidity removal, and also ORP is predominant during destabilization-hydrolysis.

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CHAPTER 5: GENERAL CONCLUSIONS

The experiments which were carried out in this study cover the reaction dynamics of the of the (1) coagulants which include FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$, (2) the metal hydroxide, $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ and the (3) flocculants which include acid-free polymers of FeCl_3 and $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ with a highly acidic AMD sample in a jar test, shaker or without mixing without pH adjustment.

In each set of experiments, a 200 mL of AMD sample (containing 6.8 g of solid particles) was dosed with the 0.021, 0.043, 0.086 or 0.1 M coagulant(s) or flocculent(s) in 20, 30, 40, 50 and 60 mL dosage respectively. The mixing or shaking rate of dispersion of the reagents in the samples was at 250 rpm for 2 minutes and reduced to 10 rpm for 10 minutes, the samples were allowed to settle for 1 hour, after which the pH, conductivity, turbidity/TSS, DO and ORP were conducted. In the set of experiments where the AMD samples were dosed with the reagents without mixing, a 1 hour settling also applied and thereafter similar measurements were carried out.

The common observation from the experimental results revealed that the turbidity removal efficiency of the coagulants and flocculants which were dosed in AMD sample is in a range of 80-99.8 %. This observation can be used along the environmental and health perspective, where the powdery $\text{Ca}(\text{OH})_2$ can be replaced by $\text{Mg}(\text{OH})_2$ and the health hazardous (Alzheimer) AlCl_3 can be replaced with FeCl_3 .

The inorganic polymers are relatively used in this study are affordable and their preparation is not complicated compared to the commercial polymers which require specialized reactors and acids. The advantage with the inorganic polymers is that Fe, Al, Mg and Ca are naturally formed minerals/elements, which are even found in abundance on the earth crust. The micrographs of the SEM showed that the optimal adsorption of the turbid materials is caused by the compact cake-like spongy structure which consists of large and small structures joined together by thread-like structures. The micrograph images do not show any possibility of a passage of the colloidal particles, a condition which is corroborated by a high turbidity/TSS removal in the AMD samples. The high turbidity/TSS removal values obtained from the treatment of highly acidic AMD without pH adjustment reveals that the adsorption the adsorption substrate (SEM micrographs) formed by the flocs of the flocculants used in the present study are compacted in such a manner that particles of all the sizes were adsorbed (turbidity/TSS values). Although the pH of the AMD sample during treatment is low, the values fall within the pH range of some of the species which are formed during hydrolysis as recommended by Peavy (1985). The first species to form during hydrolysis is Fe^{3+} , and covers an area within the pH range of 1 to 5, which is followed by $\text{Fe}(\text{OH})_2^+$ in a pH range of 2-7, the pH range obtained in this study. This indicates that charge neutralization was a predominant destabilization reaction this study. Since the degree of hydrolysis process is determined by an equilibrium state between coagulants and colloidal suspension, it therefore implies that equilibrium state in the treatment system was reached in an acidic state. Flynn (1984) stated that the shift in equilibrium reaction depends on the activity coefficient of metal ion (M^{n+})

and the ionic potential of metal salts, this indicates that the coagulants/flocculants employed in this study have high activity potential. On the contrary, the pH range of the preliminary species of Al^{3+} salts during hydrolysis (Flynn, 1985) is slightly higher compared to that of the samples treated in this study ($\text{Al}(\text{OH})^{2+}$ at pH range 3-6 and $\text{Al}(\text{OH})_2^+$ at 4-7), but still yielded an optimal turbidity/TSS removal potential. The experimental results shown in the samples with FeCl_3 dosage commensurate with those with $\text{Al}_2(\text{SO}_4)_3$, it is suggested that it is because of the similarity in physico-chemical properties (size of radii, Pauling electronegativity, charge per surface area, acidity). Owing to the fact that there is a movement of the ions induced by Brownian motion during the treatment process, an explanation was derived to prove that the rate of chemical reactions is influenced by a combination of energies stored in the coagulant/flocculent. This was employed to explain the correlation between the destabilization-hydrolysis of the colloidal suspension-metal ions and the energy associated with the electron configuration (energy levels) of the metal element in their activation state. This occurs during hybridization of the metals when they start reacting during chemical reactions (Wulfsberg, 1987). The turbidity removal values in AMD sample using Fe^{3+} or Al^{3+} salt showed that the dosing methodology, prior or during stirring (mixing or shaking) is immaterial to achieve optimal results. The values are similarly identical in corresponding samples but $\text{Al}_2(\text{SO}_4)_3$ yielded slightly lower removal efficiency in the AMD samples with dosing prior and during mixing (increasing trend with increasing dosage).

