
Masters Theses

Student Theses and Dissertations

Fall 2016

Studies on flocculation of fine mineral tailings using novel polyacrylamide based polymer

Simin Khatibi

Follow this and additional works at: https://scholarsmine.mst.edu/masters_theses



Part of the [Mining Engineering Commons](#)

Department:

Recommended Citation

Khatibi, Simin, "Studies on flocculation of fine mineral tailings using novel polyacrylamide based polymer" (2016). *Masters Theses*. 7603.

https://scholarsmine.mst.edu/masters_theses/7603

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

STUDIES ON FLOCCULATION OF FINE MINERAL TAILINGS USING
NOVEL POLYACRYLAMIDE BASED POLYMER

By

SIMIN KHATIBI

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN MINING ENGINEERING

2016

Approved by

Dr. Lana Alagha

Dr. Greg Galecki

Dr. Zeshan Hyder

ABSTRACT

One of the important features in managing or treating sulfide fine tailings is separating solids from liquid by settling test. This thesis presents results of studied conducted on flocculation of Kaolin suspensions (a model tailings) and sulfide mineral tailings. Two polymers (PAM and Al-PAM) were tested as flocculants. The zeta potential value of slurries was measured by Nano Zetasizer device.

Al-PAM was found to be more effective for flocculation of kaolinite samples and also sulfide samples while PAM with used concentration was not. This study represents the power of flocculation as a possible solution to deal with industrial tailings.

ACKNOWLEDGMENTS

First and foremost, I offer my sincerest gratitude to my advisor, Dr. Lana Alagha, who has given his valuable time, advice, criticism and correction to this thesis from the beginning up to the end of the writing.

I would like to express my appreciation to Dr. Greg Galecki, Associate Professor of Mining and Nuclear Engineering and Dr. Zeshan Hyder, Assistant Professor of Mining Engineering and Nuclear Engineering for their thoughtful and valuable comments and suggestions and helps. Many thanks to Mrs. Tina Alobaidan, Mrs. Shirley Hall and Mrs. Judy Russel for their extended administrative assistances during my education in Mining department. Many thanks to my colleges Muhammad Hayat, Ontlametse Kenneth Molatlhegi and Mostafa Khodakarami for their help and support.

I would like to express my deepest thanks to my beloved husband Hassan Zargarzadeh for his love, encouragement and mental support which without him it was impossible to accomplish this work.

TABLE OF CONTENTS

	Page
ABSTRACT.....	iii
ACKNOWLEDGMENTS	iv
LIST OF ILLUSTRATIONS.....	viii
LIST OF TABLES.....	x
NOMENCLATURE	xi
 SECTION	
1. INTRODUCTION.....	1
1.1. TAILINGS MANAGEMENT	1
1.2. CHARACTERISTICS OF TAILINGS.....	2
1.3. ISSUES RELATED TO TAILINGS MANAGEMENT	2
1.3.1. Effect of Huge Volume of MFT.....	2
1.3.2. Environmental Effects of Mature Fine Tailings (MFT).....	3
1.3.3. Fresh Water Concern.....	3
1.4. INDUSTRIAL PROCESS FOR TAILING MANAGEMENT	4
1.4.1. Consolidated/ Composite Tailings (CT) Process.	4
1.4.2. Thickened Tailings/Paste Technology.	5
1.5. RESEARCH OBJECTIVES	7
2. LITERATURE REVIEW.....	9
2.1. THE COLLOIDAL STABILITY OF PARTICLES IN SUSPENSION	9
2.2. THE ELECTRICAL DOUBLE LAYER.....	9
2.3. DELVO THEORY	11

2.4. COAGULATION AND FLOCCULATION	12
2.5. FLOCCULATING MATERIALS	14
2.6. FACTORS EFFECTING FLOCCULATION	16
2.6.1. Effect of Polymer Dosage.	16
2.6.2. Effect of Mixing Conditions.....	16
2.6.3. Effect of Polymer Molecular Weight.	16
2.6.4. Effect of Particle Size.....	17
2.6.5. Effect of pH.	17
2.7. PREVIOUS STUDIES ON FLOCCULATION APPLICATION ON TAILINGS TREATMENT.	17
3. EXPERIMENTAL WORK	20
3.1. MATERIALS.....	20
3.1.1. Materials for Model Fine Tailing.	20
3.1.2. Materials for Polymer Synthesis.	20
3.2. POLYMERS	21
3.2.1. Principle of Colloid Preparation.....	22
3.2.2. Procedure of Colloid Preparation	22
3.2.3. Al-PAM Synthesis Principles.....	23
3.2.4. Procedure of Synthesis of Al-PAM.....	23
3.2.5. Purification.	24
3.3. PREPARATION OF MODEL FINE TAILINGS	24
3.4. PREPARATION AND CHARACTERIZATION OF SULFIDE TAILINGS.	25
3.5. CRITERIA FOR SETTLING PERFORMANCE.....	27
3.5.1. Settling Tests and Methodology.....	28

3.6. ZETA POTENTIAL MEASUREMENT	29
4. RESULTS AND DISCUSSION OF FLOCCULATION AND SETTLING RATE	32
4.1. INTRODUCTION	32
4.1.1. Studies on Kaolin Suspensions (Model Fine Tailings).....	33
4.2. EXPERIMENTAL.....	33
4.2.1. Materials.....	33
4.2.2. Results and Discussion.....	33
4.2.3. Al-PAM Flocculation Performance.....	35
4.2.4. PAM Flocculation Performance.....	35
4.2.5. Comparison of Flocculation Performance of Al-PAM and PAM Polymer with Kaolinite.	35
4.3. FLOCCULATION OF SULFIDE MINERAL TAILINGS.....	36
4.3.1. Al-PAM Flocculation Performance.....	37
4.3.2. PAM Flocculation Performance.....	38
4.3.3. Comparison of Flocculation Performance of Al-PAM and PAM Polymer with Sulfide Mineral Tailings.	38
4.4. ZETA POTENTIAL MEASUREMENTS FOR SULFIDE TAILINGS	39
5. CONCLUSION	41
5.1. PROBLEM REVIEW.....	41
5.2. SUMMARY OF THESIS WORK.....	41
5.3. RECOMMENDATIONS FOR FUTURE WORK	42
BIBLIOGRAPHY	43
VITA	47

LIST OF ILLUSTRATIONS

	Page
Figure 1.1. Schematic flow chart of composite tailings process [10].....	5
Figure 1.2. Thickened tailings disposal [14].....	7
Figure 2.1. Schematic illustration of an electric double layer according to the Stern model [20]	11
Figure 2.2. Schematic diagram of the variation of free energy with particle separation according to DELVO Theory [20]	12
Figure 2.3. Schematic comparison of coagulation and flocculation	13
Figure 2.4. Schematic illustration of re stabilized by adsorb polymers [15].....	14
Figure 2.5. Illustration of polyacrylamide polymer [31]	15
Figure 3.1. Schematic of kaolin structure	20
Figure 3.2. Illustration of Al-PAM with organic polyacrylamide arms grafted on the aluminum hydroxide nano particles core	22
Figure 3.3. Experimental set up for colloid preparation	23
Figure 3.4. Schematic of Al-PAM synthesis [2].....	23
Figure 3.5. Experimental set up for Al-PAM synthesis. (A) Set up before aluminum foil was put on for protection from exposure to light. (B) Set up with aluminum foil for protection from exposure to light	24
Figure 3.6. Mineral grain size distribution for chalcopyrite, galena and sphalerite in sulfide tailings.....	26
Figure 3.7. (a) Mechanical stirrer; (b) disposable plastic pipette of 23 mL in volume ...	27
Figure 3.8. Setup for settling experiment.....	29
Figure 3.9. Schematic diagram of a typical settling rate.....	29
Figure 3.10. Zeta potential of kaolinite solution without polymer	30
Figure 3.11. Zeta potential of sulfide tailings solution without polymer	31

Figure 3.12. Zetasizer nano ZS (Malvern Instruments Inc.).....	31
Figure 4.1. 5% kaolin solution with PAM polymer.....	34
Figure 4.2. 5% kaolin solution with Al-PAM polymer	34
Figure 4.3. Comparison of PAM and Al-PAM on Kaolin.....	36
Figure 4.4. Initial settling rate of sulfide tailings with Al-PAM polymer	37
Figure 4.5. Initial settling rate of sulfide tailings with PAM polymer.....	37
Figure 4.6. Comparison of PAM and Al-PAM performance on Sulfide tailings	39
Figure 4.7. Comparison of zeta potential value for sulfide tailings with PAM and Al-PAM.....	40

LIST OF TABLES

	Page
Table.3.1. Base metal mineral and elemental distribution by sieve fraction for sulfide tailings	27
Table.3.2.Sulfide mineral associations for tailings.....	27

NOMENCLATURE

<u>Symbol</u>	<u>Description</u>
U_E	Electrophoretic Mobility
ζ	zeta potential
ε	dielectric constant
η	viscosity
$f(\kappa a)$	Henry's function
E_{vdw}	van der Waals attraction energy
E_{DL}	electrostatic repulsion (repulsive double layer) energy
E	net interaction energy

1. INTRODUCTION

1.1. TAILINGS MANAGEMENT

Tailings are usually produced at some mineral processing and mine sites. In the mining, the most part of the mines are tailings whereas the extracted minerals are just small part of all fractions. After low-grade ores has been utilized, almost 99% of main materials may finally become tailing. Therefore, tailings contain large part of waste in mining industry.

The original rock is ground and crushed almost to 0.1mm to release valuable minerals and during these processes tailings generated as waste products. For increasing the recovery of valuable minerals, water and small amount of chemical materials and reagents are used during this process.

Extracting minerals from primary ores depends on mineral types, but there are some steps which are common in the process. First, excavation of ores from underground or in open pits and then reducing the size by crushing and grinding to fine sands, slit and clay-sized particles. In the grinding process water is used and addition of small amount of chemicals expedite the separation and recovery of economic mineral. Tailings are made of two parts: solids and liquids. The solids are commonly discharged with spent process water into a tailings storage facility, most commonly a tailings dam. Tailings liquid have a tendency to contain high concentration of process chemicals. Tailings slurries can have a solids content ranging from 40% to 50%. This amount of solid is equivalent to a water content of 150% and 100% respectively, which for most soils represents slurry with fluid properties. Slurries (unrecoverable and uneconomic metals, minerals, chemicals, organics and process water) are discharged to a final storage area commonly known as a tailings

management facility (TMF) or tailings storage facility (TSF) which is a final storage area. The main concern about tailings are the physical and chemical characteristics of tailings and their method of handling and storage them.

1.2. CHARACTERISTICS OF TAILINGS

Tailings characteristics depends on the mineralogy of ore and also to the physical and chemical extraction process used for extracting the economic product. For indicating the behavior of the tailings the tailings characteristics have to be determined once they deposited in their final storage location and the potential short and long term liabilities and environmental impacts [1]. Some tailings properties which needs to ne indicated are [2]:

- ✓ Chemical content (including changes to chemistry through mineral processing) and its ability to oxidize and mobilize metals.
- ✓ Physical content and strength (static and seismic loading)
- ✓ Behavior under pressure and rates of combination
- ✓ Destruction stability (wind and water)
- ✓ Concentration behavior and drying time after accumulation and settling
- ✓ Hard pan behavior (e.g. formation of crust on top of the tailings)

1.3. ISSUES RELATED TO TAILINGS MANAGEMENT

The problems related to tailings storage is increasing. Some important issues related to disposal of fine tailings that cause challenges to industry:

1.3.1. Effect of Huge Volume of MFT. Huge volume of mature fine tailings (MFT) is one of the environmental concern. Since there is no policy for discharging tailings into the environment, the loss of water in the tailings is considerable. Losses to evaporation are small, and thus only relatively minor quantities of water are lost. The amount of

recycled water through process is more than fresh water required for make-up. Due to absence of the addition of clean dilution water, recycle of water between the process and tailings ponds in this closed loop has resulted in accumulation of fine clays and dissolved inorganic ions in the tailings pond water system, which cause a stock volume of MFT [3].

1.3.2. Environmental Effects of Mature Fine Tailings (MFT). Some MFT contain naphthenic acids and residues materials which are toxic for the environment. For example, mining and processing of sulfide ores produces large volumes of waste materials which can have serious and extensive impacts on water resources [4].

