Fall 2015

Studies on the role of organic-inorganic hybrid polyacrylamides in fine coal flotation

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STUDIES ON THE ROLE OF ORGANIC-INORGANIC HYBRID

POLYACRYLAMIDES IN FINE COAL FLOTATION

By

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A THESIS

Presented to the faculty of Graduate school of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In partial fulfilment of the requirements of the Degree

Masters of Science in Mining Engineering

2015

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ABSTRACT

The current study investigated the effect of novel organic/inorganic (hybrid) polyacrylamide polymer as ash (slimes) depressant in fine coal flotation for the possibility to enhance the combustible recovery and ash rejection. Raw coal samples contain about 25% of ash-forming minerals were crushed, grinded to -75um and floated in the presence of in-house synthesized hybrid Polyacrylamide ($Al(OH)_3$-PAM or Al-PAM) at different operational parameters. Denver flotation cell with a 5-Liters capacity was used and the parameters investigated include: Al-PAM dosage, Al-PAM conditioning time, dual use of Al-PAM and a dispersant, impeller rotation speed and pulp's pH. For comparison purposes, commercially available polyacrylamide polymers (PAMs) were also tested.

Results show a significant improvement in both combustible recovery and ash rejection at 0.25 ppm Al-PAM dosage. Further improvement in ash reduction was achieved when flotation was performed using dual dispersant/Al-PAM system. At natural pH, the maximum combustible recovery and ash rejection were obtained at Al-PAM dosage of 0.25 ppm, dispersant dosage of 0.8 ppm, conditioning time of 6 minutes and impeller speed of 1800 rpm. Zeta potential values of both raw coal and concentrates samples showed a large shift to more positive zeta potential values after flotation which indicates a significant depression of ash-forming minerals (slimes) when Al-PAM polymer was used.

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1. INTRODUCTION

1.1. BACKGROUND OF RESEARCH PROBLEM

Coal is defined as a combustible, sedimentary rock composed mainly of carbon, hydrogen and oxygen (World Coal Association, 2014). Coal started to form 400 million years ago from the remains of prehistoric dead plants and animals, which were buried between other rock strata and altered by the combined effects of pressure and heat to form coal seams. Kita et al., reported that coal is the most abundant and inexpensive fossil fuel available on earth and is found throughout the world. According the World Energy Council, it has been estimated that there are over 891,530 billion tons of proven recoverable coal reserves worldwide. (World Energy Council, 2013). The United States is ranked among the top five countries in the global coal production and has the largest coal reserves in the world, followed by Russia, China and India (as shown in Figure 1.1). According to EIA international energy statistics, the United States has about 237, 295 million tons of coal reserves, which is about 28% of the world's total reserve.

Coal has many important uses in human life, and it has been used since the 18th century as one of the main energy resources for humans (Jamil et al., 2013). Coal is used worldwide in many day-to-day goods and services such as electrical power generation, steel production, cement manufacturing, and in liquid fuels. There are two main types of coal, which are used for different purposes. Thermal coal, also known as steam coal, is mainly used in electricity generation while metallurgical coal, known as coking coal, is used for steal production and alumina refineries. Currently coal accounts for 42% of global electricity fuel, and this is set to rise to 44% by 2030. Around 70% of steel

produced globally relies on coal (Kumar & Kumar, 2015). In the United States about 80% of the coal produced is used in electrical power generation.
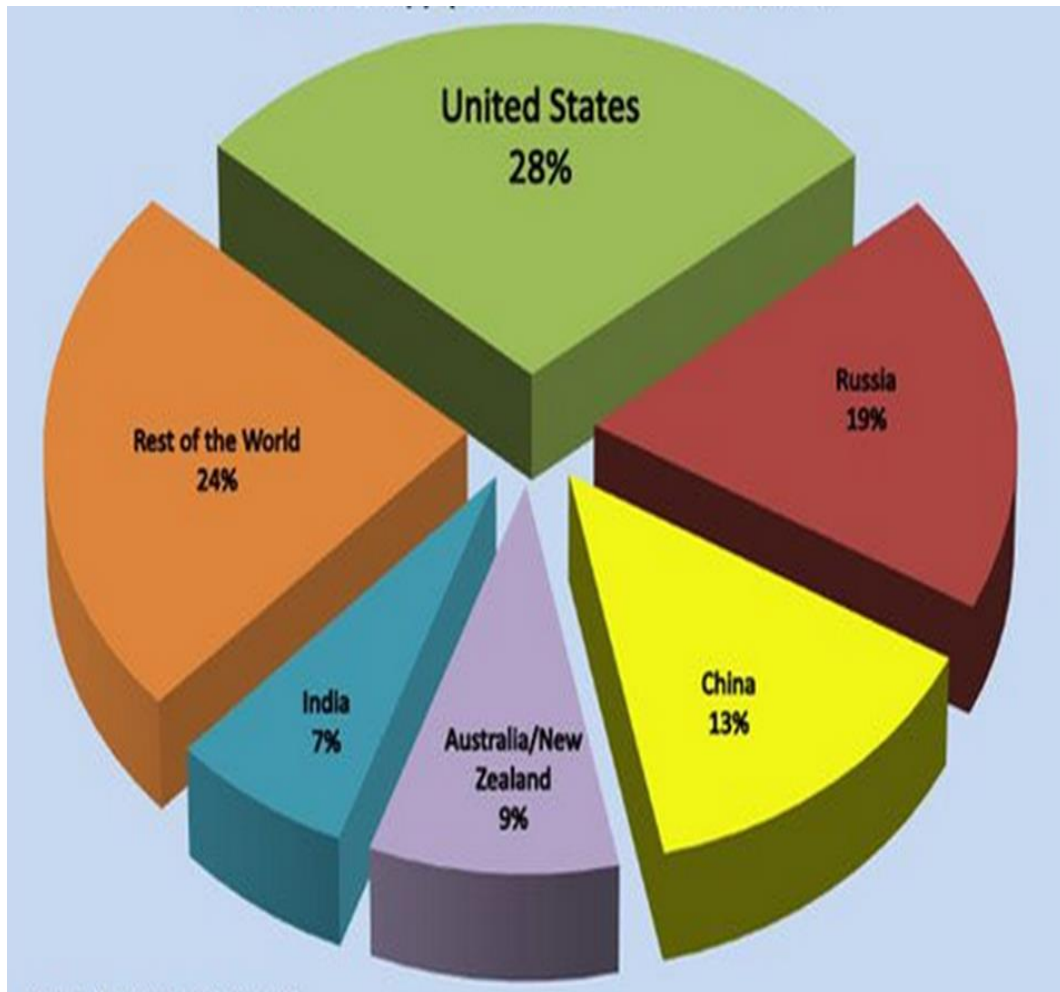
Figure 1.1. Global share of recoverable coal reserves. (Glover, 2011)

The coal run of mine (ROM) must be cleaned and sized in order to improve the quality of coal and make a consistent product that is suitable for a specific purpose. The cleaning stage involves removing extraneous, non-combustible material from the ROM.

It is well known that removing deleterious materials from the raw coal should increase the heating value of the coal. Run of mine coal varies in sizes. Hence, different cleaning devices are used for each size fraction. There are four different size classifications in coal preparation: coarse sized, intermediate sized, fine sized, and ultrafine sized. Coal preparation utilizes different units of operations that upgrade the quality of the coal by regulating the size and removal of the unwanted material. These operations include sizing, cleaning and dewatering. A typical coal cleaning circuitry is displayed in Figure 1.2. Coarse and intermediate sized fractions are cleaned by gravity based separators, while fine and ultrafine size are mainly cleaned by froth flotation. In the United States, it has been estimated that about $10 - 15$ million tons of raw fine coal are beneficiated by the froth flotation method.(Taylor, 1981)

1.2. PROBLEM STATEMENT

Coal currently provides about 40% of the world's electricity need and in the in the united states it provides about 39% of the electricity (World Coal Association, 2012). With an increasing world population and recent power shortages, the global electricity demand would also increase as more people would get access to basic electricity, especially in developing countries (International Energy Agency, 2010). The EIA reported in its annual medium term coal market report that the global coal demand will grow at an average rate of 2.3% per year through 2018 (as shown in Figure 1.3.). Due to this increase in the global coal demand and consumption, operations in coal mining and coal preparation processes are under constant expansion, employing highly mechanized machinery to cope with the increasing global coal demands. This mechanization has

increased the quantity of raw fine coal particles produced that contain high amount of ash forming minerals (slime coating). According to Ministry of Energy, Mines and Petroleum Resources the amount of fines generated from mineable seams is up to 60% of the total coal that is mined.

In the past raw fine coal particles generated from the mine were generally discarded mainly because vast amount of coal reserves was available especially those containing high-grade deposits. However, in recent years, there has been a remarkable diminution in high-grade coal reserves. With the intentions to cope with the rapid increase in global coal demand, more and more low grade, difficult to float coal is being exploited. Processing low grade coal deposits requires the comminution of coal to micron and sub-microns size in order to liberate the coal from the mineral matter.