Since mixing yields high shear stress due to high velocity gradient (v/d) (Oldshue, 1983) compared to shaking, it is expected that the turbidity removal in the former samples is low due to rupturing of the flocs. The high turbidity removal is due to the non-porous structure of the adsorption substrate (SEM micrographs). The formation of the large agglomerates which are easily adsorbed is caused by the collision of the micro-particles with the macro-particles due to Brownian motion, thus forming larger absorbable colloids. This is in agreement with Tambo *et al.* (1984) and Bolto *et al.* (2007) when stating that the aggregation of submicron particles is relatively fast if their surface chemistry is suited and if their concentration is high enough ($> 10^8/\text{ml}$). Based upon similarly equal turbidity removal efficiency shown by Fe^{3+} and Al^{3+} salts, From the environmental perspective, $\text{Ca}(\text{OH})_2$ poses a detrimental effect on human life and also clogging and damage to pipeline (scaling). The results shown by $\text{Mg}(\text{OH})_2$ confirm that it can be used as a replacement of $\text{Ca}(\text{OH})_2$.

A further investigation is necessary to determine the concentration of the hydrolysis salts are dosed to AMD without pH adjustment. Another investigation is to determine the probable type of the destabilization which occurs during such a treatment.

The coagulants/flocculants used in this study showed adsorption efficiency between 80-99.8 % of particle size between 3-109 μm in diameter. The curve in Table Z2 showed that particles with diameter of ranges of 3-9, 9-92 and 92-106 μm occupy 11, 91 and 8 % by volume respectively. This indicates that the coagulants/flocculants yielded an effective adsorption efficiency/particle size profile.