The mineralogical and geochemical structure of sulfide mine wastes are in charge of negative environmental impacts. Discharging sulfide oxidation to the shallow water will effect groundwater, and Fe(II) can further oxidize will produce additional acidity and lead to severe environmental degradation (sulfide tailing). Results from researches show that the tailings storages in the water and soils continuously release considerable amount of metals and other elements to surface and ground water [5]. Another example of tailings damages to the environment is, about coal preparation plants which produce 75-120 Kg of dry tailings per tonne of coal processed. The solid content of the slurry form of these tailings ranging between 205% and 35% (w/w) [6].

1.3.3. Fresh Water Concern. Extraction and processing useful minerals requires large volume of water which has become an issue of using water in industry. Fine tailings trap water in the pores of fine solids which decreases settling rate of them in the tailings ponds and they usually do not discharge water back to the environment. This associated with the buildup of a large amount of solids and water stockpile. Since requesting for external water use in industry is increasing, it is therefore essential to develop process to

secure a way to use the water efficiently to reduce the use of fresh water and produce less water inventory and also reduce fresh water usage [7].

1.4. INDUSTRIAL PROCESS FOR TAILING MANAGEMENT

Over the past several years various attempts have been made to increase the rate of fine tails settling to allow for water recycling and to reduce the volume of MFT. The methods employed include treatment of MFT with lime, inorganic flocculants and polymers, as well as pH control and freeze-thaw cycles. There are five different technologies, such as physical/mechanical processes (e.g. CT and TT), natural processes, chemical/biological amendments, mixtures/co-disposal and permanent storage [8]. The following section outlines two of the industrial methods that are currently being used.

1.4.1. Consolidated/ Composite Tailings (CT) Process. The CT process is a non-segregating (non-segregate tailing are mixture of tailings in which fines and coarse sand particles settle simultaneously to form a uniform deposit) disposal method to deal with MFT. In the CT technology densified extraction tailings (coarse sand from cyclone underflow of tailings, CUT) and mature fine tailings are mixed with a coagulant (typically gypsum) to produce non-segregating tailings (NST). This NST would be subsequently discharged into tailings storages and they rapidly form a solid deposit. The purpose of CT process is to run at an almost of 30% fines to produce a slurry with approximately 60% solids [9].

The successful application of the CT process has led to a reduction in MFT inventory. Due to its low cost and high consolidation rates, Ct remains the primary tailings management technique for existing and future plans of several operators, with continued effort to assess and improve deposit performance. However, there are several drawbacks

with the CT process. The addition of gypsum results in significant changes to the water chemistry. Chemical analysis of the water released from CT process has revealed high concentrations of ions such as Ca^{2+} , Na^{1+} , Cl^- and SO_4^{2-} [10]. The recycled water containing high concentrations of Ca^{2+} has been shown to have negative impact on bitumen extraction process. Some studies have shown that CT process release H_2S by anaerobic reduction of SO_4^{2-} with the residual bitumen in the tailings [8]. Schematic flow chart of composite tailings process is shown in figure 1.1.

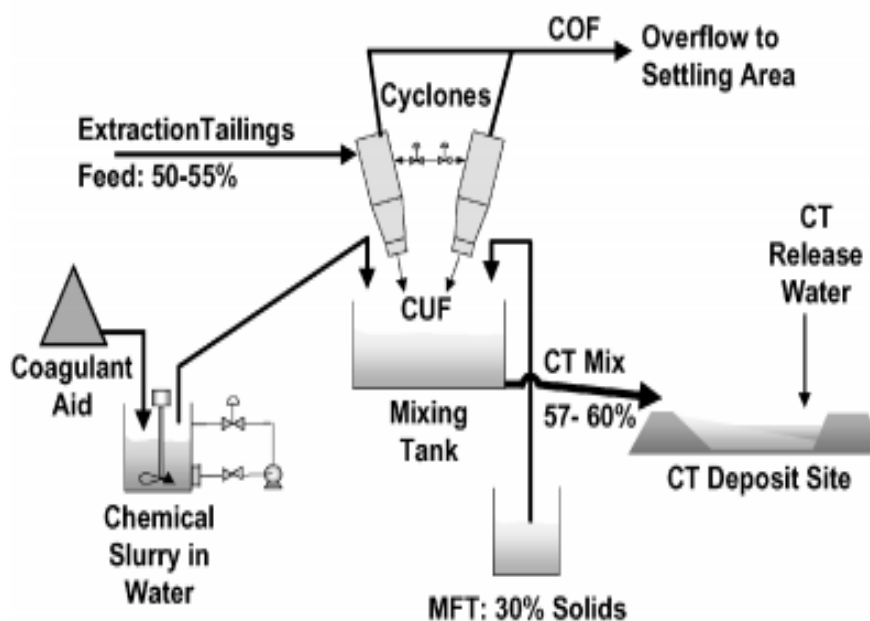


Figure 1.1. Schematic flow chart of composite tailings process [10] (MacKinnon, M. D., et al. 2001)

1.4.2. Thickened Tailings/Paste Technology. Thickened Tailings (TT) technology or paste technology (PT), includes a vessel which called thickener and it increases the settling rate of suspended fine minerals with the help of chemical aids usually flocculants. The water released after the use of flocculants is suitable for reuse and can be recycled to the extraction plant with very little heat losses. Hence this process reduces the

consumption of natural gas required to warm the process water and in turn reduces GHG (Greenhouse Gases) emissions. The flocculated fines are able to settle quickly and form a stable solid bed that can be deposited in tailings pond for land reclamation.

The most important factors influencing the performance of PT is the choice of flocculant(s) and the type of thickener. The choice to commercially apply PT to control fine tailings is deposition requirements and it is also more expensive compare to other tailings management options.

Thickeners have a smooth procedure which transport bed material to the underflow, assists dewatering of the bed material and scrapes away deposits from the base [11].

It is estimated that it takes about half an hour for a thickener to increase the solids part of suspended materials to 30%, whereas in compare with gravity settlement in a tailings pond it takes a few years to reach the same solid content. In the thickened tailings process, there is a combination of removal fine tailing materials and beach run-off streams then they inserted into a thickener. For flocculation and rapid settling of the fine solids, chemicals are added to the process.

One of the most effective polymers was used for flocculation of fine tailings is Percol 727(also known as Magnafloc 1011) or Percol LT27A which is an anionic polymer with high molecular weight and medium charge. This polymer is more effective at pH about 8.5 [12].

In summary, PT is a very promising technique to deal with fine tailings. It produces water with no charge in ion concentration that can be recycled back to the extraction plant for some extraction minerals. The resulting water is warm and hence reduces the consumption of energy. The solids after the thickening process are very stable and can be

deposited without further treatment. Since the tailings are contained in the thickener, there are no concerns of process water polluting groundwater reserves. Although promising, PT has several limitations. PT does not provide any solution to the existing inventory of MFT. It was found commercially available anionic MF1011 and lab synthesized cationic $\text{Al}(\text{OH})_3$ - PAM were ineffective in treating raw MFT. No filter cake was found even after 1 hour of filtration. PT is capital intensive since it requires design, construction and maintenance of thickener. Continuous requirement of polymers only adds operating cost of PT technology [13]. Thickened tailings disposal is shown in figure 1.2.

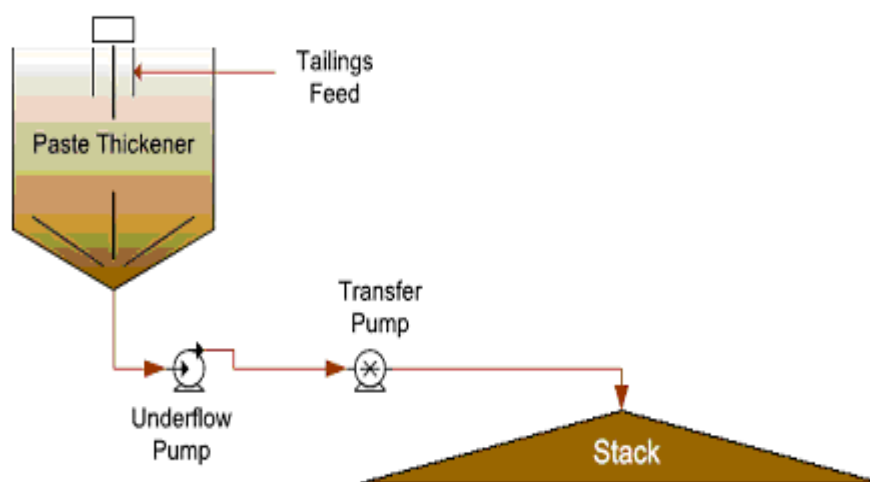


Figure 1.2. Thickened tailings disposal [14] (Paste Thickeners for Tailings Stacking n.d)

1.5. RESEARCH OBJECTIVES

This Study has investigated the effect of two polymers on flocculation and settling rate of MFT.

The major clay minerals are observed in the fine tailings are Kaolin and Illite. Typically, clay minerals in fine tailings are composed of 40-70% kaolin, 30-50% illite and

1-15% montmorillonite. The purpose of this study is to do flocculation and settling tests on both kaolin suspension (as model tailings) and sulfide mineral tailings. A series of PAM and in-house sensitized Al-PAM polymer with different concentration and dosages has been used. The settling performance was evaluated by initial settling rate.

Section 2 can be helpful for finer demonstration of flocculation process by polymers. This section express an overview on flocculation and settling rate of suspensions with fine particles. The focus of this section is on polymers flocculation and the factors that effects flocculation. Other researches work on flocculation by polymers of fine tailings is discussed and summery of their findings is presented.

Section 3 presents materials, preparation steps of Al-PAM polymer and instrument has been used for this research. Section 4 focuses on experimental works such as polymers flocculation of Kaolin suspension as a model fine tailing and sulfide tailing and results of comparing two polymers. Final conclusions from this study are presented in section 5.

2. LITERATURE REVIEW

Tailings are made of solids and liquids. The solids and spent process water are usually discharged into tailings storage facility or tailings dam. Tailings are mixtures of different size fractures such as sand, silt, and clay. For fine solids (silt and clay) it takes longer time to settle in tailings ponds.

One of the efficient ways for separating solid from liquid is flocculation. Flocculation is a process wherein colloids come out of suspension in the form of agglomerates (flocs) or flakes; either spontaneously or due to adding flocculants and/ or coagulants. Interaction of fine particles in suspension is very important to understand the effective flocculation. The following discussion is meant to give the application, definition, and mechanism of particle surface properties, nature of flocculation process as well as the effect of polymer properties and mixing conditions on the flocculation.

2.1. THE COLLOIDAL STABILITY OF PARTICLES IN SUSPENSION

The electrical charge on each particle produces electrostatic repulsion force between neighboring particle. This repulsion leads to stabilization of suspension. The Van der Waals forces are attraction forces between each molecule in colloids and this force is effective at short distances. However, the electrostatic repulsion of the surface charges prevents these attraction forces to take effect. Beside electrical repulsion, absorption of water on the particles surface from surrounding, creating salvation layers which repel each other may cause stable suspension [15].

2.2. THE ELECTRICAL DOUBLE LAYER

The charge on the surface of solid particles in the solution influences close ions forming non-uniform electric charge dispersal near the interface known as the electric

double layer (EDL) [16]. To visualize the ionic environment in the neighborhood of the charge colloid and explain the way that electrical repulsive forces occur, double layer model is used. The effect of the colloids on the ions with positive charges in the solutions is called counter-ions. Stern or counter-ions layer, is formed by a layer of positive ions around the surface of colloid due to attraction from the negative colloid [17]. Figure 2.1 is an illustration of the structure of an electric double layer for a surface with negative charges according to the Stern model.

There is a repulsion between the stern layer and other positive ions that are also trying to approach the colloid and the additional positive ions that are still attracted by the negative particles in the solution. Formation of a diffuse layer of counter ions is a result of this dynamic equilibrium. The concentration of these ions is high near the surface and it decreases gradually with increasing the distance until it attains equilibrium [18].

The potential at the shear plane between the stern layer and the diffuse layer is known as Zeta potential(ζ).

With considering electrostatic repulsion, the zeta potential is more notable than potential at the surface [19]. Zeta potential value is useful for predicting and controlling the stability of suspension with fine particles. Schematic illustration of an electric double layer according to the Stern model is shown in figure2.1.