The grinding of low rank coal has resulted in the production of large quantities of fine coal particles which has gained an increasing level of importance in coal preparation and mineral processing industry. The large amount of coal fines that have been generated from both mining and beneficiation processes has been reported as a chronic problem to both fine coal preparation and utilization as these fines contain a high amount of ash-forming minerals. Ash forming minerals are defined as impurities that do not burn during combustion of coal. This include; clay minerals, quartz, oxides, carbonates, sulphides and phosphate. The presence of high ash forming minerals in coal adversely affects the utilization of coal. High ash is said to increase the handling cost of coal. High ash content also affect coal's combustion and reduces boiler efficiencies causing clinkering and slagging.
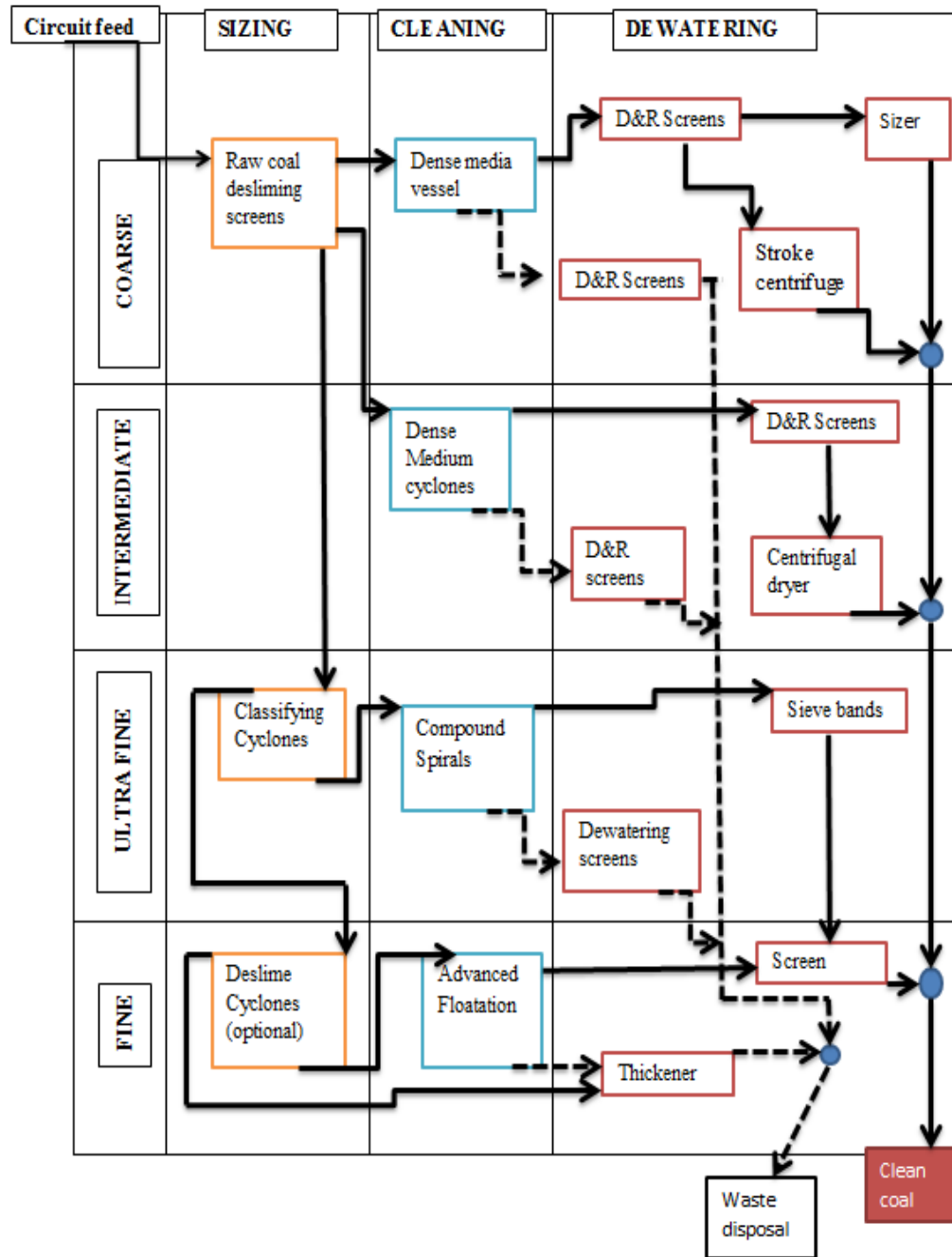
Figure 1.2. Typical coal cleaning circuitry

It is also a common perception that fine coal impoundments are environmental hazards,

leaching toxins into rivers and streams. This perception has resulted in a greater emphasis

on cleaning and recovering fine coal. In addition, improving coal prices and technology have also made the recovery of coal fines discarded by previous generation more viable today. Klimpel and Hansen et al., reported that discarded coal fines represent a notable economic value.(Klimpel & Hansen, 1987)
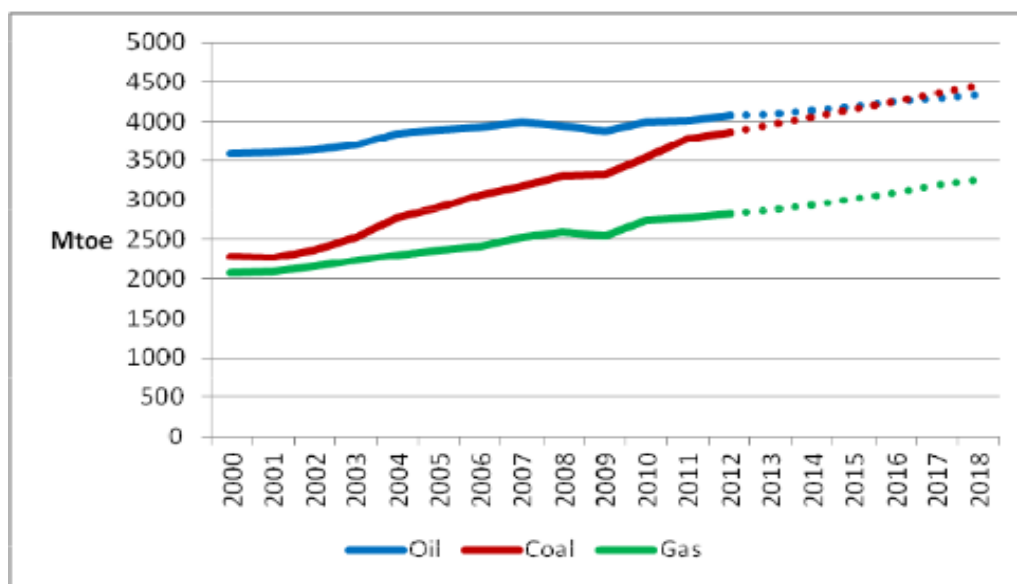
Figure 1.3. Global energy demands from fossil fuels (EIA, 2013)

In the past, conventional froth flotation was the most effective method used to clean and recover discarded coal fines. The process utilizes the differences in surface hydrophobicity properties between the coal and the inorganic matter. However, the process has always been challenging, problematic and costly due to the presence of fine slime coating in the flotation circuit. In coal preparation slimes are defined as any particle less than 5μm. Mishra et al,.reported that slimes present during fine coal cleaning are

mainly generated by the degradation of particles composing of the feed, and particularly by the disintegration of clay water.(Mishra, 1978) Coal seams are said to include bands of clay minerals, which are associated with slime coating characteristics. Due to the modern full seam mechanized mining, these bands of clay minerals remain in the feed to a cleaning process. Aplan et al., have reported that the major constituents of ash-forming minerals in U.S.A coal are clay minerals such as kaolinite, montmorillonite and illite. The presence of ash- forming minerals (slimes) in fine coal flotation has always been considered undesirable. Conventional froth flotation for fine coal cleaning suffers mainly from three major problems:

o Low recovery of ultrafine coal particles due to slime coating by ash-forming minerals. Slime coating on both valuable ore and air bubbles inhibit bubble-particle attachment and has been proposed to explain the observed reduction in flotation recovery especially when fine grinding is required.

o The lack of selectivity, which results in the flotation of middlings and entrainment of mineral fines in the froth (Polat et al., 2003). In this case mineral matter may be degraded to extremely fine or colloidal sizes thereby creating difficulty in parts of the water clarification process such as flotation.

o The presence of slimes in the flotation circuit also leads to high consumption of reagents due to their increase in the solid/liquid interfacial area, colloidal size and high ion exchange capacity. High consumption of reagents due to presence of slimes coating cause a problem to the floatation circuit because it reduces the availability of reagents to targeted minerals (coal particles).

Coal research has been largely devoted to developing efficient coal cleaning technologies to produce clean coal through the depression of ash forming mineral matter (slimes) in coal flotation circuits. Using novel ash depressants will help contribute to existing technologies regarding ash depression in coal flotation.

1.3. OBJECTIVES

The primary objectives of this study were to improve the efficiency of a conventional coal froth flotation process in order to produce clean coal through the depression of ash forming mineral matter (slimes) in coal flotation circuits and to increase the overall combustible coal recovery. In order to achieve these objectives, a novel organic-inorganic (hybrid) polyacrylamide polymer (Al-PAM) was proposed to serve as an ash-depressant. The polymer was added to the flotation pulp and anticipated to selectively adsorb at the surface of ash particles and flocculate them which will result in slime depression

1.4. PROPOSED APPROACH

The proposed hypothesis of ash depression by a novel organic-inorganic (hybrid) polyacrylamide polymer, Al $(OH)_3$-PAM is illustrated in Figure 4. The polymer system used in this work contains inorganic nanoparticles Al $(OH)_3$ dosed within the polymer structure during the polymerization process. Integrating the $Al(OH)_3$ as a functional group into the PAM molecular structure is anticipated to improve the adsorption of the polymer on fine ash-forming mineral particles exist in flotation pulp. These fine and

ultrafine mineral particles form a layer of slimes at the surface of coal thus decreasing its hydrophobicity. $Al(OH)_3$ adsorb on the surface of slimes by electrostatic attractive forces due to the cationic nature of the polymer. The adsorption of $Al(OH)_3$-PAM leads to the reduction of electrostatic repulsion among the mineral particles in the flotation pulp by partial or complete charge neutralization while the arms (branches) of PAM help to bridge the particles and flocculate them thus depress their flotation. This depression results in decreasing the total amount of ash in froth (better froth quality). In the meantime, the surface of the coal particles is free of slimes, which increase the particle's hydrophobicity and consequent recovery.