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Appendix A

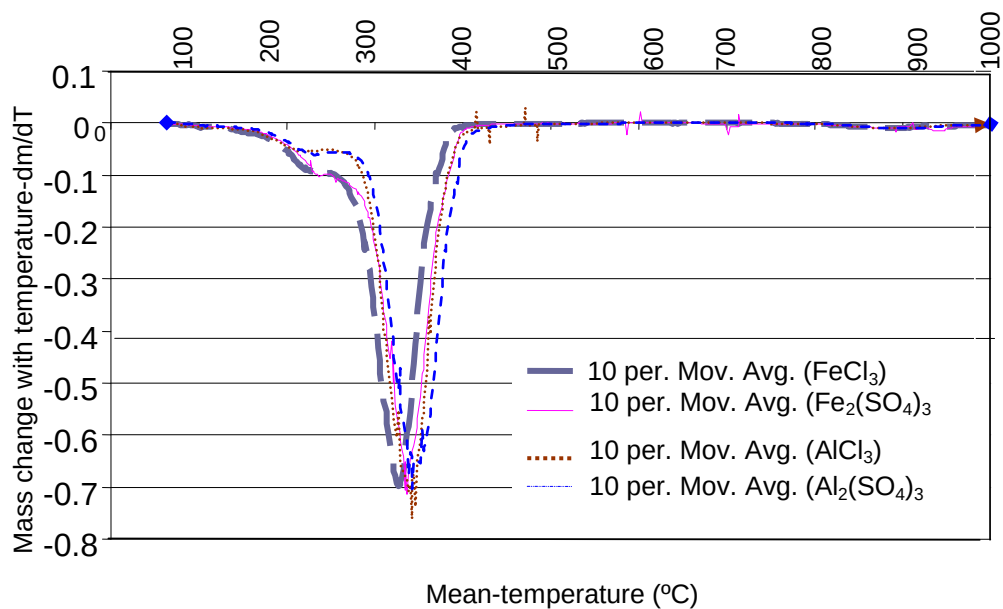


Figure S1: TGA graph of dry paint sludge dosed with 0.043 M Al^{3+} and 0.043 M Fe^{3+} salts.

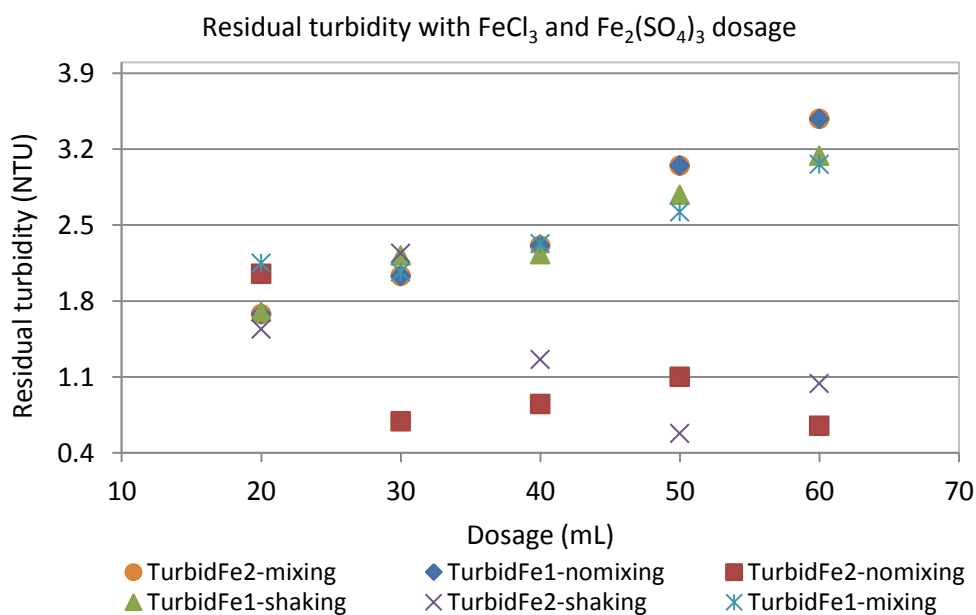


Figure S2: Residual turbidity in AMD sample with Fe^{3+} salts dosage with mixing, shaking and without mixing.