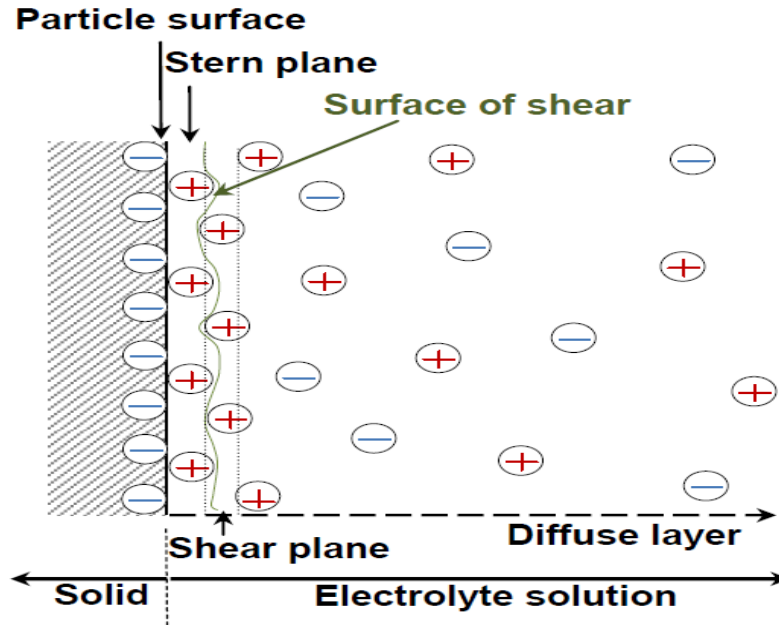


Figure 2.1. Schematic illustration of an electric double layer according to the Stern model [20] (Guo,Lina, 2012)

2.3. DELVO THEORY

The DELVO theory (named after Derjaguin, Landau, Verwey and Overbeek) is the classical statement of the stability of colloids in suspension [20].

The DELVO theory explains the propensity of charged particles to agglomerate or remain discrete by combining the van der Waals attraction energy E_{vdw} (curve) with the electrostatic repulsion (repulsive double layer) energy E_{DL} (curve) to form the net interaction energy E (curve) which is represented in equation 2.1 and shown in figure 2.2 [6].

$$E = E_{vdw} + E_{DL} \quad (2.1)$$

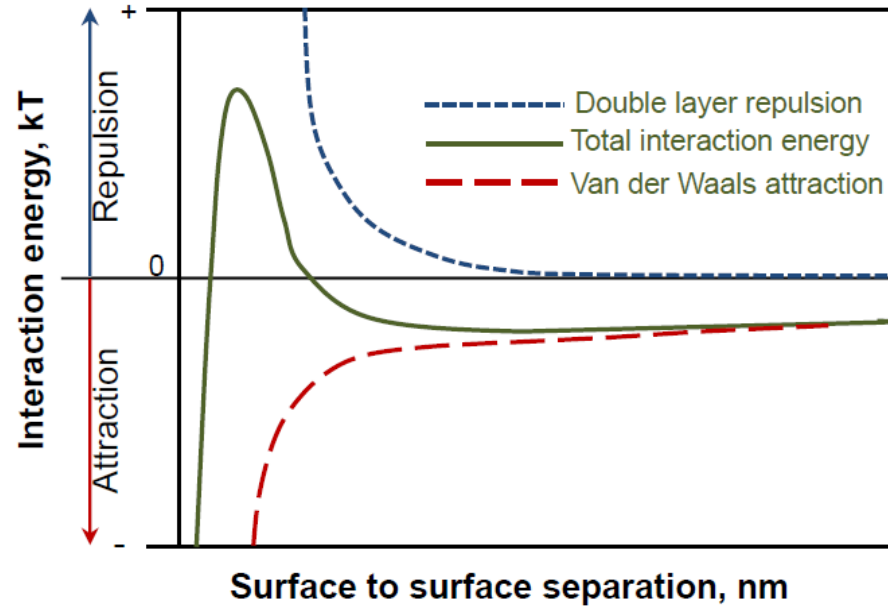


Figure 2.2. Schematic diagram of the variation of free energy with particle separation according to DELVO Theory [20] (Guo,Lina, 2012)

2.4. COAGULATION AND FLOCCULATION

Coagulation is defined as the addition of inorganic salts for its importance at destabilizing fine solids suspension. Combination of colloidal particles and suspensions with very fine solid particles can form large agglomerates in coagulation process. Separation of coagulation may happen by way of flocculation, filtration, centrifugation, sedimentation or other separation methods. Adding coagulant or different types of chemicals to the suspension assist destabilization of the colloid dispersal and agglomeration of individual colloidal particles which it helps to achieve coagulation [21].

In some concentrations, surfaces of negatively charged particles will reduce through the addition of metal cations (coagulant). Increasing of concentration of ions leads to a reduced thickness of the electric double layer, resulting in decay of the repulsive double layer interaction. Therefore, the attraction van der Waals interaction becomes more prevalent and hence the probability of particle aggregation will increase [22].

The slightly large particles, formed by coagulation are called microflocs, which are in small size but more compact and they are not visible to naked eye. Increasing particle size from submicroscopic micro floc to visible suspended particles is flocculation. The floc size continues to build through additional collisions and interactions with inorganic polymers formed by the coagulant or with organic polymers added. The comparison between coagulation and flocculation is shown in figure 2.3.

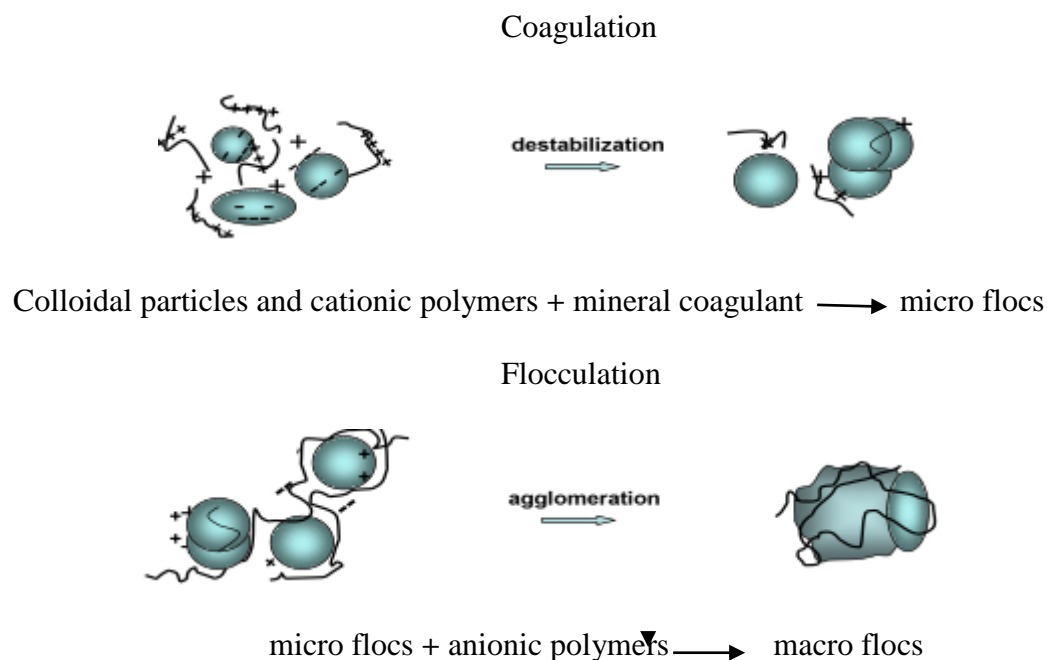


Figure 2.3. Schematic comparison of coagulation and flocculation (comparison of coagulation and flocculation n.d)

In flocculation, agglomerations of destabilized particles form large particles which is a microscopic aggregation of suspended particles process. For better flocculation, increasing the floc size by adding high molecular weight, water soluble organic polymers help particles settle down faster [23]. The flocculating agent should be mixed at a slow speed so that small flocs can easily attaches into large particles, and finally settle down. During coagulation, coagulant adds the particles together and form a clump. In flocculation larger clumps form due to mixing solution gently and gathering small clumps

from coagulation. The large flocs easily settle down and thus can be separated [24]. The most important mechanism of agglomeration is flocculation by bridging [25].

When optimum dosage of polymer is added, the individual chains of polymer take in onto another particle, therefore other particles will attach together through bridging [26]. This mechanism requires particle surface to be available for polymer chain attachment. When polymer concentration is lower than optimum, there are insufficient bridging links between polymer chains and particles, thus there exists unlinked particles in the supernatant of the suspension [27]. On the other hand, when excess polymer is added, particle surface will not be free any more to be attached to polymer's chain or part, and this leads to destabilization of the suspension (also known as steric stabilization). Hence there exists an optimum dosage of the polymer at which the particles are sufficiently covered with polymer chains, leading to destabilization of the suspension [28]. Schematic illustration of re stabilized by adsorb polymers are shown in figure 2.4.

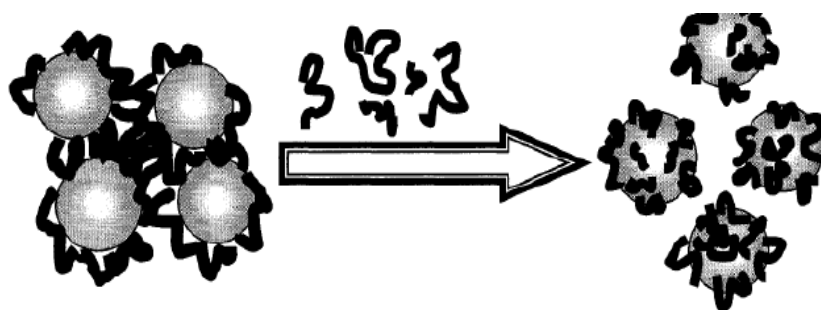


Figure 2.4. Schematic illustration of re stabilized by adsorb polymers [15] (Modified from Tridib et al., 2006)

2.5. FLOCCULATING MATERIALS

There are two kinds of flocculants; inorganic and polymeric. Polymeric flocculants has more benefits in compare with inorganic flocculants. Polymeric flocculants form more rapidly flocs and the flocs are larger and stronger than inorganic flocs. The polymer dosage

requirement for polymeric flocculants is less than inorganic flocculants (almost 1% and 20% respectively on a dry weight basis) [15, 27]. Inorganic flocculants plus being cheap are useful for economic reasons.

Polymeric flocculants such as natural and synthetic polymers use bridging for flocculation [20]. Natural polymers have less molecular weight in compare with synthetic polymers and they are also very expensive and may be toxic. Synthetic polymers are able to achieve good flocculation and by making some changes in their molecular weight or structure can be suitable for some application [29].

Polyacrylamide and its derivative are most commonly used synthetic flocculants [29,30]. Polyacrylamide is generally non-ionic and the ionic part is divide to anionic and cationic groups. Anionic polyacrylamide may be prepared by partial hydrolysis of polyacrylamide or by polymerization of acrylic acid and acrylamide together. Polymerization of acrylamide with some derivatives of it, forms cationic polyacrylamides. Depending on the application the type of cationic material is changeable [31]. Figure 2.5 is schematic of polyacrylamide polymerization.

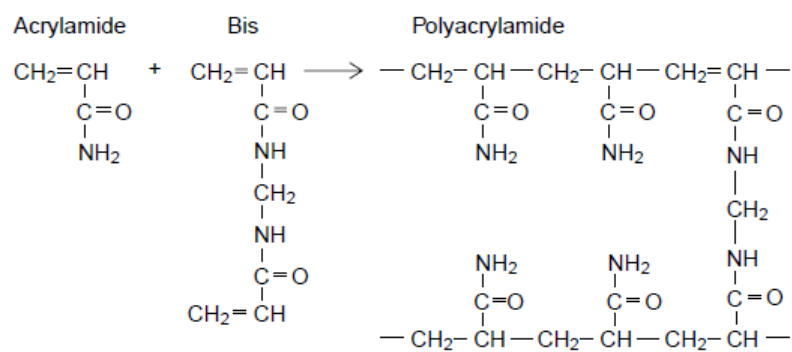


Figure 2.5. Illustration of polyacrylamide polymer [31] (Polyacrylamide structure n.d)

2.6. FACTORS EFFECTING FLOCCULATION

2.6.1. Effect of Polymer Dosage. Polymer dosage effects the degree of flocculation. Efficiency of the flocculation process decreases by adding polymer more than its optimum dosage [32]. At the optimum dosage of polymer which is the maximum amount of polymer, half the area of the solid is covered with the polymer and solid can be utilized for flocculation. At the polymer concentration higher than optimum, some layers of polymer will cover the surface of particle, which makes the suspension very stable. Therefore, the separation won't be easy [33, 34].