To further investigate the polymer's adsorption on the fine ash-forming mineral (slime coating), electrokinetic (zeta potential) measurements of coal/water slurries were conducted. Since froth flotation is a surface dependent process, it is of paramount importance to understand the interfacial phenomena (zeta potential) in order to improve the process. It is well explained that the ash forming minerals (slime coating) are electrostatically attracted to the surface of the coal particles and the attachment is heavily dependent on the magnitude and sign of the zeta potentials of the coal particles and the fines. Therefore, zeta potential measurements may provide information on the coal surface properties and the interactions among coal particles in the suspension. The findings will be used/ related to the existing unit of operation of froth flotation.

Zeta potential measurement of coal slurries before and after flotation and different pH were conducted to achieve this. In addition the surface properties of the coal particles and the ash forming minerals will be controlled by changing the dosage of $Al(OH)_3$-PAM and the pH of the suspension. It is explained that pH is one of the most important factors

in controlling slime coating due to the electrostatic attraction between the ash forming minerals and coal particles. For this reason, froth flotation experiments and zeta potential measurements were carried out at different pH's.

1.5. STACTURE OF THESIS

This thesis is organized into 6 chapters. Chapter 1 provides the introduction to this study. Chapter 2 contains the theoretical considerations and a comprehensive literature review relevant to the existing body of knowledge in the subject of polymeric depressants in fine coal flotation. Chapter 3 comprises the extensive experimental work and the theoretical studies. The experimental setup, measurement techniques and procedures of the study are also described in this chapter. Chapter 4 presents the results and discussion, while Chapter 5 discusses the main conclusions of the study and recommendation.
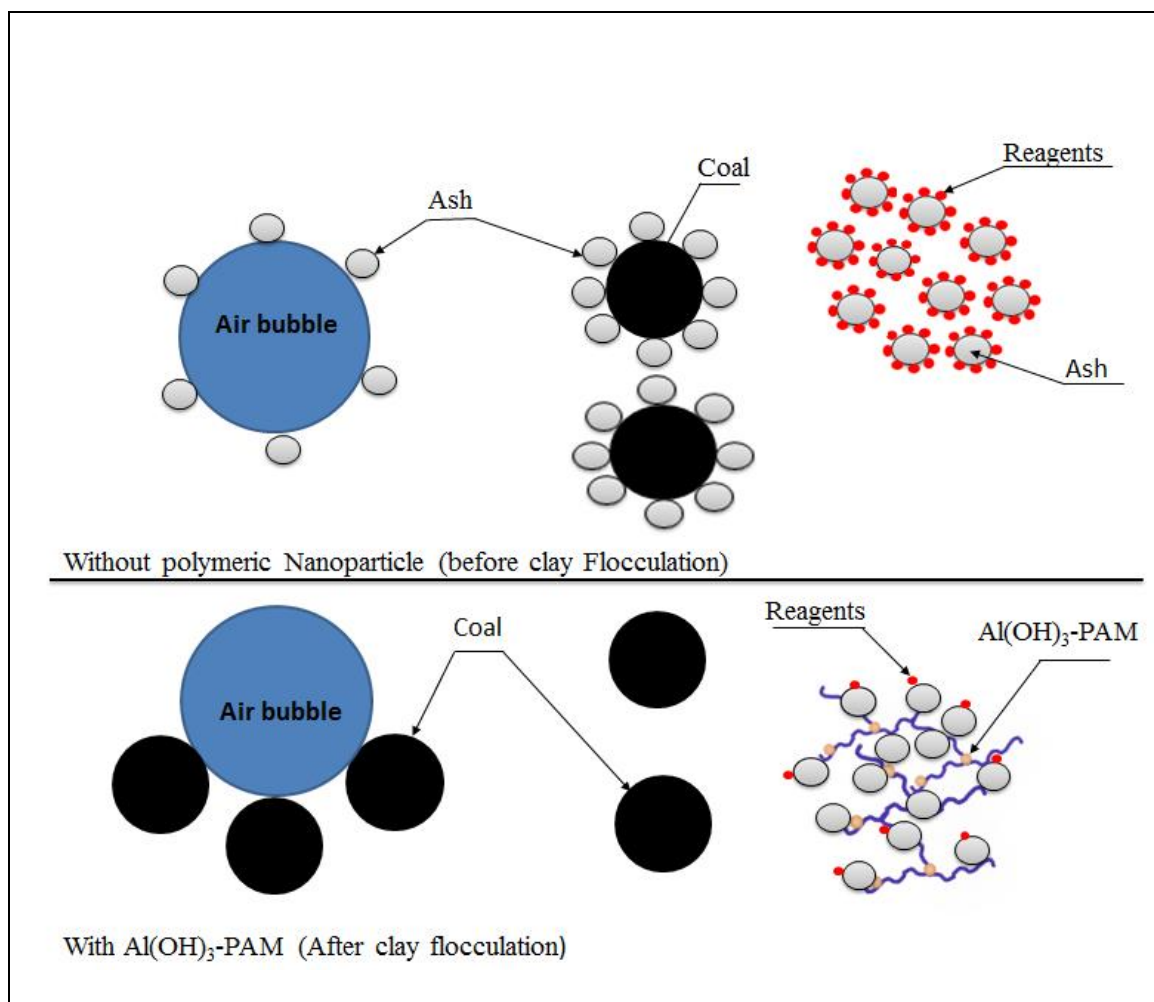
Figure 1.4. Proposed hypothesis on Al(OH)3-PAM role in fine coal flotation

2. LITERETURE REVIEW

2.1. HISTORY OF COAL FROTH FLOTATION

Fuerstanau et al., 2007 defined Froth flotation as a physiochemical process used to separate finely ground particles from their associate gangue by means of surface hydrophobicity (Fuerstanau, Jameson, & Yoon, 2007). To facilitate this process air bubbles are introduced into the pulp to selectively attach to the surfaces of hydrophobic particles and carry them to the froth while the inorganic minerals, which are hydrophilic stay wetted in the liquid. The hydrophilic particles are later removed as the tailings. According to (Frank, 1933), basic coal froth flotation technology was derived from its ore flotation sibling. The coal froth flotation technology was developed in 1910 by an Australian plant that used air for bubble generation. In the United States the first commercial coal flotation plant was built in 1911 by Superior Copper Corporation. By 1915 the first laboratory studies on coal froth flotation were established (Ralston and Wichmann, 1922). The increasing mechanization of coal mining machinery has led to a decrease in the size and grade of products from the mine and to an increasing need for coal cleaning to improve the grade before sale. With an increasing proportion of fines in the product, froth flotation has assumed a greater importance as a cleaning process for coal.

2.2. COAL FROTH FLOTATION FUNDERMENTALS

The fundamentals of the froth flotation process of coal are based on the selectivity of valuable coal particles being attached to air and recovered at the froth zone(Dube,

2012). The valuable coal particles attached to air bubbles are referred as hydrophobic while particle that remain the pulp are hydrophilic. According to Oss and Giese, (1995) the boundary between hydrophobic and hydrophilic particles in the pulp occurs when the difference between the apolar attraction and the polar repulsion between coal particles immersed in water is equal to the cohesive polar attraction between the water molecules. Thus, under these conditions the interfacial free energy of interaction between coal particles immersed in water is exactly zero. Pawlik, (2009) concluded that the selectivity process of valuable coal particles is dependent on the relative strength of the particle-water bubble and particle water interactions. The interaction of the coal surface with water, sometimes referred to as coal wettability, is mainly important in the coal froth flotation process. The schematic of froth flotation principle is shown in Figure 2.1.

The coal particle's attachment to air bubbles is mainly determined by interfacial energies between three solid-water, water-gas and solid-gas interfaces. This is applied by Young's equation

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \tag{1}$$

Where γ_{sg}, γ_{sl}, and γ_{lg} are the interfacial tensions of solid-gas, solid-liquid and liquid-gas interfaces respectively and theta is the contact angle. Another equation (2), describing the relative adhesion of the liquid phase itself as compared to the solid phase is pointed out by Adam. The equation is extracted from Young's equation.