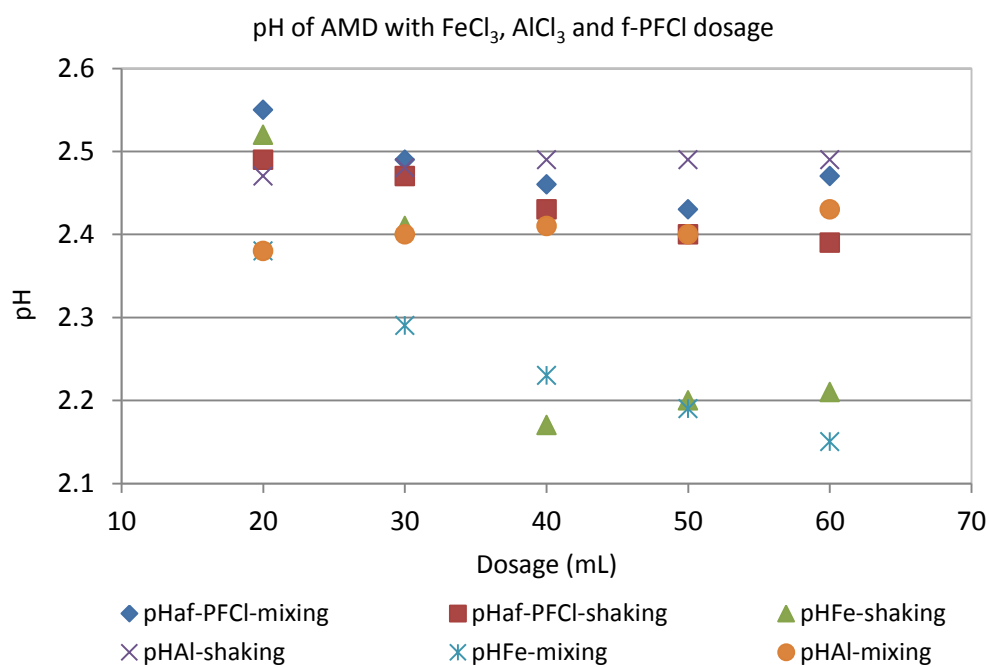


Figure S3: Residual turbidity in AMD sample with FeCl_3 , AlCl_3 and af-PFCl dosage with mixing and shaking.

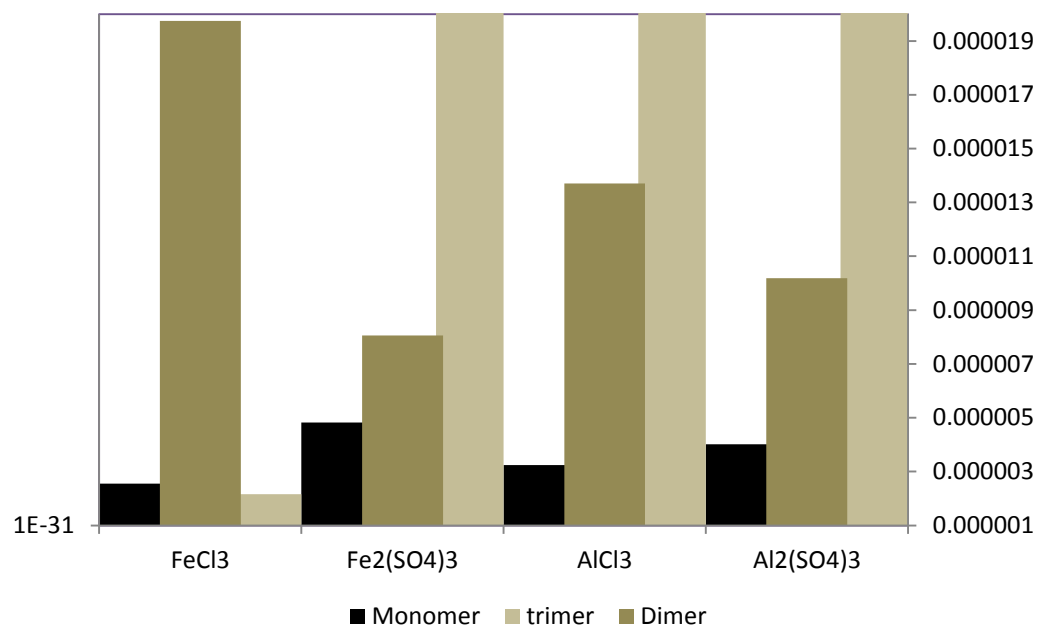


Figure S4: Hydrolysis species of Fe^{3+} and Al^{3+} salts.