2.6.2. Effect of Mixing Conditions. Floc breakage occurs due to excessive agitation of flocculation suspension. This may decrease flocculation efficiency and settling rate as the smaller flocs form. Floc breakage produces new particle surface into the solution which increase the capacity of flocculation by polymer adsorption onto particle surface, but because of repulsion due to excess adsorption, efficiency of flocculation will be low. So the optimum dosage of polymers is depending to special amount of mixing.

2.6.3. Effect of Polymer Molecular Weight. Better flocculants is a result of higher the molecular weight and synthetic bridging polymers. After adsorption of high molecular weight of polymer, it can be far from the particle surface and it takes more time to reach equilibrium. Consequently, increasing particle size and number of collision will increase flocculation efficiency [15]. Even though polymers with similar molecular weight may give different flocculation results, their performance still might be different and depends on properties of polymer and slurry. Therefore, molecular weight is not the only factor for successful flocculation [35].

2.6.4. Effect of Particle Size. One of the important parameter for flocculation is particle size. Experiments showed coarse particles (greater than 100 μm), which normally do not agglomerate, they will if appropriate molecular weight (high) of flocculants was applied. For fine particles (less than 50 μm) the flocculation is best option. Generally, decreasing particle size will increase flocculation process [36].

2.6.5. Effect of pH. Changing pH of solution effects the colloid surface charge and the optimum dosage needed for effective flocculation. The degree of ionization of the polymer may be effected by pH. pH altering will affect the polymer chain charge, so that determining the amount of extension of the polymer. Bridging flocculants can happen at certain range of pH which depends on type [37].

2.7. PREVIOUS STUDIES ON FLOCCULATION APPLICATION ON TAILINGS TREATMENT.

Tailings dewatering is a necessary process in most mining operations. Typically, Sedimentation or/and filtration accomplish final dewatering. Dewatering streams with very fine particles (less than 5 μm), needs a necessary pretreatment step which is flocculation for such systems, the performance and the capacity of the dewatering system may be determined by effectiveness of the flocculation.

It has been shown that dynamic effects such as stirring time are important in the action of polymeric flocculation in suspensions. According to these results, increasing mixing time will increase flocculation rate and also, the results from using different cationic polymers indicated that the flocculation increased with a polymer with higher molecular weight. These tests have been done on different suspensions such as kaolin at pH=7 [33].

Some interesting early work on flocculation of fine tailings, who tested anionic and nonionic polyacrylamide as potential flocculation reagents for fine tailings at different pHs.

His results showed that flocculation at pH=3.3 with anionic polymer was not as good as results at pH=7. He showed low pH for polymers containing 30% and above of anionic groups, prevents ionization which affects the flocculation process. For nonionic polymers, adjusting pH from 3.3 to 7 led to same results for flocculation. These behaviors indicated the influence of low pH conditions on anionically charged polymer [31].

Bigges's (2000) [28] study showed using slightly overdosed cationic polymer (SNF Floeger it is one of the derivative of polyacrylamide polymer and it was high molecular polymer), did not prevent flocculation, but it did slow down the process of aggregates. In this study, 0-100 concentration of polymer at pH=6 has been used. At highest polymer dosage (5ppm), bridging flocculation was efficient due to choosing high molecular weight polymer which makes easier the interaction between particles and polymer.

More recently, studies on coal tailings showed that isoelectric point (iep) of +0.045mm tailings happens at pH=2 and zeta potential value for -0.045mm and +0.045mm tailings is between -25 and -27 at pH=8-8.5. The results have been indicated that settling rate increased at natural pH of coal tailing slurry (i.e. pH= 8.3) by using low and medium anionic flocculants (charge densities of 16-40%) having high molecular weight polymer while its turbidity decreased. For this experiment the derivative of polyacrylamide polymer has been used [38, 39].

Further studies on flocculation mechanism on fine tailings confirmed that for a known kind of polymer, higher molecular weight, mixing time, which would result in a

more effective flocculation of small particles, leading to flocs formed with more particles, and hence increased the settling rate [40].

The aforesaid studies suggest measuring turbidity or clarity of supernatant and amount of solid in residue, initial settling rate and turbidity or clarity of supernatant is a good way for finding flocculation efficiency by polymer. Flocculation by anionic polyacrylamide with medium charge and high molecular weight for fine tailings such as coal and sulfide tailings can be effectual. As it mentioned earlier, some factors such as optimization of polymer dosage, water chemistry (e.g. pH of tailing), and mixing condition can influence good flocculation results.

3. EXPERIMENTAL WORK

3.1. MATERIALS

3.1.1. Materials for Model Fine Tailing. Kaolin clay that was used in this study as an example of model fine tailings was purchased from Fisher Scientific. Kaolin clay is an aluminasilicate that comprise of a single tetrahedral silica sheet bonded to a single octahedral alumina sheet through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheets [41]. The general chemical composition is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (figure 3.1).

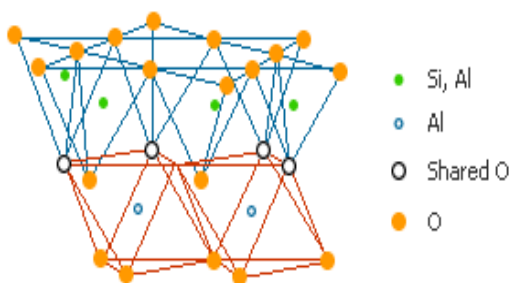


Figure 3.1. Schematic of kaolin structure (Schematic of kaolin structure n.d)

Kaolin has a negative surface charge in aqueous suspension due to replacement of Al^{+3} with Si^{+4} in the tetrahedral sheet of the clay surface. This mechanism is known as isomorphous substitution of ions. Electrical potential of kaolin depends on ion concentration, pH, valence of cations and also other things [41].

Kaolin was chosen in this work because of its application in many different ways including ceramic processing, composite materials design, paper making, coal processing, industrial waste management and oil sands extraction.

3.1.2. Materials for Polymer Synthesis. The chemicals used for polymer synthesis are: acrylamide (monomer), aluminum chloride anhydrous (>99%) and

ammonium carbonate (for synthesize the aluminum hydroxide nanoparticles); ammonium persulfate (98%) and sodium hydrogen sulfite (95%) (used as initiators in the polymerization of acrylamide); acetone (>99.5%) and; pH modifiers were sodium hydroxide (NaOH) and hydrochloric acid (HCl). All these chemical were purchased from Fisher Scientific (FisherSci, USA).

3.2. POLYMERS

Below is the list of polymers used in this study:

- A. Polyacrylamide (PAM) was used as flocculant in settling tests, is almost white powder which is soluble in water with a molecular weight of about 5×10^6 Dalton. This polymer is manufactured and distributed by Pfaltz & Bauer Rare and Fine Chemical Company [42].
- B. Aluminum polyacrylamide (Al-PAM) is in-housed synthesized organic-inorganic hybrid polymer with a star like-structure. Al-PAM chemical formula is $\text{Al}(\text{OH})_3$ polyacrylamide, which it has an ionic bond between $\text{Al}(\text{OH})_3$ colloids and polyacrylamide chain [42].

The three major steps for preparing Al-PAM polymer are: 1) preparation of the aluminum hydroxide colloidal nanoparticles, 2) polymerization of acrylamide monomer in $\text{Al}(\text{OH})_3$ colloid to produce Al-PAM, and 3) purification of the Al-PAM polymer by precipitation in acetone. Al-PAM polymer should have a star-like structure as proposed earlier in literature [43,44]. Figure 3.2 is an illustration of the proposed star like structure of Al-PAM polymer Al-PAM structure.

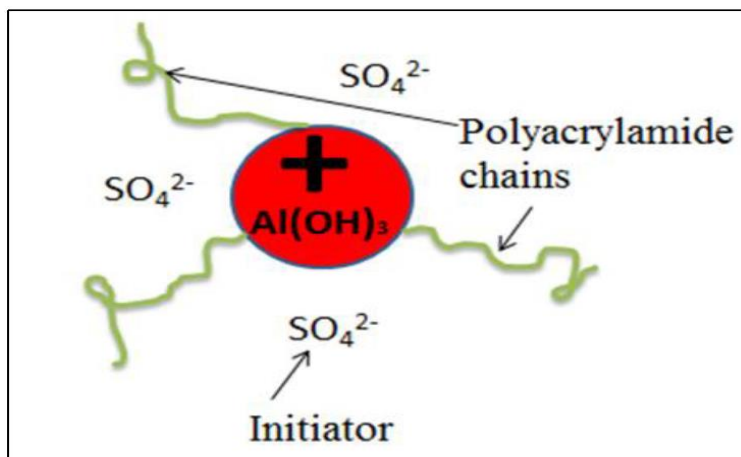


Figure 3.2. Illustration of Al-PAM with organic polyacrylamide arms grafted on the aluminum hydroxide nano particles core (Al-PAM structure n.d)

3.2.1. Principle of Colloid Preparation. Preparation, synthesis and characterization of Al-PAM colloid discussed in detail in the work of [42,44] but will be mentioned briefly here.

The chemical reaction involved in the synthesis of $\text{Al}(\text{OH})_3$ colloid is:



3.2.2. Procedure of Colloid Preparation. 25 g of 0.01M (AlCl_3) solution has been prepared in a beaker by dissolving 0.33g of aluminum chloride anhydrous (>99%) (AlCl_3) in distilled water. In a separate beaker, about 0.48 g ammonium carbonate (NH_4)₂CO₃ was dissolved in distilled water to make 50 g of 0.1M (NH_4)₂CO₃ solution. The prepared (NH_4)₂CO₃ solution was added to AlCl_3 solution by using Master FLEX mini pump at a rate of 0.5 g/min. The addition rate of (NH_4)₂CO₃ solution to AlCl_3 solution was controlled by an electronic balance. Two solutions have been mixed with an IKA RW20 mechanical stirrer at initial constant rate 500 rpm. Adding extra amount of (NH_4)₂CO₃ solution through the pump was stopped after about 36-37 g of the (NH_4)₂CO₃ solution has been added into 25g of AlCl_3 . The solution was stirred for 30 minutes at the rate of 300rpm for completing

the reaction. The zeta potential value and particle size of the prepared $\text{Al}(\text{OH})_3$ colloid suspension was measured by using Zetasizer Nano Ltd instrument, which were +30 mV and 50nm respectively. The experimental set up for colloid preparation is shown in Figure 3.3.

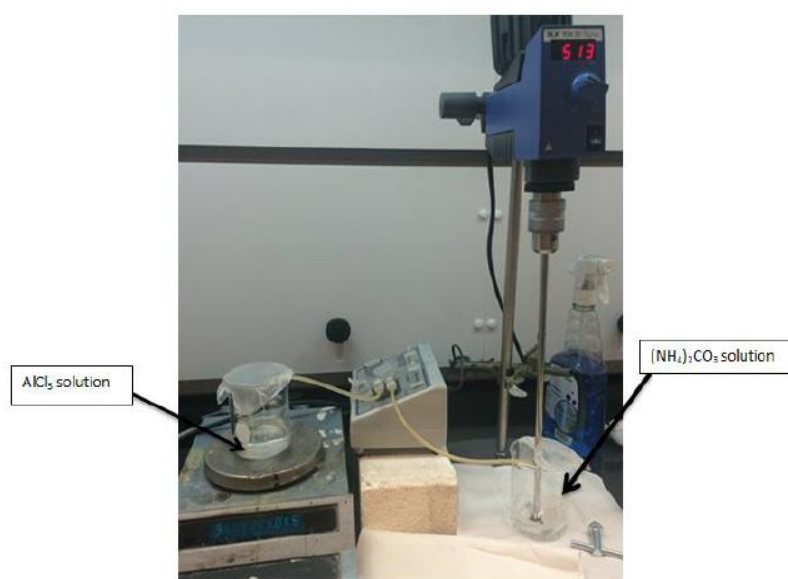


Figure 3.3. Experimental set up for colloid preparation

3.2.3. Al-PAM Synthesis Principles. Figure 3.4 is a schematic of synthesis mechanism of Al-PAM.

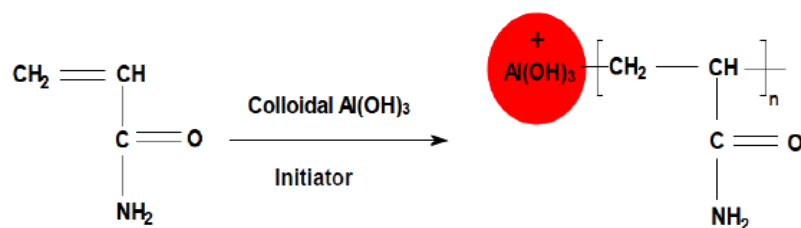


Figure 3.4. Schematic of Al-PAM synthesis [2] (Al-PAM synthesis n.d)

3.2.4. Procedure of Synthesis of Al-PAM. 4.5 grams of acrylamide monomer were added to 25 grams of colloid suspension in a 100 mL flask under magnetic stirring at 20

rpm. From beginning to the end of reaction, nitrogen gas was used to the mixture to avoid any oxidation. The process was maintained at a constant by using oil bath which it was temperature of 40 degrees Celsius. Aluminum foil was used for covering flask from being exposed to light. After 30 minutes of agitation under nitrogen gas, initiators (1 mL of 2 g/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 1ml of 1g/L NaHSO_3) were added within 30 minutes through a 10-mL glass funnel. The reaction was kept for 4 to 8 hours until the formation of transparent gel. Figure 3.5 shows the set up for Al-PAM synthesis.