$$W_A = \gamma_l (1 + \cos\theta) \tag{2}$$

Where, W_A is the work of adhesion of the liquid phase to the solid phase. Another work done by Dupre showed that work of adhesion for two immiscible liquids in contact is represented by Equation (3).
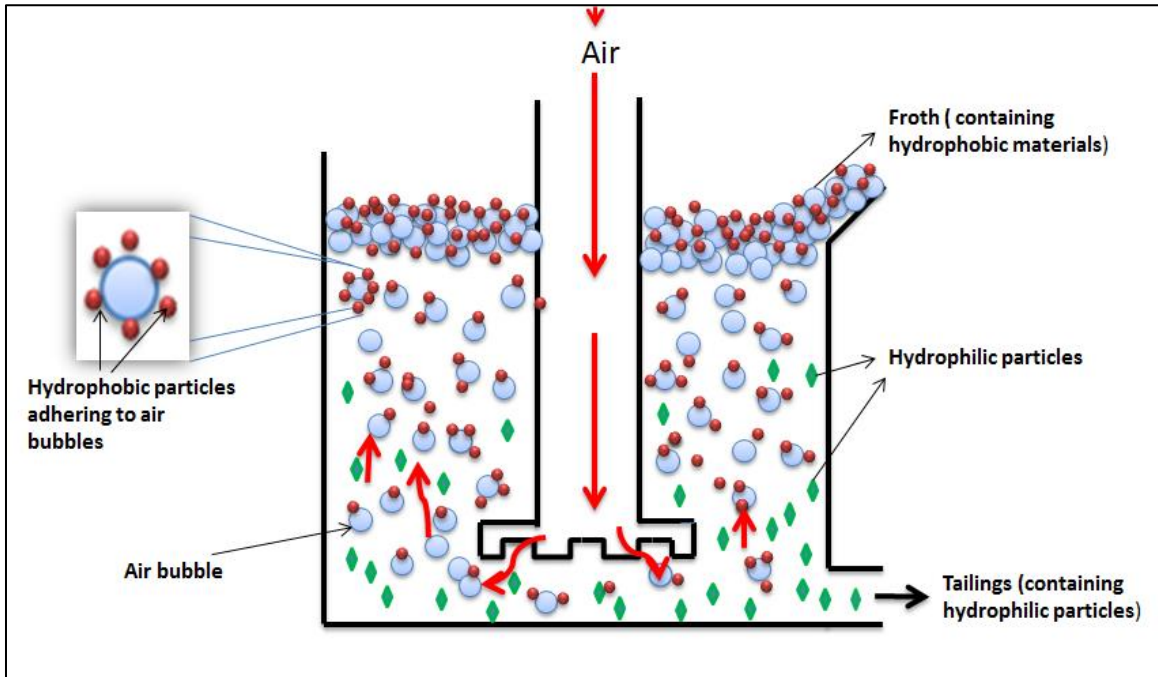
Figure 2.1. Schematics of froth flotation principle

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \tag{3}$$

Where a and b represent the two condensed phases. The work of adhesion from this equation can be determined by measuring the surface tensions of a and b and the interfacial tensions at the interface ab. In the case where a or b is a solid, surface tensions cannot be measured directly. However W_{AB} can then be determined by substituting Young's equation into equation (4) which is the same as Equation (3)

$$W_{AB} = \gamma_{so} + \gamma_{lv} - \gamma_{sl} \tag{4}$$

Where γ_{S0} denotes the solid placed in a vacuum. Combining 1 and 4 results the following relationship known as Young and Dupré equations (5) which is shown below.

$$W_{AB} = \gamma_{so} - \gamma_{sv} + \gamma_{lv}(1 + \cos\theta) \tag{5}$$

Fowkes (1964) assumed that the difference between γ_{S0} and γ_{SV} is equal to zero when water is used as a liquid in solid surfaces. Therefore, the Young and Dupré equations may simply be written as

$$W_{AB} = \gamma_l (1 + \cos\theta) \tag{6}$$

Equation (6) shows that the contact angle (theta) is function of the surface tension of the liquid. The contact angle is measured through the liquid, where the liquid/ vapor interface comes into contact with a solid surface. Figure 2.2 depicts the schematic representation of the three phase contact between liquid, vapor and solid phases. If the contact angle is very large, it will result in very strong bubble attachments, if angle is small, it will results in a lesser bubble attachment. For effective froth flotation, the coantact angle should be close to 90^0.

2.3. COAL FLOTATON PARAMETERS

Coal's froth flotation process involves three dispersed phases that form the flotation pulp: coal particles, oil droplets and air bubbles. During the froth flotation process, these phases interact with water as a median through various sub-processes. Hence, the sub-processes are affected by several parameters that also affect the overall froth flotation performance. According to Polat, Polat and Chander (2003) these parameters are classified into four classes as shown in Figure 2.3. These include material, chemical, operational and equipment parameters.
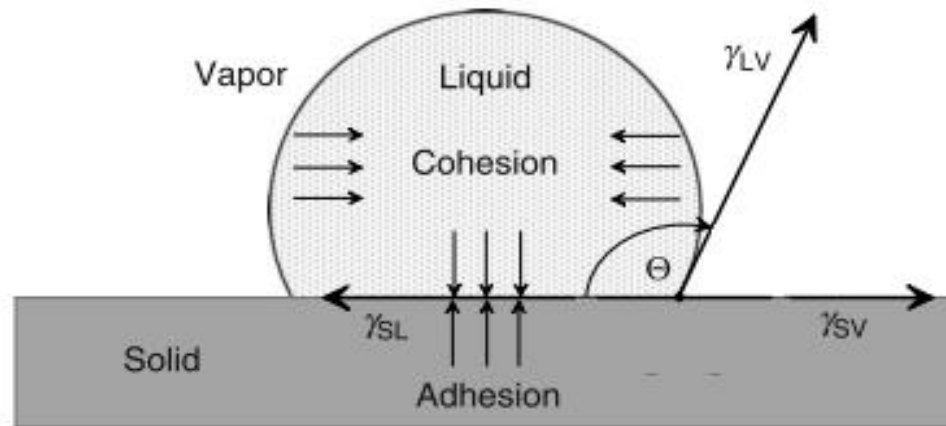
Figure 2.2. Schematic representation of the three phase contact between liquid, vapor and solid phases

2.4. FLOTATION REAGENTS

Reagents are the most important part of the fine coal froth flotation process since much attention; time and energy are spent on the selection of reagents when developing an effective flotation treatment process. In commercial plants, the control of reagent additions is the most important part of the flotation strategy (Ores, 2007). Fine coals that have been considered difficult to float can be recovered with the use of the proper reagent. Coal froth flotation is dependent on the surface properties of coal particles and these surfaces properties are controlled by various regulating chemical agents (Components et al., 1995).

MATERIAL PARAMETERS	CHEMICAL PARAMETERS
- Particle size - oxidation - minerology	-Reagent type - Reasgent concentration - Mineral(s)solution chemistry
OPERATIONAL PARAMETERS - Impeller speed - aeration - Conditioning time -Pulp level - pH -Froth removal time	EQUIPMENT PARAMETERS - Type of cell - Cell design
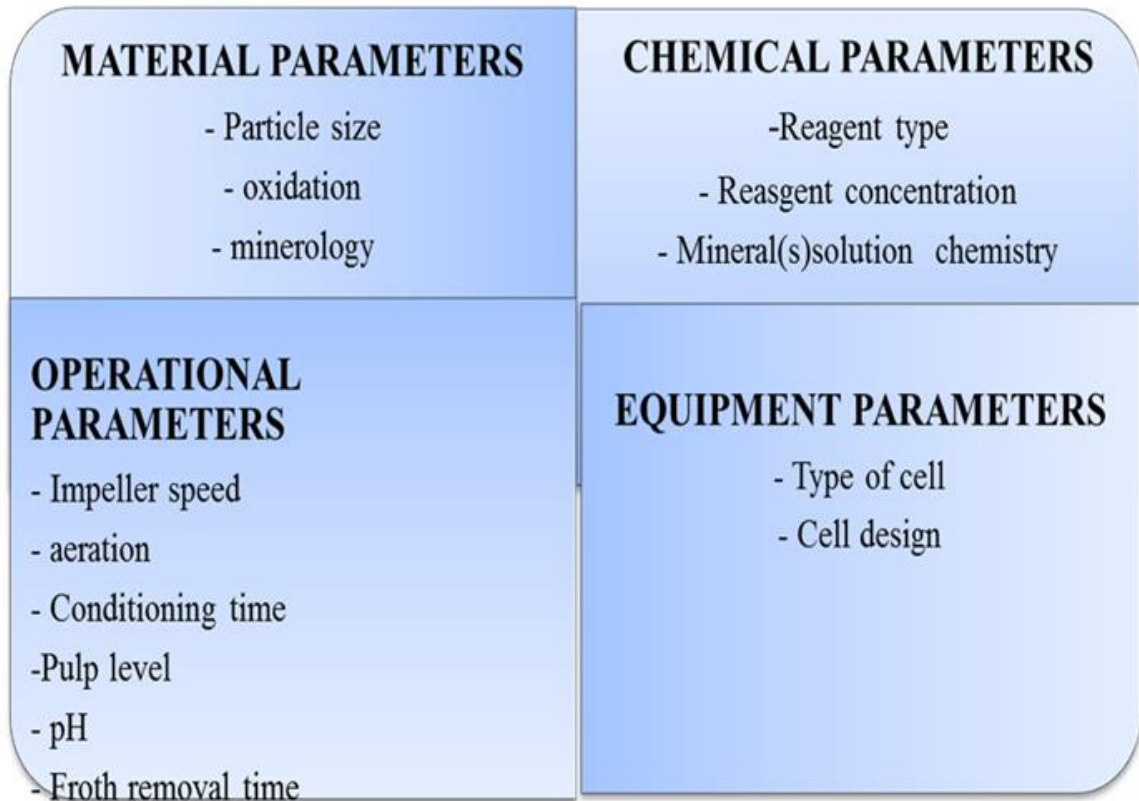
Figure 2.3. Various flotation parameters

These chemical reagents include frothers, Collectors, Activators, Depressants, pH controller. The use of reagents both promoters, depressants and emulsifies can lead to improvement of the fine coal recovery.