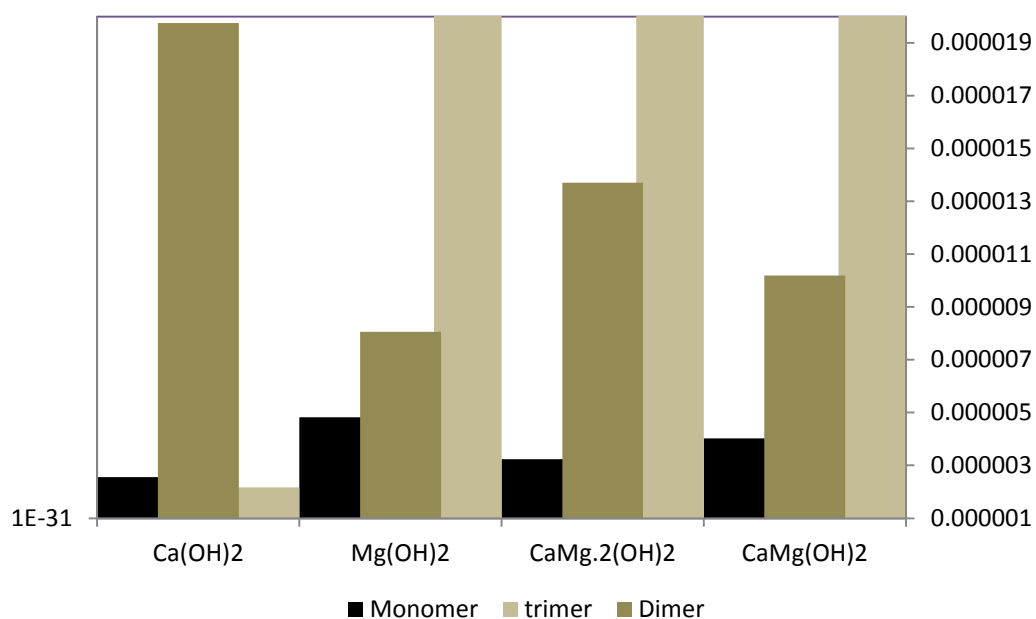


Figure S5: Hydrolysis species of Ca^{2+} salt.

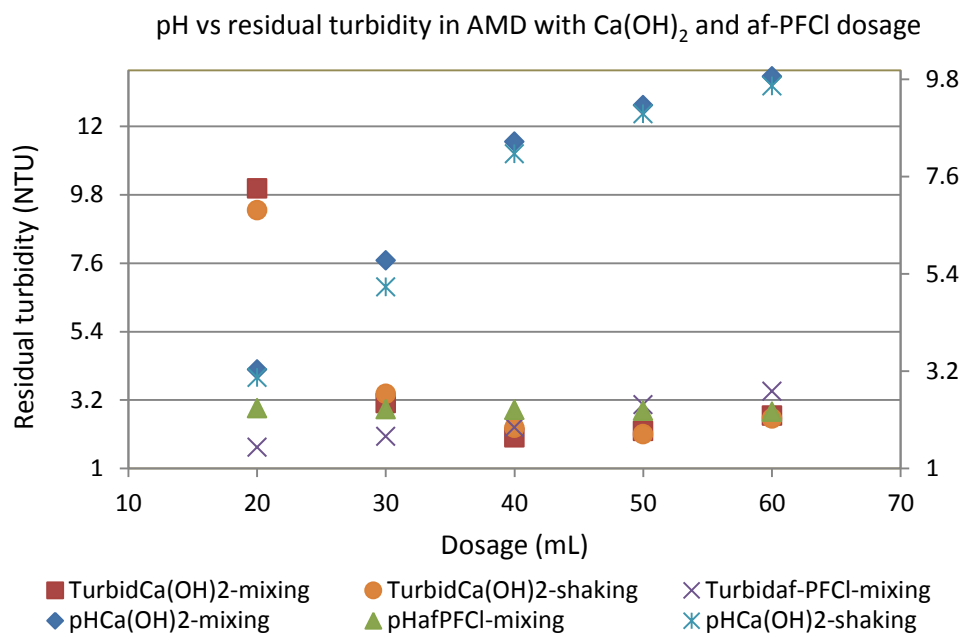


Figure S6: pH vs residual turbidity in AMD sample with af-PFCl and Ca(OH)_2 with mixing and shaking.