3.2.5. Purification. The purpose of purification of Al-PAM polymer gel is for removing unreacted monomer and initiators form product gel. For purification, the gel was first diluted with distilled water to 10 wt. % and placed in a mechanical shaker for 2 days. The prepared polymer solution was then dropped-wise in acetone and precipitated. Finally, the purified polymer was transferred to a Teflon dish, and the dish was placed for drying at 60 degrees Celsius in a vacuum oven overnight.



(A)

(B)

Figure 3.5. Experimental set up for Al-PAM synthesis. (A) Set up before aluminum foil was put on for protection from exposure to light. (B) Set up with aluminum foil for protection from exposure to light

3.3. PREPARATION OF MODEL FINE TAILINGS

For understanding flocculation process, flocculation performance of polymer model tailings was used. An aqueous slurry contained 5 wt.% kaolin (Fisher Scientific)

was prepared by dissolving 50 g of Kaolin into 950 mL of distilled water in a 1000 mL beaker. The solution was mixed with a three blade impeller at 500 rpm for almost 24 hours in order to be sure that kaolin was dispersed before flocculent addition. The pH of the suspension was adjusted to 8.5 using NaOH while stirring.

The reason that kaolin was chosen as model fine tailing is that many tailing wastes consist mostly of phyllosilicate minerals such as clays, illite, and the majority is being kaolinite. In addition, Kaolin has been used in a myriad of applications including papermaking, manufacturing of polymer nanocomposites, ceramic processing, cosmetics, etc.

3.4. PREPARATION AND CHARACTERIZATION OF SULFIDE TAILINGS

Sulfide tailing produced from flotation process of sulfide minerals; galena, sphalerite and chalcopyrite was used in this work as an example of industrial tailing waste to investigate the potential of using both organic and hybrid polyacrylamide polymers as flocculants. The sulfide mineral tailing wastes were bought from Doe Run Company. Since samples were stocked in 5 gallons containers, it was important to make sure that the slurry is homogeneous and the sub-samples taken for the purpose of characterization have the same composition. Isokinetic sampling was performed by mixing the solids in the slurry using mechanical agitator. Samples were mixed at 500 rpm for 24 hours prior to taking sub-samples. Sub-samples were taken during agitation. The solid content of sulfide mineral tailing was determined to be 20% by weight. Characterization of sulfide mineral tailings was done at CAMP (The Center for Advanced Mineral and Metallurgical Processing). The tailings were found to contain sphalerite at 0.10%, galena at 0.05%, chalcopyrite at 0.05% and pyrite at 1.9%. Chalcopyrite grain size distribution P_{80} was between 100 to 200 μm

whereas the composite particle size distribution P_{80} s was approximately 125 μm . The grain size of sphalerite and galena in the tailings was slightly smaller than 32 μm (figure3.6).

The gangue material was mainly carbonate with dolomite at 95% in the tailings. The best metal mineral and elemental distribution for tailings is presented in table3.1. More than 50% of the lead and zinc in the tailing was in the -500 mesh fraction; however, 84% of the remaining copper was found in the +200 mesh fraction.

The sulfides show even greater association with the gangue, which is expected since it is likely that the more poorly liberated grains persisted in the tailings (table 3.2). The sub-samples from kaolin slurry and sulfide mineral tailing were prepared using a disposable pipette to transfer (<100 g) of tailings into the beaker of 250 mL under mechanical mixing. Figure 3.7 (a) and (b) shows a picture of mechanical stirrer and disposable pipette.

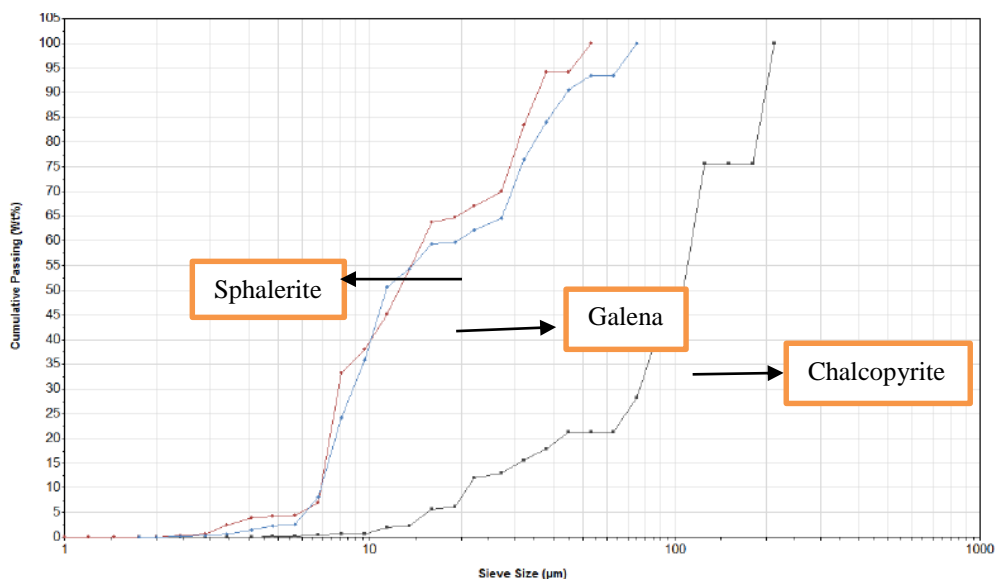


Figure 3.6. Mineral grain size distribution for chalcopyrite, galena and sphalerite in sulfide tailings

Table 3.1. Base metal mineral and elemental distribution by sieve fraction for sulfide tailings

Mineral	Modal Concentration					Mineral/Elemental Distribution				
	+200	200 X 400	400 X 500	-500	Modal	+200	200 X 400	400 X 500	-500	Total
Chalcopyrite	0.19	0.02	0.02	0.04	0.10	84.5	3.7	1.7	10.1	100.0
Galena	0.04	0.01	0.02	0.10	0.05	35.2	5.5	3.4	56.0	100.0
Sphalerite	0.05	0.00	0.02	0.11	0.05	39.8	0.9	2.9	56.4	100.0
Cu (Wt. %)	0.07	0.01	0.01	0.01	0.04					
Pb (Wt. %)	0.03	0.01	0.02	0.09	0.04					
Zn (Wt. %)	0.03	0.00	0.01	0.08	0.04					
Mass Dist. (%)	44.8	21.1	7.3	26.8	100.0					

3.5. CRITERIA FOR SETTLING PERFORMANCE

The effectiveness of polymer flocculants for tailings treatment was determined by measuring two parameters:

- Initial settling rate
- Electrokinetics measurements

Table 3.2. Sulfide mineral associations for tailings

Mineral	Chalcopyrite	Dolomite	Galena	Pyrite	Quartz	Sphalerite	Free Surface
Chalcopyrite		5.8	0.0	8.2	2.0	0.0	84.0
Galena	0.0	19.8		2.0	4.3	2.0	71.8
Siegenite	0.0	22.4	0.0	0.3	1.5	0.0	75.7
Sphalerite	0.0	17.4	1.2	0.6	1.6		78.7



Figure 3.7. (a) Mechanical stirrer; (b) disposable plastic pipette of 23 mL in volume

3.5.1. Settling Tests and Methodology. Standard settling tests were applied to the Kaolinite model fine tailings. The initial settling rates (ISR) as a function of polymer dosage are based on changing rate of settling by recording mudline over time. For finding ISR, slope of the settling curve was calculated and its unit is meter per hour (m/hr).

Mineral solutions of 5% wt. solids were prepared by dispersing 5gr Kaolin into 95ml of Distilled water in a glass beaker. The suspension was stirred with a three blade impeller at 500 rpm for 24 hours to ensure complete dispersion before flocculants addition. The pH of the suspension was adjusted to the 8.5 using the pH modifiers (NaOH) while stirring. The flocculant solutions were added drop by drop while the solution was mixing under 280 rpm speed of impeller. The polymers were then added at dosages of 15, 25, 35,45,55,65, and 75 ppm (part-per-million), respectively into 5 wt.% Kaolin suspensions. After last drop of polymer was added, mixing was stopped immediately due to sensitivity of flocs to the mixing condition such as mixing rate. The flocculated tailings were then poured to a 100 mL graduate cylinder. The descent of the supernatant- sediment interface (mud line) was recorded as a function of time after inverting the cylinder for 3 times. There are two ways for finding settling rates: for every 5-mL volume of mud line going down record the time in second, or for every 5 seconds of settling record the volume of the mud line. The picture of set up is shown in figure 3.8.

As it is shown in picture 3.8, h is the mud-line height at time t and H is the initial mud-line height or suspension height at time zero. The initial settling rate which is the slope of the initial linear portion of the plot, was determined by plotting of the supernatant height versus time as it is shown in figure 3.9.

3.6. ZETA POTENTIAL MEASUREMENT

Zeta potential measurements were conducted using Malvern ZetaSizer Nano ZS (Malvern Instruments Inc., Westborough, Massachusetts) (Figure 3.12). First, the Capillary cell was rinsed with distilled water. Then, after 5 minutes of settling, 25 mL of supernatant of tailings slurry (with and without polymer) was transferred to the Capillary cell for finding zeta potential. The measurements were conducted at pH=8.5 and temperature of 22°C (figure 3.10 & 3.11).

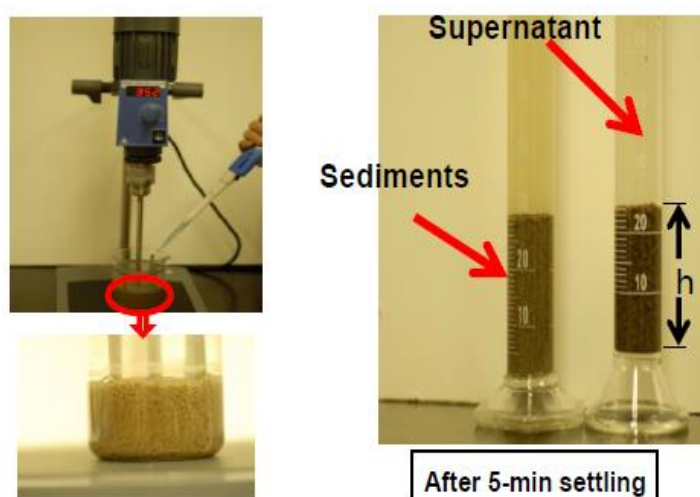


Figure 3.8. Setup for settling experiment

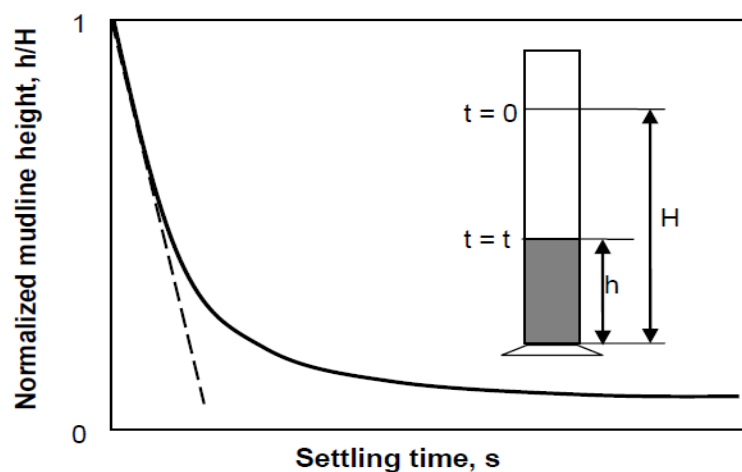


Figure 3.9. Schematic diagram of a typical settling rate (Guo,Lina, 2012)

The instrument uses the particles electrophoretic mobility to calculate zeta potential. Charged particles in the electrolyte are attracted towards the electrode of the opposite charge due to apply an electric field across an electrolyte. Electrophoretic mobility is the velocity of the particles in unit electric field strength. The software calculates zeta potential using the following Henry equation:

$$U_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta} \quad (1)$$

Where U_E is electrophoretic mobility, ζ is zeta potential, ε is dielectric constant, η is viscosity and $f(\kappa a)$ is called Henry's function. In the Henry's function κ is the thickness of double layer and a is the particles ratio and it is about the ratio of the particle radius to the electrical double layer thickness. Zeta potential of kaolinite solution without polymer, zeta potential of sulfide tailings solution without polymer and zetasizer nano ZS devise are shown in figure 3.10, 3.11 and 3.12 respectively.