2.4.1. Collectors. Collectors are a fairly large group of organic chemical compounds, that differ in chemical composition and function (Wheeler & Keys, 1940). The main purpose of collectors in coal froth flotation is to selectively concentrate on the solid-liquid interface and form a hydrophobic layer on the coal particles in the flotation pulp, providing a suitable condition for the clean coal particles to be attached to the air bubbles and collected at the froth layer (Ores, 2007);Polat et al., 2003). Collectors are

generally classified into two distinct groups (as shown in Figure 2.4.) due to their ability to dissociate in water. These groups are ionizing and non – ionizing collectors. The non – ionizing collectors are usually used as collector for coal flotation.

2.4.2. Frothing Agents. Frothres are heteropolar surface-active compounds made up of a polar group and a hydrocarbon radical capable of adsorbing in the air-water interface (Khoshdast & Sam, 2011). The frother molecules are set up in the air-water interface such that the hydrophilic or polar groups are aligned into the water phase and the hydrophobic or non-polar hydrocarbons chains in the air phase. Frothers have to main purpose in the froth flotation- to stabilize and decrease the size of the air bubbles so they remain well dispersed in the slurry. They also create a more stable froth. Frothers are classified in different classes as shown in Table 2.1. Frothers that are commonly used in coal flotation are MIBC, pine oil, and various water- soluble polyglycol types.

2.4.3. Regulators. Regulators, sometimes known as modifiers, are added to the flotation process mainly to perform two main duties within the flotation pulp, to alter the action of the collector on the coal surface / any valuable mineral and to govern the selectivity of the flotation process. Coal flotation regulators are mainly classified/ grouped into three main groups:

- Activators

- pH regulators

- Depressants
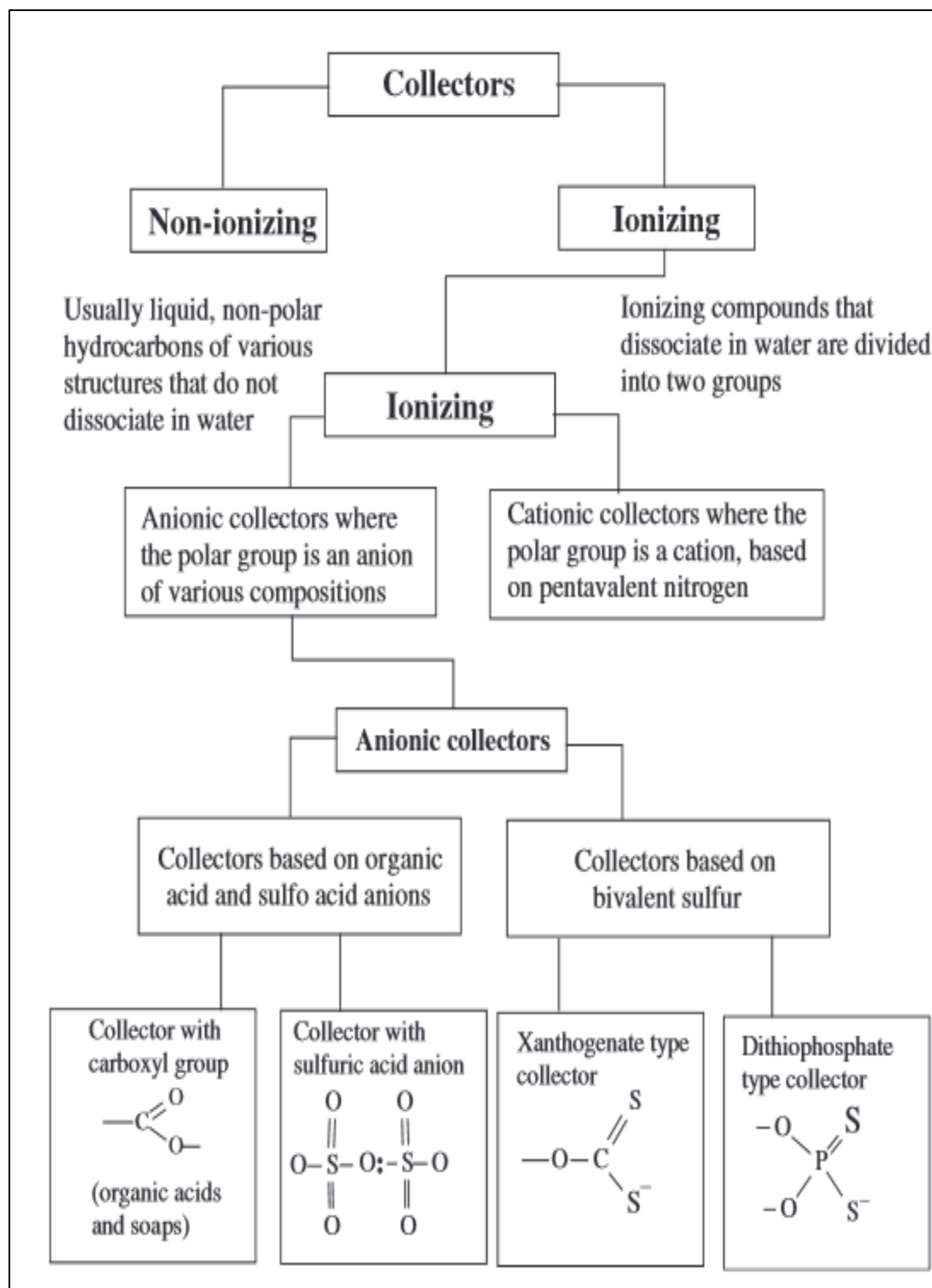
Figure 2.4. classifications of collectors.(Bulatovic, 2007)

Table 2.1. classification of frothers

GROUP	NAMES	SOLUBILITY IN H_2O
Aliphatic Alcohols	MIBC	Low
	2-Ethyl hexanol	Low
	2,2,4- Trimethyl pentanediol / 1,3- monoisobutyrate (Texanol)	Insoluble
Cyclic Alcohols	α – terpineol (active constituent of pine oil)	Low
	cyclohexanol	low
Aromatic Alcohols	Cresytic acid (mixture of cresols and xylenols)	low
Polyglycol- type	DF 250	All very good
	DF1012	
	AeroFroth 65/ DF 400	
	DF- 1263	↓

2.4.4. Coal Depressants. Depressants are said to have the opposite effect of the collector. (Hu, Sun, & Wang, 2009) Defined a depressant as an agent that when added to the flotation system, inhibits the adsorption of a collector on a given mineral surface or adsorbs on the mineral surface to make it hydrophilic thereby preventing it from floating. The depression mechanism has been subjected to controversy and various hypotheses have been proposed by several researchers to explain this phenomenon. (Klimpel, Hansen, & Fazio, 1989) proposed four theories; that the depressant chemically reacts with the coal /mineral surface which lead to production of the insoluble protective film on the surface of the mineral resulting in a failure to react with the collector; the depressant

(by various physical-chemical mechanisms such as surface adsorption and mass reaction effects) inhibits the formation of the collector film; the depressant acts a solvent for an activating film naturally associated with the mineral and lastly that it acts as a solvent for collecting films. Various types of depressants are used in flotation, including; inorganic depressants such as zinc sulphate, lime sodium sulphide etc. and organic depressants such as polyacrylamide polymers containing various functional groups.

2.5. NOVEL INORGANIC- ORGANIC HYBRID POLYMERS

Inorganic-organic hybrid materials are defined as wild, manifold and existing categories of systems derived from and intimate combination; often mediated by the formation of a chemical bond, of organic and inorganic building blocks (Carraro & Gross, 2014). In recent years, there has been a rapidly growing attention devoted to developing an inorganic – organic hybrid membrane made up of a polymer matrix and inorganic nanoparticle. The reason for this is because the addition of inorganic materials to organic polymers endows the polymer materials with many unique physical and chemical properties(Wang, Qian, Zheng, & Yang, 2006). Organic – inorganic hybrids are said to create high performance and high function due to synergism of the two components(Yang, Qian, & Shen, 2004). The unique multifunctional character of the inorganic – organic hybrid polymers makes them potentially useful in a variety of processes involving; dispersion/ flocculation, structural materials, electronic and optical materials and various water treatment processes (Chujo, 1996)(Wei, Jin, Wei, Yang, & Xu, 1998)(Novak, 1993). Currently, different kind of inorganic nanoparticles have been successfully introduced into the polymer matrix to prepare the inorganic/ organic hybrid

nanoparticle membrane.(Samadi, Khalilian, & Tabatabaee, 2014) This include; SiO_2, Al_2OH_3, Fe_3O_4, ZnO, ZrO_2, TiO_2 and CdS. Inorganic- organic hybrid polymers are generally classified into 3 classes based on the method used to synthesize them. The first class involves assembling the performed organic and inorganic components into the form of particles which are the elementary units that constitute the building blocks of the resulting hybrid colloid. The second class involves the in situ polymerization of the organic polymer in the precursor in the presence of the performed inorganic particle. The third class involves the organic polymer and inorganic molecular precursor reacting simultaneously Bourgeat-lami (1918). Figure 2.5 depicts the three classes of Inorganic-organic hybrid polymers.