Appendix B



Figure S7: Polluted area by coal mine AMD-Brugspruit valley



Figure S8: AMD concentrated with heavy metals



Figure S9: A guy swimming in AMD



Figure S10: AMD pumped from underground

Appendix B

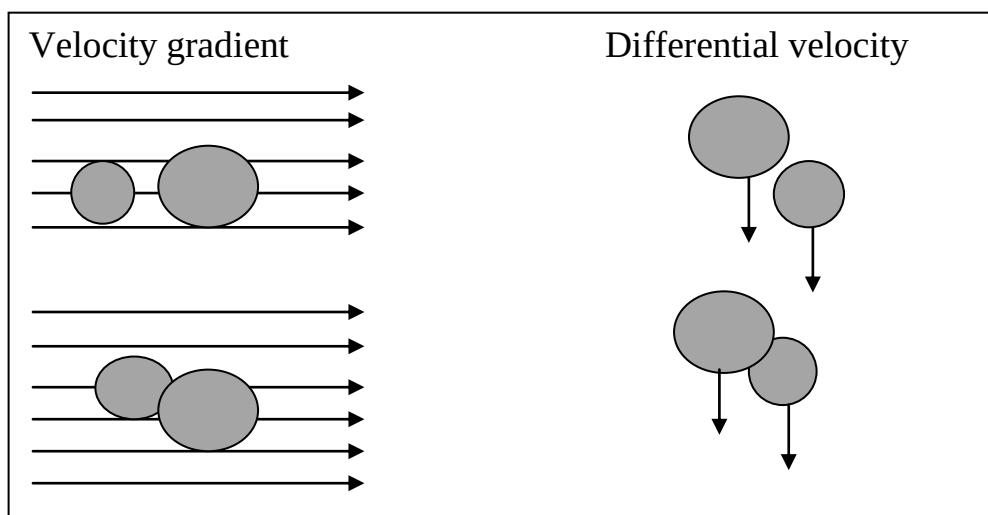


Figure S11: Flocs formation in a colloidal system due to Brownian motion showing a velocity gradient and differential velocity.

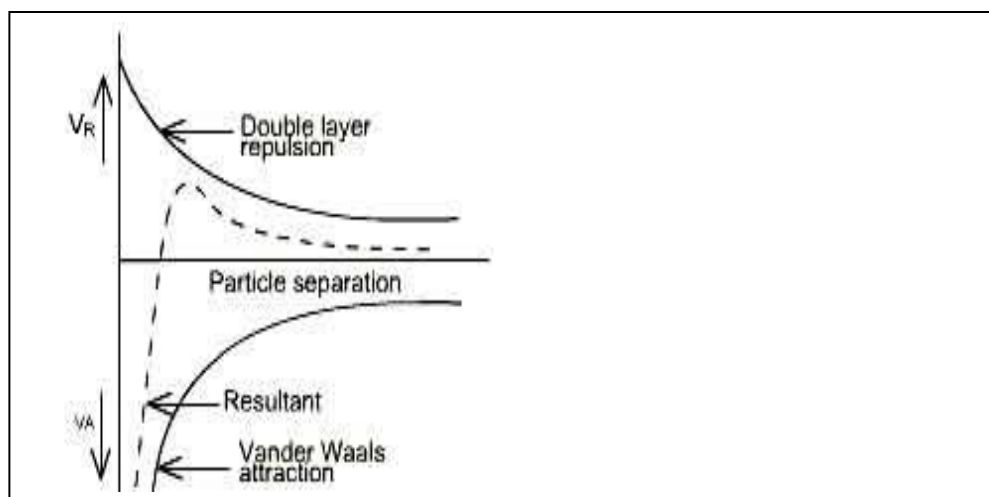


Figure S12: Forces exerted between the colloidal particles (Lee, 2001).