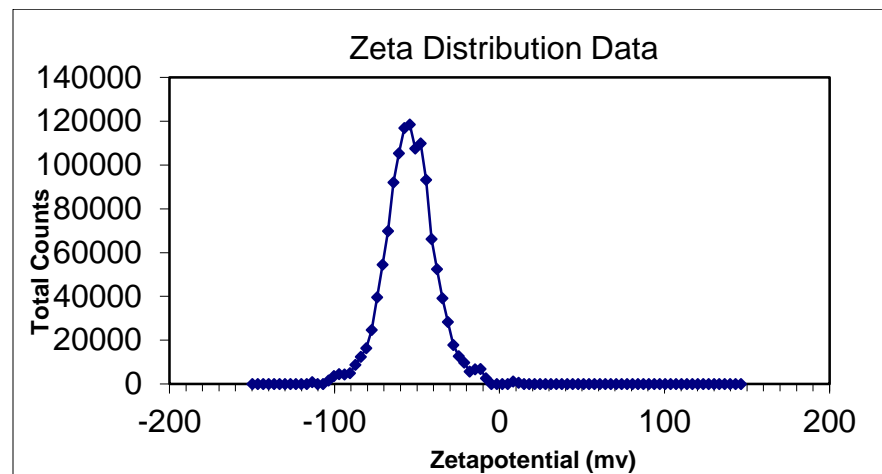


Figure 3.10. Zeta potential of kaolinite solution without polymer

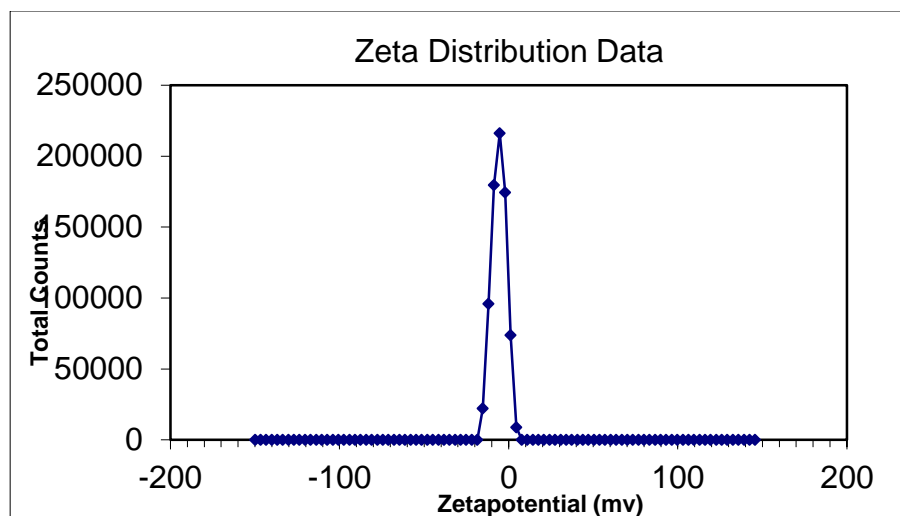


Figure 3.11. Zeta potential of sulfide tailings solution without polymer

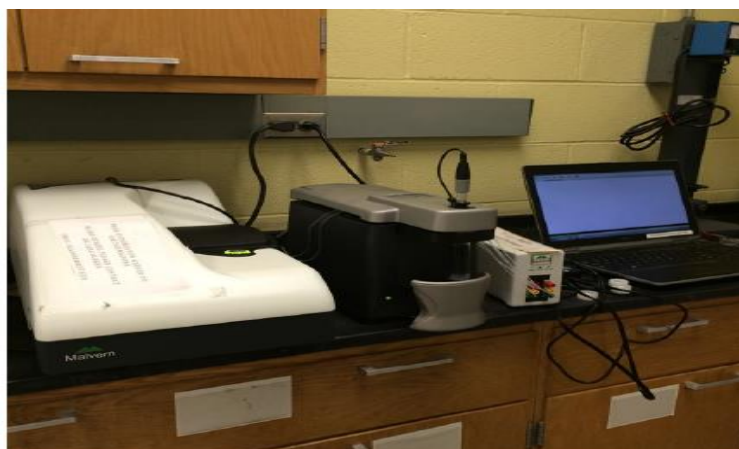


Figure 3.12. Zetasizer nano ZS (Malvern Instruments Inc.)

4. RESULTS AND DISCUSSION OF FLOCCULATION AND SETTLING RATE

4.1. INTRODUCTION

In this section, details about basic principles, data processing, example discussion for settling and polymer effects, and result of polymer addition on flocculation and settling of fine tailings have been discussed. This work was performed in two parts: studies on kaolin suspension (as model tailings) and studies on sulfide mineral tailings. Kaolinite tailings are produced in the mineral processing industry. The natural pH of Kaolinite tailings shows, Kaolinite particles have negative charge and they tend to form stable solution with poor flocculation characteristics. Two kinds of polymer were used. Aluminum polyacrylamide (Al-PAM) which is an organic- inorganic and polyacrylamide (PAM) which is an organic polymer was used.

The flocculation of kaolin suspension using Al-PAM, as in-house synthesized polymer prepared by polymerization of acrylamide in $\text{Al}(\text{OH})_3$ colloidal solution (all the process has been described in section 3 has been described.

Fine particles flocculation may occur by different mechanisms such as: polymer bridging, charge neutralization, polymer-particle surface complex formation and depletion flocculation, or may be combination of these mechanisms. In the bridging mechanism, the polymer chains adsorb on the particle surface with few points of attachment. Effective bridging mechanism does not happen due to surface saturation and because of strong adsorption, fine particles destabilize. So, strong adsorption does not aid flocculation process [45]. In the flocculation with Al-PAM which is a cationic polymer due to short micro-ion length bridging mechanism is not the primary mechanism. Since Al-PAM has strong adsorption on to negative particles, thus charge neutralization becomes would be

avored. In this processes, polymer will change particles surface charge. Flocculation of Kaolinite with negatively charge with nonionic PAM polymer, bridging mechanism has the major importance, whereas charge neutralization will be of secondary or little importance [45,47].

The settling rate results from kaolin solution with Al-PAM showed the flocs are denser and larger due to electronic interaction between the positive $\text{Al}(\text{OH})_3$ core and the negative particle f kaolin as well as the adsorption-bridging effect of polyacrylamide chains in Al-PAM, in compere with PAM.

4.1.1. Studies on Kaolin Suspensions (Model Fine Tailings). This section focuses on flocculation of 5% wt. Kaolin suspensions and Sulfide tailing with PAM and Al-PAM polymer. The objective of this study was to investigate the effect of polymers dosage. Performance was measured in terms of settling rate.

4.2. EXPERIMENTAL

4.2.1. Materials. The materials used in this study include Kaolin clay, Polyacrylamide (PAM), Al-PAM, pH modifiers (i.e. reagent grade NaOH and HCl), and distilled water.

4.2.2. Results and Discussion. The initial settling rate of the kaolin suspension was calculated from the results of the settling tests in Figure 4.1. Figure 4.2 shows the results of the initial settling rate as a function of concentration of PAM and Al-PAM polymer respectively. Initial settling rate was found by adding trend line to the graph. The slop of trend line was multiplied to 3600 to convert it from ml to m/h. For 500ppm of stock solution of PAM and Al-PAM at highest dosage 75ppm, settling rate was 21.6 and 31.4 m/h for both polymers respectively.

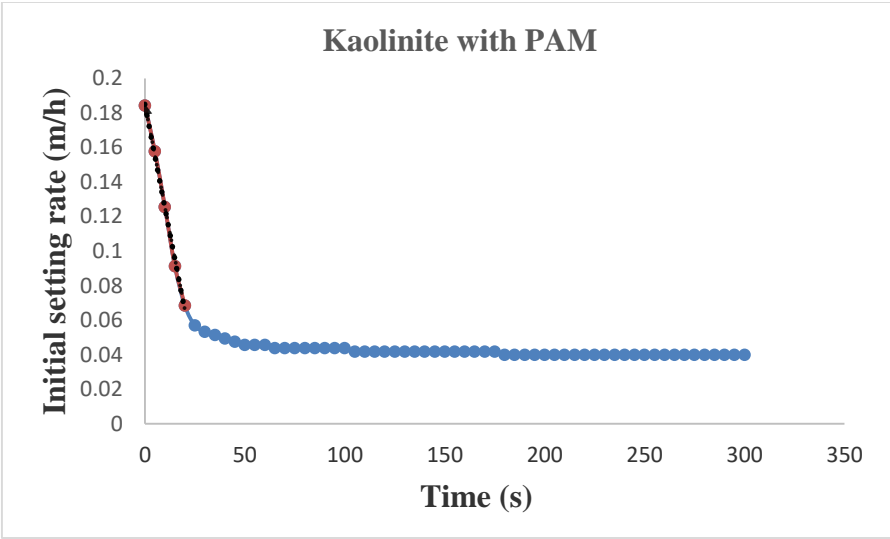


Figure 4.1. 5% kaolin solution with PAM polymer

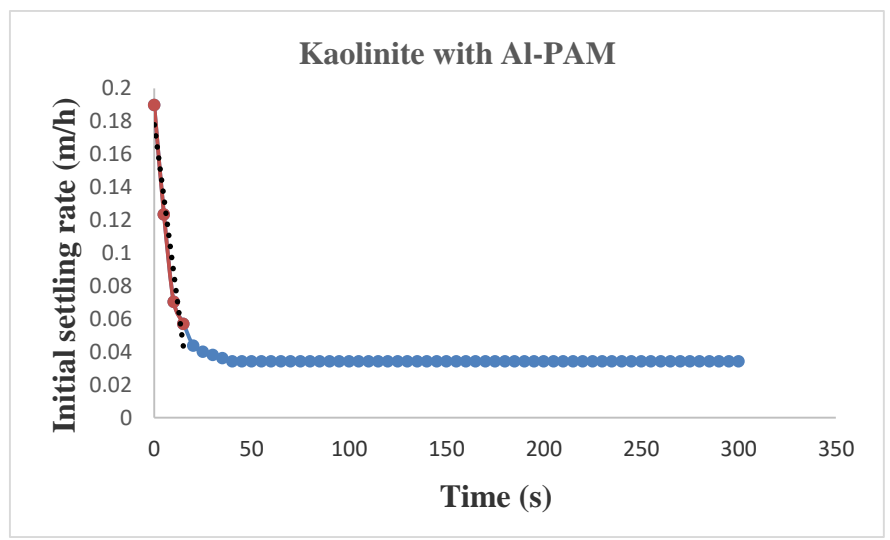


Figure 4.2. 5% kaolin solution with Al-PAM polymer

According to the results from the settling rate of kaolin suspension, the optimum dosage of flocculation of PAM polymer is 35ppm which ISR is 29.16 m/h. At this optimum concentration bridging mechanism happens between polymer molecules and also Kaolin particles due to partially covered by adsorbed PAM polymer on the Kaolin surface particles. Increasing polymer dosage results in full coverage of kaolin particles surface

therefore steric barrier forms and prevent to be close to each other. So, density of suspended solid particles will increase and slurry becomes more stabilized.