Al $(OH)_3$- PAM or Al-PAM is a hybrid organic-inorganic polymer, developed in the early 2000 in china, derived in part from research on synthesizing hybrid organic-inorganic composite materials (Chow, Contreras, Zhou, & Li, 2012). The composite is composed of positively charged sub-micron size particles of aluminum hydroxide dosed within the polyacrylamide structure which has been polymerized in the presence of charged particles. The polymer is prepared by following three main steps; the first step involves preparing the aluminum hydroxide colloid. The second step involves synthesizing the Al $(OH)_3$- PAM hybrid and the last step involves purifying and drying of the polymer. Al $(OH)_3$- PAM hybrid polymer has a star like structure (as shown in Figure 2.6) (Guo, 2012)

Al $(OH)_3$- PAM hybrid polymer has many application in industries including mining, mineral processing, waste oil recovery, gas processing, treatment of tailings and waste water in the oil industry. The hybrid polymer has been used mainly as a flocculent

for enhancing the separation of solids from liquid in aqueous suspension. Haihong Li et al., investigated the effects of $Al(OH)_3$- PAM hybrid polymer on recovery of bitumen during froth flotation. In the study two polymers were synthesized $Al(OH)_3$- PAM and Magnafloc 1011.
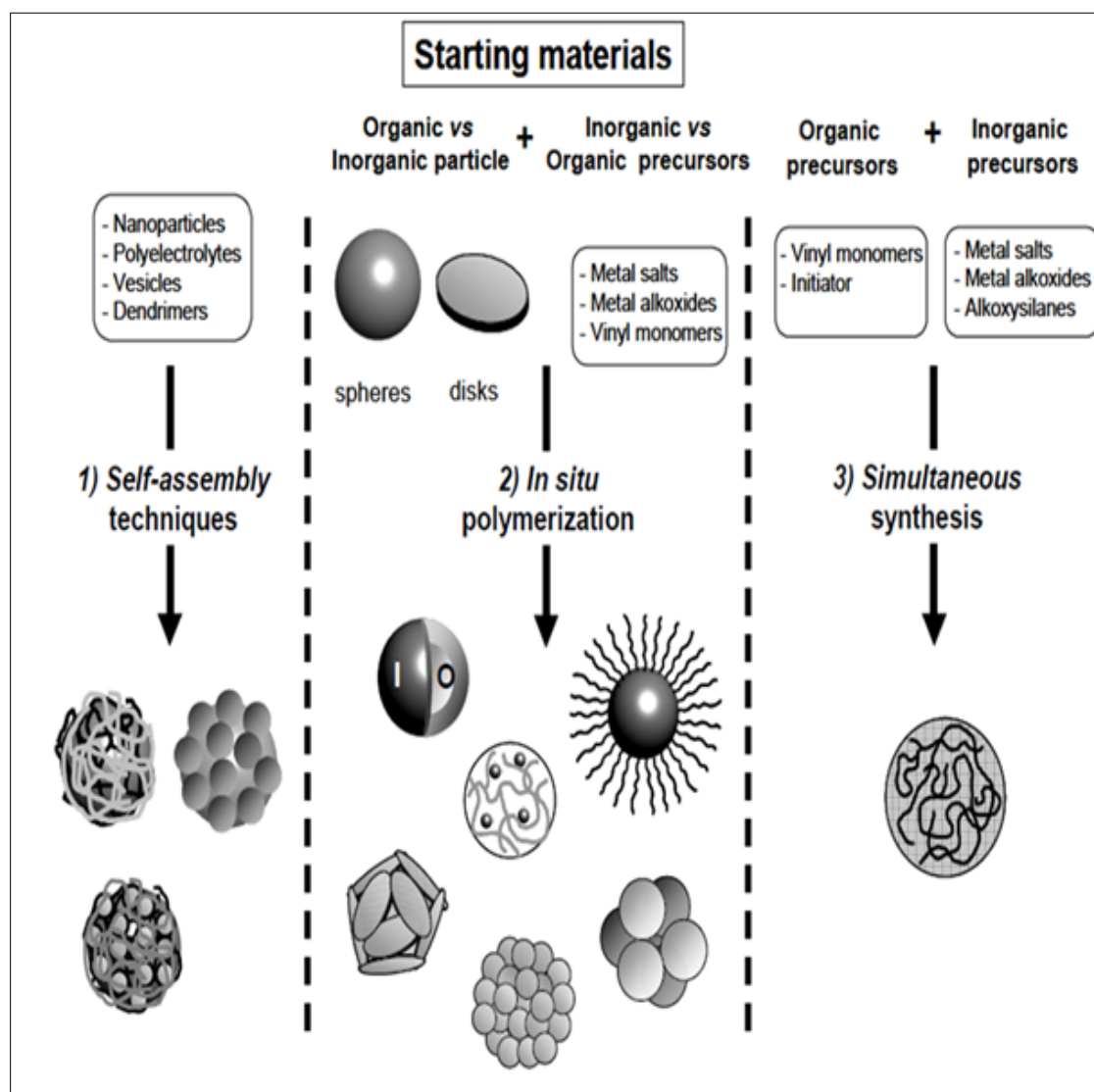
Figure 2.5. three classes of Inorganic- organic hybrid polymers(Bourgeat-lami, 1918)

From the flotation experiments it was found that the use Al(OH)$_3$- PAM alone led to deterioration in bitumen recovery due to formation of large bitumen lumps during froth flotation. However, holistic improvements in bitumen recovery, froth quality and tailings settling were achieved when Al(OH)$_3$- PAM was used in combination with magnafloc 1011 at low dosage.(Li, Haihong; Long, Jun; Xu, Zhenghe; Misliyah, 2008). There is no literature available on the use Al (OH)$_3$- PAM hybrid polymer in coal flotation.

2.6. POLYMER APPLICATION IN FINE COAL FLOTATION

Polymers have been successfully used in mineral processing/ coal preparation mainly as gangue depressants or dispersants. (Pikkat-Ordynsky & Ostry, 1972). Branched polymers with lower molecular weight are very good dispersants or depressants while high molecular weight polymers are good flocculants. It is concluded from literature that flocculants are very likely to depress coal during flotation.
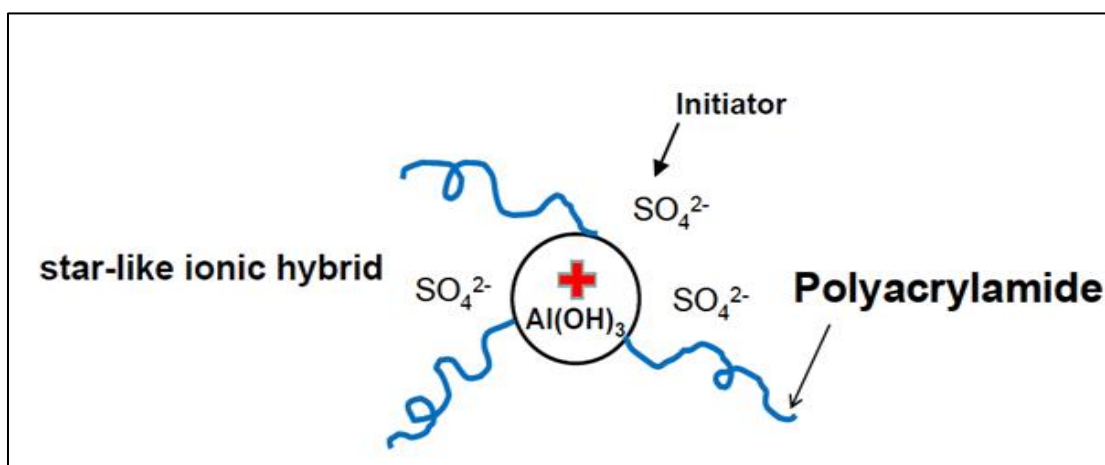
Figure 2.6. Star like structure of Al (OH)$_3$- PAM hybrid polymer.

Aimone & Booth, (1956) investigated the effects of flotation gangue depressants consisting of water soluble linear polymers of mono cyclo octatetraene olefins. The polymers have a molecular weight of 10,000 and contain water soluble salts. Flotation experiments were conducted using Pb-Zn sulphide ores in the presence of water soluble linear polymers of mono cyclo octatetraene olefins. The results showed that flotation recovery of the sulphide ores was greatly improved when 0.1 lb/ton of the sodium salt of hydrolyzed polyacrylonitrile was added. Similar effects were noticed in fine coal flotation. However, the study did not fully show the depression of ash forming minerals by polymers in flotation of fine coal.

Fedorova et.al, carried out a study to test the flotation of coal fines using different flotation agents . The agents were waste generated by the petroleum industry. The agents were polymer residues collected: A(after the distillation of isooctylene fraction), B (after the distillation of isopropylbenzene) and C (after the alkylation of C6H6 and distillation of isopropylbenzene) (Fedorova, 1958) . In the study, the polymer residues were mixed with the alkylate residue (obtained from the production of alkylbenzene) and petrolatum's (oxidized and saponified). Other reagents which include kerosene, crude oil, desiel fuel and oxidized gas oil for comparison were also used. Among all these reagents, the most effective and cheapest flotation agents were polymer residue mostly collectors and to a considerable lower degree foam forming substance. However the study did not explain the interaction of the polymer residue with ash forming minerals in coal fines during flotation.

Davydkov N.I (1959) also tested the use of flotation reagents together with the polymers to improve plant process recovery in the Karaganda plant. Before the study, the

original plant produced a concentrate containing 9% ash from feed containing 19.5% ash while recovering 55% of the feed product. A continuous pilot plant with 15 kg /hr of solids was used to conduct the study. Sulfonated kerosene was used together with 450 g/ton of polymer (unspecified composition) as reagents. The results showed that the product could be altered to yield a concentrate of 70% of the feed at 9% ash. The pilot results were successful; however the industrial scale operation was only partially successful in a continuous 8- chamber installation. It would be necessary to reprocess the intermediate product to obtain high a product yield due to the large fraction collected.