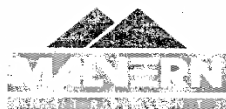
Appendix C

Table Z1: Aluminum* and Iron(III)⁺

Equilibria Reaction	log K (25 C)
1. $\text{Al}^{3+} + \text{H}_2\text{O} = \text{AlOH}^{2+} + \text{H}^+$	-4.97
2. $\text{AlOH}^{2+} + \text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + \text{H}^+$	-4.3
3. $\text{Al}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Al}(\text{OH})_3 + \text{H}^+$	-5.7
4. $\text{Al}(\text{OH})_3 + \text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + \text{H}^+$	-8.0
5. $2\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}_2(\text{OH})_4^{2+} + 2\text{H}^+$	-7.7
6. $3\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-13.94
7. $13\text{Al}^{3+} + 28\text{H}_2\text{O} = \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+} + 32\text{H}^+$	-98.73
8. $\text{Al}(\text{OH})_3(\text{am}) = \text{Al}^{3+} + 3\text{OH}^-$	-31.5
9. $\text{Al}(\text{OH})_3(\text{c}) = \text{Al}^{3+} + 3\text{OH}^-$	-33.5
10. $\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$	-2.2
11. $\text{FeOH}^{2+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + \text{H}^+$	-3.5
12. $\text{FeCOH}^{2+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{H}^+$	-6.0
13. $\text{Fe}(\text{OH})_3 + \text{H}_2\text{O} = \text{Fe}(\text{OH})_4^- + \text{H}^+$	-10.0
14. $2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-2.9
15. $3\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-6.3
16. $\text{Fe}(\text{OH})_3(\text{am}) = \text{Fe}^{3+} + 3\text{OH}^-$	-38.7
17. $\text{a-FeOOH}(\text{c}) + \text{H}_2\text{O} = \text{Fe}^{3+} + 3\text{OH}^-$	-41.7

*Baes and Mesmer (1976) and ⁺Flynn (1984)

Table Z2: Particle size distribution of AMD sample



MASTERSIZER 2000

Result Analysis Report

Sample Name:
AMDraw1 - Average
Sample Source & type:
Supplier = Malvern
Sample bulk lot ref:
195325

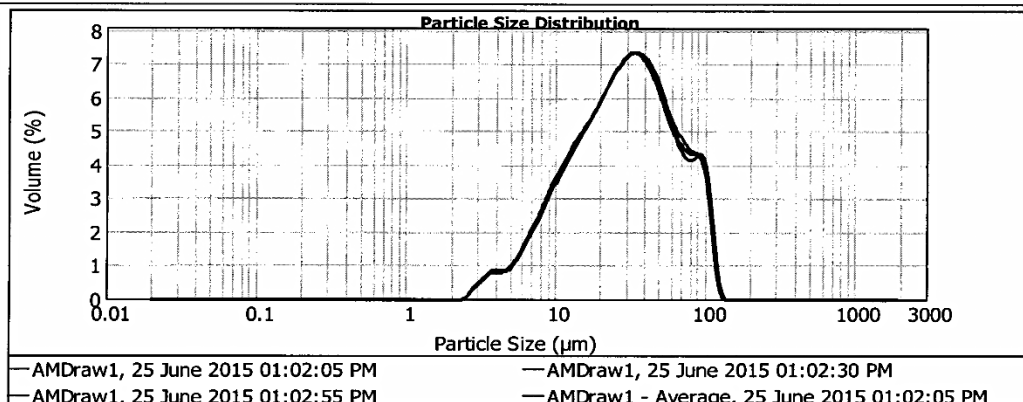
SOP Name:
Measured by:
micron
Result Source:
Averaged

Measured:
25 June 2015 01:02:05 PM
Analysed:
25 June 2015 01:02:06 PM

Particle Name: Silica 0.0	Accessory Name: Hydro 2000MU (A)	Analysis model: Single narrow mode (spherical)	Sensitivity: Enhanced
Particle RI: 1.544	Absorption: 0	Size range: 0.020 to 2000.000 um	Obscuration: 14.62 %
Dispersant Name: Water	Dispersant RI: 1.330	Weighted Residual: 1.881 %	Result Emulation: Off