4.2.3. Al-PAM Flocculation Performance. AL-PAM polymer has Al colloid core with positive charge. The aluminum content (Al content) in the Al-PAM has an important role in Al-PAM function. Adding of Al-PAM polymer with positive charge to the kaolin solution with negative charge cause an electrostatic attraction force between polymer molecules and kaolin particles. By increasing the concentration of Al-PAM, the number of positively charge particles will increase which led to neutralization of more negatively charged on the kaolin particles surface in suspension.

4.2.4. PAM Flocculation Performance. For nonionic PAM, bridging procedure has main role in flocculation process. In the case of nonionic PAM, the major driving force for bridging is H-bonding. There is an electrostatic repulsion between particles and polymer molecule which causes long distance interaction between them and also allows the polymer to be extended. The formation of open structures flocs is due to this extension of polymer molecules. Thus, bridging mechanism and aggregation with open structure happens for flocculation process.

4.2.5. Comparison of Flocculation Performance of Al-PAM and PAM Polymer with Kaolinite. Figure 4.4 shows the initial settling rate of 5% kaolin with Al-PAM and PA polymer at 500ppm (high concentration stock solution). Comparison of graphs shows, at 25ppm of polymer the ISR for Al-PAM was 8.28 m/h in compare to 25.2 m/h when PAM was used as flocculent. At highest dosage 75ppm, ISR for Al-PAM was 32.4 m/h while it was 21.6 m/h for PAM. Even though for some polymer dosage the value of ISR with PAM is larger, but it is obvious the ISR is almost increasing by increasing the polymer

dosage for Al-PAM polymer. Since ISR is a function of size of aggregation, this result indicates that the aggregates formed using Al-PAM will be larger and faster than using PAM. This is most likely because of the difference in the interaction mechanism of the two polymers with Kaolin particles. Figure 4.3 shows that the settling rates increases with increasing polymer dosage up to an optimum (between 50-75ppm), adding more polymer cause to decrease flocculation efficiency.

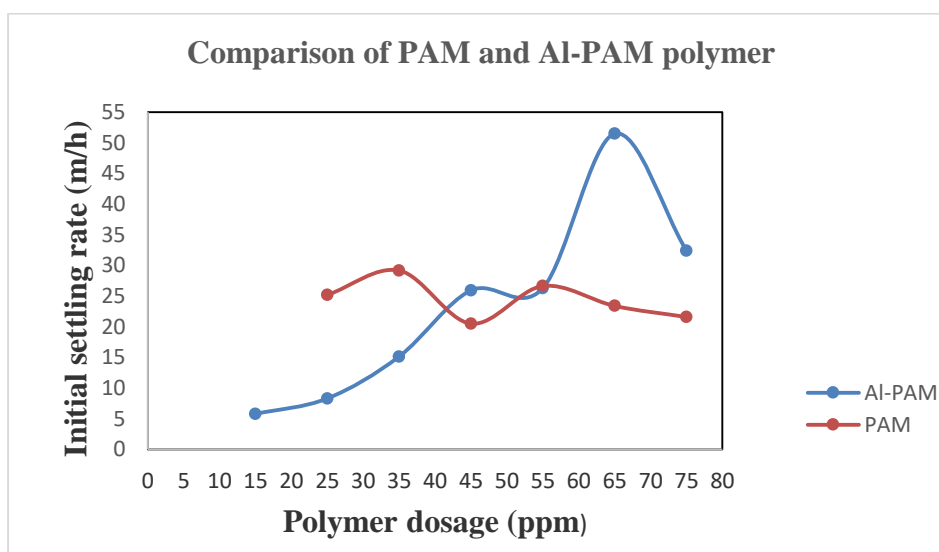


Figure 4.3. Comparison of PAM and Al-PAM on Kaolin

4.3. FLOCCULATION OF SULFIDE MINERAL TAILINGS

The ability of Al-PAM and PAM polymer to flocculate sulfide mineral tailings was examined. The natural pH of slurry was 8.05 and solid content was 20wt%. The composite particle size distribution P_{80} 's was approximately 125 μ m for tailing. Dolomite is the primary gangue mineral at 95% in this sulfide tailing. The ISR has been found in the same as for Kaolin solution. For 500ppm of stock solution of PAM and Al-PAM at highest dosage 75ml, settling rate was 24.48 and 45.72 m/h for both polymers respectively. The settling test results are shown in figure 4.4 and 4.5.

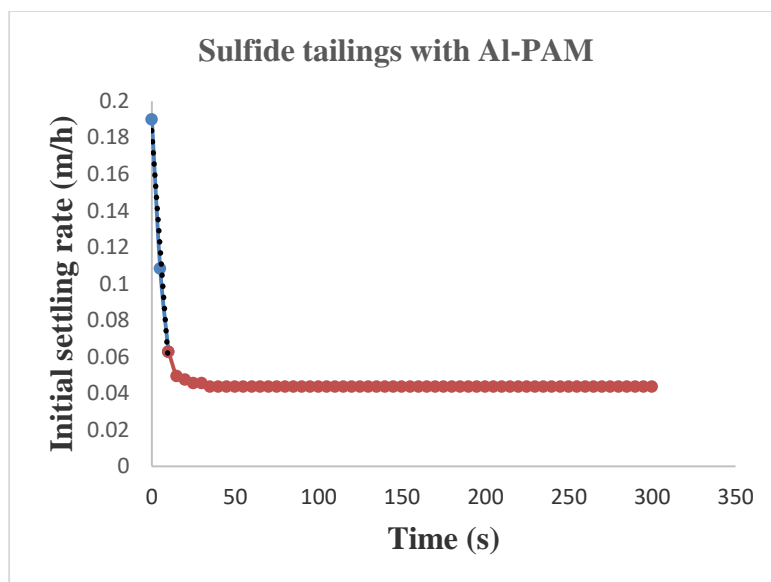


Figure 4.4. Initial settling rate of sulfide tailings with Al-PAM polymer

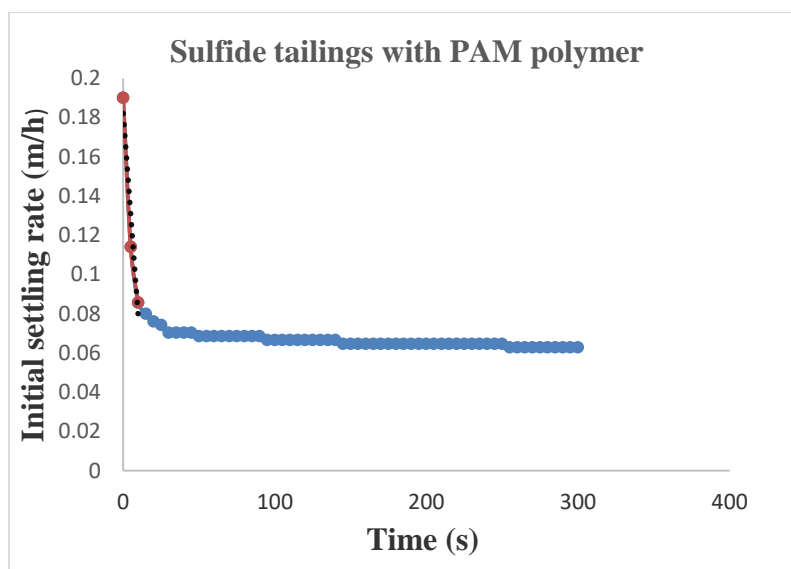


Figure 4.5. Initial settling rate of sulfide tailings with PAM polymer

4.3.1. Al-PAM Flocculation Performance. As it mentioned before, Al-PAM polymer has positive charge due to Al colloid core. Zeta potential of sulfide tailings was negative due to Dolomite particles in tailings. So, adding of Al-PAM polymer with positive charge to the sulfide mineral tailings with negative charge cause an electrostatic attraction

force between polymer molecules and tailings particles. Increasing the dosage of Al-PAM will lead to neutralization of more negatively charged sites on the surface of sulfide tailings particles in suspension due to large amount of positively charge particles.

4.3.2. PAM Flocculation Performance. Polyacrylamide polymer (PAM) which was used for this study was nonionic flocculants which bridging mechanism is primary force in this case. The major driving force for bridging is H-bonding. There is an electrostatic repulsion between particles and polymer molecule which causes long distance interaction between them and also allows the polymer to be extended. The formation of open structures flocs is due to this extension of polymer molecules. Thus, bridging mechanism and aggregation with open structure happens for flocculation process.

4.3.3. Comparison of Flocculation Performance of Al-PAM and PAM Polymer with Sulfide Mineral Tailings. Comparison of sulfide tailings with PAM and Al-PAM at high concentration (500ppm) was shown in figure 4.6. From these graphs, at 15ppm of polymer dosage the ISR for PAM was 9.36 m/h in compare to 23.76 m/h when Al- PAM was used as flocculent. At highest dosage 75ppm, ISR for PAM was 24.48 m/h while it was 45.72 m/h for Al-PAM. It is obvious the ISR is increasing by increasing the polymer dosage for Al-PAM polymer. It can be seen from the graphs that Al-PAM makes better settling rates, specifying that they are capable flocculants for sulfide tailing. Al-PAM improved settling rates at a dosage of 45ppm for 500 concentrations. The results also indicate that Al-PAM even at lower dosage, produces higher ISR with higher concentration. Al-PAM needs lower dosage to reach optimum dosage and higher ISR.

Electrostatic phenomena are the primary mechanism of adsorption of polymers on sulfide mineral tailings. This adsorption depends on surface charge of particles and ionic

and nonionic character of polymer. Therefore, cationic Al-PAM polymer is much more strongly adsorbed on dolomite particles than a nonionic polymer [48]. Larger ISR with Al-PAM, indicates larger aggregation minerals in compare with PAM. According to figure 4.7 increasing polymer dosage up to an optimum (between 35-50ppm) for Al-PAM and (between 45-65) for PAM will increase settling rates, beyond which further addition of the polymers result in decrease efficiency.

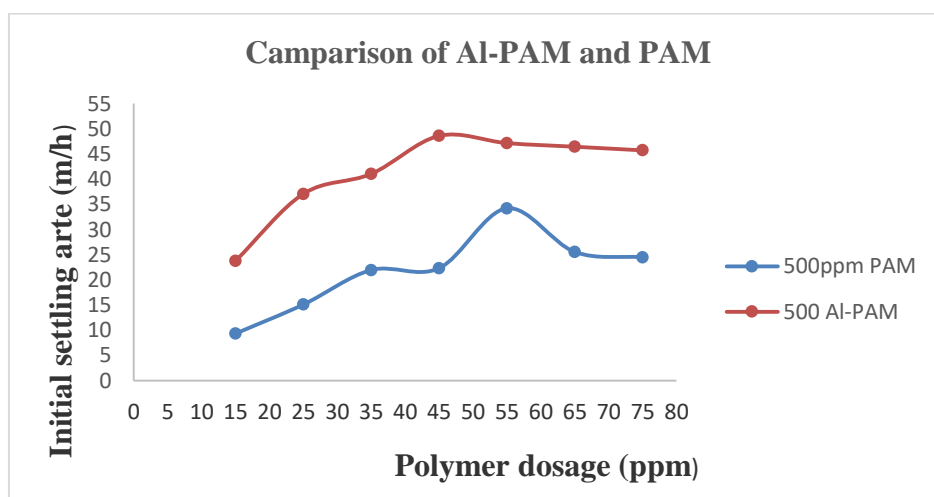


Figure 4.6. Comparison of PAM and Al-PAM performance on Sulfide tailings

4.4. ZETA POTENTIAL MEASUREMENTS FOR SULFIDE TAILINGS

In this study zeta potential measurements were done by using supernatant of the tailings before and after adding polymers. 25 ml of supernatant was injected into capillary cell. The cell was placed in ZetaSizer Nano machine and measures was done. These measurements were performed at natural pH for sulfide mineral tailings which it was 8.05.

The zeta potential value of sulfide tailings at natural pH before adding polymer was -2.84. After adsorption of polymers PAM (optimum dosage 55ppm) and Al-PAM (optimum dosage 45ppm) the value of zeta potential changed to -1.1 and -1.13 respectively. So zeta potential values for sulfide tailings, before and after adding polymer is low.