Snow and Bell, (1980) used water soluble polymers of partially hydrolyzed polyacrylamide to reduce the amount of clay floated and to increase the overall recovery of coal. Polymers were added to the flotation circuit so as to flocculate clays associated with coal and discharge them as tailing. Using the collector alone, recovery of 89% was achieved with 10.54% ash. When 2 lb/ton of polymer was added to the flotation pulp, the recovery was increased to 90% with an ash content of 9.88%. When the polymer dosage was increased to 4 lb/ton recovery was decreased to 86% with an ash content of 11.11%. However, further study needs to be conducted to see the effect of the polymer when fuel oil is reduced.

(Williams and Unlu, 1987) investigated the effects of various polyacrylamide flocculants on the floatation of different coal samples. The effects of ionic character, concentration and age of polymer on the percentage recovery of coal and ashes were studied. Batch flotation tests were complemented by contact angle measurements tests measured as a function of pH, inorganic electrolyte and polymer concentrations. From the results, the contact angle measurements tests demonstrated that polyacrylamide

flocculants rendered the coal's surface hydrophilic. The pH was also found to affect the contact angles, with the maximum values occurring just below neutral pH. Flotation results showed that the presence of polyacrylamide flocculants during the flotation of four different coal slurries resulted in decreased recoveries, increased coal ash and decreased ash in tailings. The reduction in recoveries was mainly due to three things: the depressant effect of the polyacrylamide on the coal, the flocculation of particles into large , strong flocs and the increased pulp viscosities reducing the efficiency of particle / bubble collisions.

(Moudgil, 1989) studied the effects of nonionic polyacrylamide and the partially hydrophobic, nonionic polymer, polyethylene oxide (PEO) on the flotation of fine coal slurries. The results showed a dramatic decrease in the recovery of floated coal at higher dosages of polyacrylamide, when polyethylene oxide (PEO) was used the recovery of the floated coal were partially decreased. However the depressant action was found to be less severe at higher dosages as compared to nonionic polyacrylamide. A conclusion was made that the depressing action of the polyacrylamide was due to the adsorption of the hydrophilic polymer molecules on coal particles, rendering the surface polar in nature. However, the study failed to show the interfacial studies of the interaction of both polymers and the coal particles.

Xu and Aplan, (1994) investigated the dual use of a mineral matter dispersant with polymeric depressant system during the flotation of fine coal. The polymeric depressant and the mineral matter dispersant were both added in the flotation pulp so as to enhance the separation of fine coal particles from the ash and pyrite minerals. Flotation experiments were first conducted with only the use of the mineral matter dispersant. The

second set of experiments was conducted with the joint use of the dispersant and the polymeric depressant. The results showed that using the dispersant alone did not enhance the ash reduction while the dual use of the dispersant and polymeric depressant reduced the ash content that had been accidentally entrapped or collected in the froth mass. However, the study failed to show the effects of the polymer at different pH levels.

Chander, Polat and Polat, (1996) investigated the potential use of the triblock copolymers of PPO (polypropylene oxide) and PEO (polyethylene oxide) to improve the combustible recovery of coal flotation process in the presence of an insoluble collector. The study was conducted on high rank and low rank coal samples. Non- selective agglomeration was found to be the main problem in coal flotation in the absence of tri-block co-polymers. Agglomeration was promoted by mechanical emulsification of the collector. The results showed that adding the polymer 2 minutes before the collector improved the flotation by allowing the polymer to adsorb and modify the surface of the coal. This allowed triblock copolymers to increase selectivity of flotation for high rank coal, increasing hydrophobicity and the recovery. For low rank coal, the polymers acted as both emulsifies for the collector and surface modifiers for coal particles. The recovery slightly increased while the amount of ash content in the froth was decreased. However, the study failed to determine the optimum dosage of the polymer needed.

Parkekh et. al investigated the floatability of the polymer-flocculated fine coal slurry using column flotation. The slurry used in their experiments was first flocculated with polymers and concentrated to 10% (by weight) before it was floated in column flotation. From their results they were able to show that fine coal slurry flocculated with cationic, nonionic and anionic polymers could be floated effectively. Zeta potential and

contact angles measurements showed that the presence of polymers on the surface of the coal did not lower its hydrophobicity, and in some cases, it even improved its hydrophobicity. However the study did not investigate the interaction of polymers with ash-forming minerals (slimes).

Pawlik, (2005) studied the effects of low molecular weight polymers (MW< 100,000) on the surface properties of a medium – volatile bituminous coal in concentrated aqueous suspensions through adsorption, flotation and electroacoustic and rheological measurements. Flotation tests were conducted using carboxymethy cellulose, hydroxyethyl cellulose, humic acids, polystyrene sulfonate, dextrin and hydroxyl propyl cellulose that were used as ash depressants. Flotation experiments showed that polymeric dispersants completely depressed the coal hence reducing the recovery. Anionic polymers were found to quickly decrease the surface charge towards more negative values, increasing electrostatic repulsion between the particles while anionic polymers stabilized coal particles towards aggregation by a combination of steric effects and electrostatic repulsion.

Tao, Ghen, Fan, Zhou, and Zhao, (2006) conducted a study on coal and potash samples to evaluate the performance of a clay binding agent developed by Georgia Pacific Resins Inc. Flotation tests were conducted using both mechanical and column flotation. The clay binders used in the study were low molecular weight polymers that were the condensation products of urea and formaldehyde, reacted under acidic conditions. To evaluate the performance of the clay binders, the following flotation parameters were optimized; impeller speed, binder dosage, collector dosage and residence time. The flotation results showed that the use of the clay binder significantly

enhanced flotation efficiency under different conditions. More significant benefit of the clay blinders were observed at a higher impeller speed of about 1500 rpm. Decreasing the residence time also improved the flotation performance. However, the study did not evaluate how the pH affected the performance of the clay binder in flotation of both coal and potash.

Ofori, O'brien, Firth, and Mcnally (2012) also studied the use of tri block copolymers surfactants of PPO (polypropylene oxide) and PEO (polyethylene oxide) as flotation promoters to enhance the recovery of the poorly floating components of coal. Since (Chander et al., 1996) did not show how the polymer influenced the poorly floating components of the coal, flotation experiment were complimented by the use of a coal grain analysis tool that allowed an assessment to determine which components of the flotation feed were most influenced by the use of the tri block copolymers. Both their experiments and full scale flotation experiments showed that tri block copolymers surfactants of PPO (polypropylene Oxide) and PEO (polyethylene Oxide) significantly improved the flotation recovery of coal when added in small amount before adding the conventional collector. However, there was a slight increase in the ash content of the froth. The coal grain tool results also showed that recovery of each coal components was improved more than that of fine fractions by using tri block copolymers with coarse grain components.

3. EXPERIMENTAL WORK

3.1. MATERIALS

3.1.1. Polymer Synthesis Chemicals.
All the chemicals used for polymer Synthesis was purchased from Fisher Scientific (FisherSci, USA). These chemicals include, acrylamide (monomer), aluminum chloride anhydrous (>99%) and ammonium carbonate (which were used to synthesize the aluminum hydroxide nanoparticles), ammonium persulfate (98%) and sodium hydrogen sulfite (95%) (Which were used as initiators in the polymerization of acrylamide), acetone (>99.5%) by weight and nitrogen gas (which was used to remove the dissolved oxygen from the reaction vessel).

3.1.2. Flotation Reagents.
All chemicals used in the flotation Experiments were purchased from Fisher Scientific Company, USA. This includes: kerosene (which was used as a collector), methyl isobutyl carbinol (MIBC) (which was used as a frother), sodium metasilicate (which was used as a dispersant), and sodium hydroxide (NaOH), and hydrochloric acid (HCl) (which were used to adjust the pH of the flotation pulp as needed).

3.2. SAMPLE ACQUISITION

Coal samples used in this study were obtained from a mine located in Illinois. The coal samples were mainly raw coal obtained directly from the mine. The samples were collected in 20 gallon buckets. When the samples arrived at the lab, a representative

sample was obtained from the bucket for analysis and characterization in accordance with standard practices for preparing coal samples for analysis (ASTM D2013).

3.2.1. Crushing and Grinding. The as-received run of mine coal was first crushed in a jaw crusher (8X5 model, Sturtevant Inc, USA) used as a primary crusher and it was then further crushed in a roll crusher as a secondary crusher (8x5 model roll crusher, Sturtevant Inc, USA) (shown in Figure 3.1. and 3.2.). Lastly, a laboratory ball mill was then used to grind the coal samples to a finer size (shown in Figure 3.3). After crushing and grinding a representative sample of the ground coal was screened to different sizes using US standard sieves of 500,300, 150, 75 and 38 μm and further analyzed for proximate and size distribution analysis was conducted as per ASTM D4749-87(2012) standards.

3.2.2. Size and Ash Distribution. Particle size distribution of the grounded coal samples was measured by dry sieving analysis using US standard sieves of 500, 300, 150, 75 and 38 μm. The fraction between 75 and 38 μm was further analyzed using US standard sieves of 75, 63, 53, 45 and 38 μm as it was used as a feed in all floatation experiments. The ash content of each particle size distribution was determined in accordance with ASTM D3174-12.

3.2.3. Proximate Analysis. Proximate analysis of the flotation raw coal samples was determined using a TA Instruments Q50 Thermogravimetric Analyzer (TGA), (TA instruments, Delaware, USA) (Figure 3.4.). Proximate analysis is a standard methodology used to determine the fixed carbon, volatile matter, moisture, and ash percentages of the coal samples.