Concentration: 0.0411 %Vol	Span : 2.386	Uniformity: 0.705	Result units: Volume
Specific Surface Area: 0.311 m ² /g	Surface Weighted Mean D[3,2]: 19.262 um	Vol. Weighted Mean D[4,3]: 36.695 um	

d(0.1): 8.989 um d(0.5): 29.327 um d(0.9): 78.954 um



Size (µm)	Volume in %	Size (µm)	Volume in %	Size (µm)	Volume in %	Size (µm)	Volume in %	Size (µm)	Volume in %	Size (µm)	Volume in %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	1.72	50.238	4.49	355.656	0.00
0.022	0.00	0.159	0.00	1.125	0.00	7.962	2.08	56.368	4.02	399.052	0.00
0.025	0.00	0.178	0.00	1.262	0.00	8.934	2.46	63.246	3.58	447.744	0.00
0.028	0.00	0.200	0.00	1.416	0.00	10.024	2.81	70.963	3.31	502.377	0.00
0.032	0.00	0.224	0.00	1.589	0.00	11.247	3.13	79.621	3.25	563.677	0.00
0.036	0.00	0.252	0.00	1.783	0.00	12.619	3.42	89.337	3.18	632.456	0.00
0.040	0.00	0.283	0.00	2.000	0.00	14.159	3.69	100.237	2.48	709.627	0.00
0.045	0.00	0.317	0.00	2.244	0.00	15.887	3.96	112.468	0.82	796.214	0.00
0.050	0.00	0.356	0.00	2.518	0.12	17.825	4.25	126.191	0.04	893.357	0.00
0.056	0.00	0.399	0.00	2.825	0.32	20.000	4.56	141.589	0.00	1002.374	0.00
0.063	0.00	0.448	0.00	3.170	0.47	22.440	4.90	158.866	0.00	1124.683	0.00
0.071	0.00	0.502	0.00	3.557	0.61	25.179	5.20	178.250	0.00	1261.915	0.00
0.080	0.00	0.564	0.00	3.991	0.62	28.251	5.43	200.000	0.00	1415.892	0.00
0.089	0.00	0.632	0.00	4.477	0.65	31.698	5.52	224.404	0.00	1588.656	0.00
0.100	0.00	0.710	0.00	5.024	0.81	35.566	5.46	251.785	0.00	1782.502	0.00
0.112	0.00	0.796	0.00	5.637	0.81	39.905	5.25	282.508	0.00	2000.000	0.00
0.126	0.00	0.893	0.00	6.325	1.09	44.774	4.92	316.979	0.00		
0.142	0.00	1.002	0.00	7.096	1.40	50.238		355.656			

Operator notes: Experimental batch 4

Jar test and a shaker table

Table Z3: Run 1

Beaker	FeCl ₃ (mL)	Fe ₂ (SO ₄) ₃	FeSO ₄ (mL)	AlCl ₃ (mL)	Al ₂ (SO ₄) ₃
1	20				
2	30				
3	40				
4	50				
5	60				

Table Z4: Run 2

Beaker	FeCl ₃ (mL)	AlCl ₃ (mL)	Combined FeCl ₃ +AlCl ₃ (mL)	
1	20			
2	30			
3	40			
4	50			
5	60			

Table Z5: Run 3

Beaker	FeCl ₃ ml added	Combined FeCl ₃ and Ca(OH) ₂ ml added	Combined AlCl ₃ and Ca(OH) ₂ ml added	Combined FeCl ₃ and Mg(OH) ₂ ml added	FeCl ₃ -Ca(OH) ₂ polymer ml added	FeCl ₃ -Mg(OH) ₂ polymer ml added
1	20					
2	30					
3	40					
4	50					
5	60					