Consider suspension of sulfide tailings containing small amount polymer (<35 ppm), and the influence of progressive addition of the polymer. The first additions of polymers lead to an increase of electrostatic repulsive force between the particles. By increasing the polymer dosage (>45 ppm), the zeta potential value is almost constant. Therefore, the electrostatic repulsions remain constant, and polymer concentration won't be so effective. So increasing the steric stabilization will improve dispersion. The comparison of zeta potential values for sulfide tailings before and after adding PAM and Al-PAM has shown in figure 4.7.

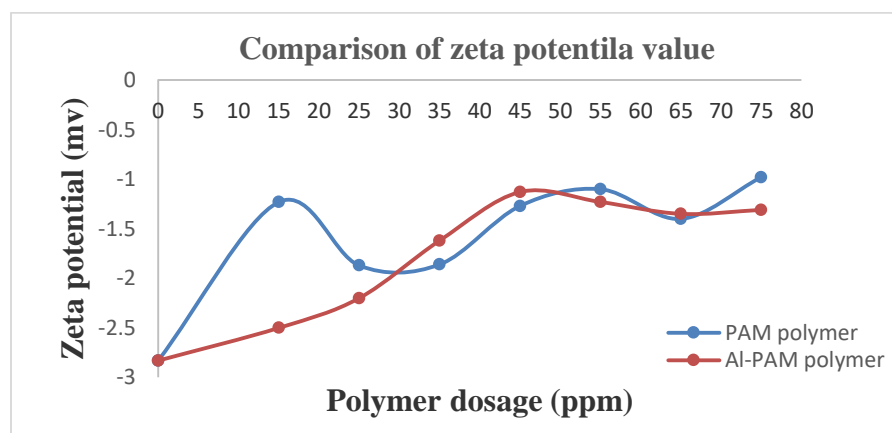


Figure 4.7. Comparison of zeta potential value for sulfide tailings with PAM and Al-PAM

5. CONCLUSION

5.1. PROBLEM REVIEW

Fluid fine tailings which is generated during production is one the main challenges for industry. Mature fine tailings (MFT) are fin tailings which are stored in large settling pond from a stable slurry structure. It would take a long time to consolidate MFT into a solid material. For preventing that, they remain in a fluid state. Environmental effects of MFT (has been discussed in section 1) has raised many concerns regarding long term management of them.

Some technologies for dealing with accumulated MFT such as tailings handling technologies has been improved over the years. In the Thickened Tailings Technology (TT), anionic flocculants in thickener vessels have been applied for creating a densified underflow that is similar to MFT. Mixing coarse sand tailings with MFT is another industrial practice for modifying fluid MFT and it is called Composite Tailings (CT) Technology.

Even with the successes gained with current industrial tailings management practice, the search for alternative methods of dealing with MFT continues.

5.2. SUMMARY OF THESIS WORK

The key to managing/treating tailings is promoting accelerated fine solids settling in tailings pond.

This thesis explored this concept by conducting flocculation studies on both Kaolin suspension (i.e. model tailing) and sulfide mineral tailings. The performance of two polymers PAM and Al-PAM as flocculants on treating MFT was investigated. The results of the tests have been presented and discussed in earlier sections of this thesis. In this study,

Al-PAM has shown better results in flocculation performance on MFT in compare with PAM. It will be interesting to find out other derivatives of polyacrylamides that could perform much better. More research in this field, will bring more success and accelerate tailings dewatering industry. This could in turn result in significant improvements such as elimination of new tailings ponds, more rapid recycle of process water, less fresh water draw creation of a more readily reclaimable tailings deposit. These improvements are crucial to tailings management.

5.3. RECOMMENDATIONS FOR FUTURE WORK

Following are some recommendations for future research and also for understanding the mechanism of polymer assisted CT process:

1. Study the effect of different molecular weight, and charge density of polymer settling behavior,
2. Study the effect of residual polymer in tailings water,
3. Measure the interaction forces between clays and sand with polymer at various dosages.

BIBLIOGRAPHY

- [1] Ritcey, Gordon M. "Tailings management: problems and solutions in the mining industry." (1989).
- [2] Treatment, BREF Surface. "Draft Reference Document on Best Available Technique for the Surface treatment of Metals and Plastics." European Commission, Directorate JRC, Draft April (2004).
- [3] Peachey, Bruce, and P. Eng. "Strategic Needs for Energy Related Water Use Technologies: Water and the EnergyINet." *New Paradigm Engineering* (2005): 34-36.
- [4] Espana, Javier Sánchez, et al. "Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications." *Applied geochemistry* 20.7 (2005): 1320-1356.
- [5] Kesimal, Ayhan, et al. "Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill." *Materials Letters* 59.28 (2005): 3703-3709.
- [6] Ryu, Changkook, et al. "Pelletised fuel production from coal tailings and spent mushroom compost—Part I: Identification of pelletisation parameters." *Fuel Processing Technology* 89.3 (2008): 269-275.
- [7] Balkau, F. "Environmental issues in tailings management—Case studies on tailings management." *International Council on Metals and the Environment (ICME), United Nations Environment Programme (UNEP)* (1998): 11.
- [8] Kasongo, Tshitende, et al. "Effect of clays and calcium ions on bitumen extraction from Athabasca oil sands using flotation." *The Canadian Journal of Chemical Engineering* 78.4 (2000): 674-681.
- [9] Caughill, David Leslie, N. R. Morgenstern, and J. D. Scott. "Geotechnics of nonsegregating oil sand tailings." *Canadian Geotechnical Journal* 30.5 (1993): 801-811.
- [10] MacKinnon, M. D., et al. "Water quality issues associated with composite tailings (CT) technology for managing oil sands tailings." *International Journal of Surface Mining, Reclamation and Environment* 15.4 (2001): 235-256.
- [11] Yuan, S., and R. Lahaie. "Thickened tailings (paste) technology and its applicability in oil sand tailings management." *Proceedings of the 13th International Conference on Tailings and Mine Waste, Banff, Alta. 2009.* BGC Engineering 2010.

- [12] Cymerman, G., et al. "Thickening and disposal of fine tails from oil sand processing." The 3rd UBC-McGill Int. Sym. Fund. of Mineral Processing (CIM), Quebec City QC (1999).
- [13] Alamgir, Aurangzeb, et al. "Al-PAM assisted filtration system for abatement of mature fine tailings." *Chemical engineering science* 80 (2012): 91-99.
- [14] <http://www.pastethickassoc.com/?view=tailingsstacking>. May 2016.
- [15] Tripathy, Tridib, and Bhudeb Ranjan De. "Flocculation: a new way to treat the waste water." (2006).
- [16] Glawdel, Tom, and Carolyn Ren. "Zeta Potential Measurement." *Encyclopedia of Microfluidics and Nanofluidics*. Springer US, 2008. 2199-2207.
- [17] Incorporation, Zeta-Meter. "Zeta Potential: A Complete Course in 5 Minutes." Zeta-Meter, Inc 765 (2005).
- [18] Henderson, Douglas. "Recent progress in the theory of the electric double layer." *Progress in Surface Science* 13.3 (1983): 197-224.
- [19] Masliyah, Jacob H., and Subir Bhattacharjee. *Electrokinetic and colloid transport phenomena*. John Wiley & Sons, 2006. Section 1,5.
- [20] Guo, Lina. *Understanding Al-PAM assisted oil sands tailings treatment*. Diss. University of Alberta, 2012.
- [21] Hogg, R. "Flocculation and dewatering." *International Journal of Mineral Processing* 58.1 (2000): 223-236.
- [22] Wang, Chen, et al. "Current state of fine mineral tailings treatment: A critical review on theory and practice." *Minerals Engineering* 58 (2014): 113-131.
- [23] Nasser, M. S., and A. E. James. "The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions." *Separation and purification technology* 52.2 (2006): 241-252.
- [24] Lyklema, Johannes. *Fundamentals of interface and colloid science: soft colloids*. Vol. 5. Academic press, 2005. Section 2.
- [25] Sworska, A., J. S. Laskowski, and G. Cymerman. "Flocculation of the Syncrude fine tailings: Part I. Effect of pH, polymer dosage and Mg²⁺ and Ca²⁺ cations." *International journal of mineral processing* 60.2 (2000): 143-152.
- [26] Adachi, Yasuhisa, Azusa Kobayashi, and Motoyoshi Kobayashi. "Structure of colloidal flocs in relation to the dynamic properties of unstable suspension." *International Journal of Polymer Science* 2012 (2012).

- [27] Bolto, Brian, and John Gregory. "Organic polyelectrolytes in water treatment." *Water research* 41.11 (2007): 2301-2324.
- [28] Biggs, Simon, Michael Habgood, and Graeme J. Jameson. "Aggregate structures formed via a bridging flocculation mechanism." *Chemical Engineering Journal* 80.1 (2000): 13-22.
- [29] Renault, François, et al. "Chitosan for coagulation/flocculation processes—an eco-friendly approach." *European Polymer Journal* 45.5 (2009): 1337-1348.
- [30] Bratby, John. "Coagulation and flocculation." England: Uplands (1980).
- [31] Moody, G. "The use of polyacrylamides in mineral processing." *Minerals Engineering* 5.3 (1992): 479-492.
- [32] Menter, Paul. "Acrylamide Polymerization—A Practical Approach." Bio-Rad Tech Note 1156 (2000).
- [33] Gregory, John. "Polymer adsorption and flocculation in sheared suspensions." *Colloids and Surfaces* 31 (1988): 231-253.
- [34] Hogg, R. "Agglomeration models for process design and control." *Powder technology* 69.1 (1992): 69-76.
- [35] Mark, James E., ed. *Physical properties of polymers handbook*. New York: AIP Press, 1996.
- [36] Moudgil, Brij M., Sanjay Behl, and T. S. Prakash. "Effect of particle size in flocculation." *Journal of colloid and interface science* 158.2 (1993): 511-512.
- [37] Besra, L., D. K. Sengupta, and S. K. Roy. "Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions." *International Journal of Mineral Processing* 59.2 (2000): 89-112.
- [38] Sabah, E., and I. Cengiz. "An evaluation procedure for flocculation of coal preparation plant tailings." *Water research* 38.6 (2004): 1542-1549.
- [39] Sabah, E., and Z. E. Erkan. "Interaction mechanism of flocculants with coal waste slurry." *Fuel* 85.3 (2006): 350-359.
- [40] Alamgir, Aurangzeb, et al. "Al-PAM assisted filtration system for abatement of mature fine tailings." *Chemical Engineering Science* 80 (2012): 91-99.
- [41] Yukselen, Yeliz, and Abidin Kaya. "Zeta potential of kaolinite in the presence of alkali, alkaline earth and hydrolyzable metal ions." *Water, Air, and Soil Pollution* 145.1-4 (2003): 155-168.

- [42] Yang, W. Y., J. W. Qian, and Z. Q. Shen. "A novel flocculant of Al (OH) 3–polyacrylamide ionic hybrid." *Journal of colloid and interface science* 273.2 (2004): 400-405.
- [43] Sun, Wei, et al. "Study of Al (OH) 3– Polyacrylamide-Induced Pelleting Flocculation by Single Molecule Force Spectroscopy." *Langmuir* 24.24 (2008): 14015-14021.
- [44] Alagha, Lana, et al. "Adsorption kinetics of a novel organic–inorganic hybrid polymer on silica and alumina studied by quartz crystal microbalance." *The Journal of Physical Chemistry C* 115.31 (2011): 15390-15402.
- [45] Pearse, M. J., and J. Barnett. "Chemical treatments for thickening and filtration." *Filtration and Separation* 17.5 (1980): 465-468.
- [46] Nasser, M. S., and A. E. James. "The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions." *Separation and purification technology* 52.2 (2006): 241-252.
- [47] Mporfu, Patience, Jonas Addai-Mensah, and John Ralston. "Investigation of the effect of polymer structure type on flocculation, rheology and dewatering behaviour of kaolinite dispersions." *International Journal of Mineral Processing* 71.1 (2003): 247-268.
- [48] Van Lierde, A. "Flocculation and dispersion of dolomite by acrylate polymers." *International Journal of Mineral Processing* 1.1 (1974): 81-100.

VITA

Simin Khatibi is from Tehran, Iran. He received her B.S degree in Physics in spring 2006 from Razi University of Science and Technology. She received her M.Sc. in Physics in spring 2013 form Missouri University of Science and Technology. She started her second master in Mining Engineering in Fall 2014 in Missouri University of Science and Technology where she held position of research assistant while working on solid liquid separation project. In December 2016, Simin received her Master of Science degree in Mining Engineering from Missouri University of Science and Technology.