Figure 3.1.Laboratory jaw crusher

Figure 3.2.Laboratory Roll crusher

Figure 3.3. Laboratory ball mill

Figure 3.4. Q50 Thermogravimetric Analyzer (TGA)

3.2.4. X-ray Diffraction Analysis. An x-ray diffraction analysis of the coal

sample was used to reveal the qualitative information on the mineral matter composition

of raw coal samples used in this study. XRD was also used to analyze the froth obtained

under optimum flotation conditions. The raw coal samples used in XRD spectroscopic

characterization were further grounded using mortar and a pestle and the sample was

packed and pressed to match the top of sample holder before it was analyzed. The x-ray

diffraction analysis was performed using the PANalytical X'Pert Pro Multi-Purpose

Diffractometer (MPD) (PANalytical Inc., MA, USA) system with Cu (k-alpha) as a

source of x-ray and the radiation was generated at a tube voltage of 40 kV. From the

analysis, the XRD patterns of 2θ against intensity were obtained and the Joint Committee

on Powder Diffraction Standard's mineral powder diffraction files then used to interpret

the diffractograms using hanawalt methods of qualitative analysis. The diffractometer

system used for the analysis is shown in Figure 3.5.

3.3. RELEASE ANALYSIS

Release analysis is analogous counterpart in the coal froth flotation to float and

sink method in the gravity concentration of coal. Its main objective is to obtain the best

possible separation performance by any froth flotation process. The flotation release

analysis was carried out in a conventional laboratory flotation cell. A diagram of the

timed release analysis procedure is shown in Figure 3.6.

3.3.1. Experimental Procedure for Timed Release Analysis. The timed

release analysis procedure was initiated by adding about 253 grams of the coal sample

into a 5 liter batch flotation cell. About 4800 mL of tap water was then added to fill the

cell. This produced slurry had a 5 wt.% of coal/water. The slurry was then conditioned for 5 minutes to allow wetting of the coal. After conditioning, 200 μL of collector (kerosene) were added and allowed another 3 minutes for further conditioning. Then, 300 μL of frother (MIBC) was added to the slurry and conditioned for 2 minutes. At the beginning, the impeller speed and air flow rate were set at minimum of 1200 rpm and 4 lpm, respectively.

Figure 3.5. PANalytical X'Pert Pro Multi-Purpose Diffractometer (MPD) at MS&T

The purpose of using a lower agitation speed and air flow rate at the beginning was to ensure the removal of the most readily floatable coal particles.

3.3.2. Float 1. Froth 1 was collected in Basin 1 for 30 seconds at 1200 rpm (agitation speed) and 4 lpm (air flow rate). The second froth was collected for 60 seconds at 1500 rpm and 5 lpm. The third fraction was collected for 90 seconds at 1700 rpm and 6 lpm, fourth froth was collected for 120 seconds at 1800 rpm and 7 lpm. Lastly, the firth froth was collected for 150 seconds at 1900 rpm and 8 lpm. The tailings from the cell were emptied into a bucket and saved for analysis. The operating procedure for Float 1 is summarized in Table 3.1.

Table 3.1.Summary of operating procedure for Float 1

Pan	Air Rate (Lpm)	Impeller speed (Rpm)	Collection Time (s)
1	4	1500	30
2	5	1600	60
3	6	1700	90
4	7	1800	120
5	8	1900	150

3.3.3. Refloat A. To start the second phase of the experiment, the first Froth from Float 1 was added to the cell and tap water was added to fill the cell. The slurry was conditioned for 5 minutes. After that, about 200 µL of collector were added to the

previously conditioned slurry and conditioned for an additional 3 minutes. Lastly, 300 μL of frother was added and further conditioned for 2 minutes. The first portion of Froth 1A was collected for 15 seconds at 1200 rpm and 4 lpm. Air was turned off and Froth 2 from Float 1 was added to the cell. The refloating was continued for an additional 15 seconds to finish the collection of Froth 1A. The first portion of Froth 2A was then collected for 30 sec at 1600 rpm and 5 lpm before Froth 3 from Float 1 was added to the cell. After adding froth 3 from Float 1, flotation was continued for 30 seconds to finish the collection of Froth 1A .The first portion of froth 3A was collected for 45 seconds at 1700 rpm and 6 lpm. The air flow rate was then turned off, and Froth 4 from Float 1 was added to the cell. Flotation was continued for another 45 minutes to finish collection of Froth 1A. After Froth 3A was removed, the first portion of Froth 4A was collected for 60 seconds at 1800 rpm and 7 lpm. The air flow was turned off and Froth 5 from Float 1 was added to cell. The air was turned on and flotation was continued for an additional 60 seconds to finish the collection of Froth 4A. After removing Froth 4A, the final Froth 5A, was collected for 150 seconds at 1900 rpm and 8 lpm to finish collection of Froth 5A. The tailings from the cell were emptied into a bucket and saved. The operating procedure for Refloat A is summarized in Table 3.2.

3.3.4. Refloat B. To complete the third phase of the flotation release experiment, the procedure shown in Table 3.1 was repeated, except that the products from Refloat A were not added to the cell until the froth collection time had progressed two-thirds of the way through the collection time of the proceeding froth, as shown in Table 3.3. The five collected concentrates and the three tailings products were combined as one and were then filtered, dried and analyzed for ash.

Table 3.2. Summary of operating procedure for refloat A

Pan	Air Rate (Lpm)	Impeller speed (Rpm)	Collection Time (s)	
1A	4	1500	15 sec collect Add 2A & collect for 15 sec	1B
2A	5	1600	30 sec collect Add 3A & collect for 30 sec	2B
3A	6	1700	45 sec collect Add 4A & collect for 45 sec	3B
4A	7	1800	60 sec collect Add 5A & collect for 60 sec	4B
5A	8	1900	Collect for 150 sec to complete 5B	5B

Table 3.3. Summary of operating procedure for refloat B

Pan	Air Rate (Lpm)	Impeller speed (Rpm)	Collection Time (s)	
1B	4	1500	20 Sec collect Add 2B & collect for 10 sec	1C
2B	5	1600	40 Sec collect Add 3B & collect for 20 sec	2C
3B	6	1700	60 sec collect Add 4B & collect for 30 sec	3C
4B	7	1800	80 Sec collect Add 5B & collect for 40 sec	4C
5B	8	1900	Collect for 150 sec to complete 5C	5C
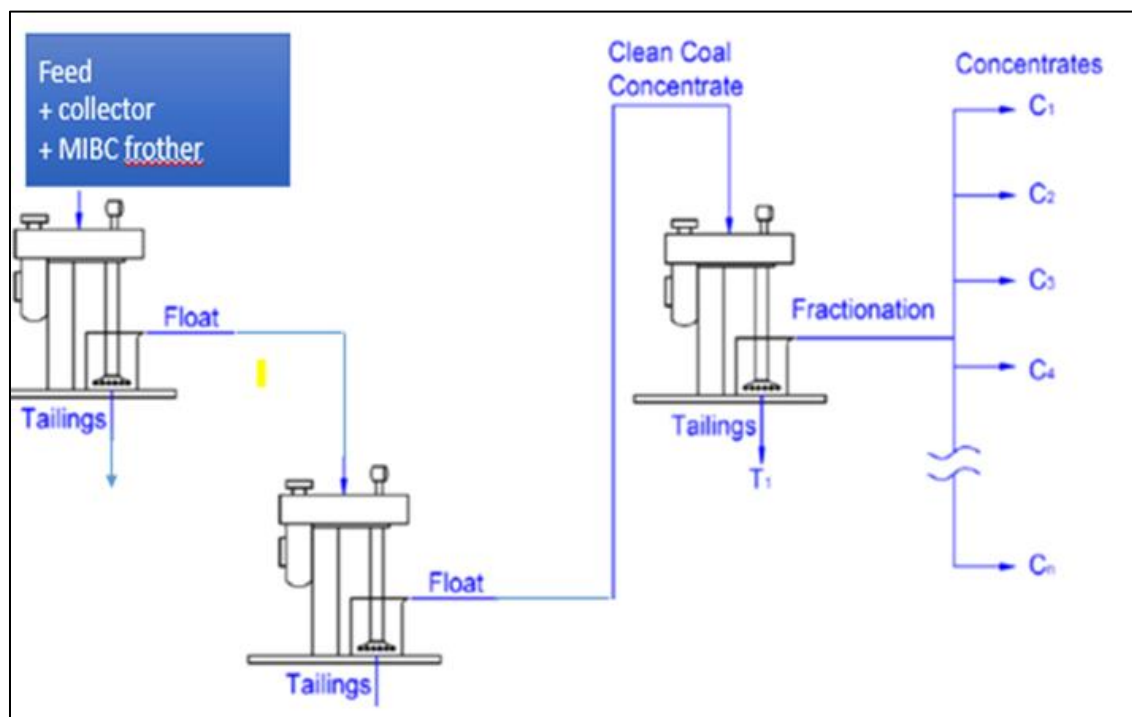
Figure 3.6. Flow diagrams for timed release analysis procedure

3.4. ZETA POTENTIAL

Zeta potential measurements were conducted using a raw coal (flotation feed) and fine clean coal (3.91 % ash) which was obtained from a timed release analysis test of the flotation feed. Isoelectric graphs of both clean coal and the raw coal were established and compared. All the experiments were conducted using pure KCI for supporting electrolytes for zeta potential tests. HCL and NaOH were used for pH adjustments. Zeta potential measurements were carried out using Zetasizer nano ZS (Malvern Instruments Inc., Westborough, Massachusetts) (Figure 3.7.). In a typical zeta potential experiment, the sample is first prepared
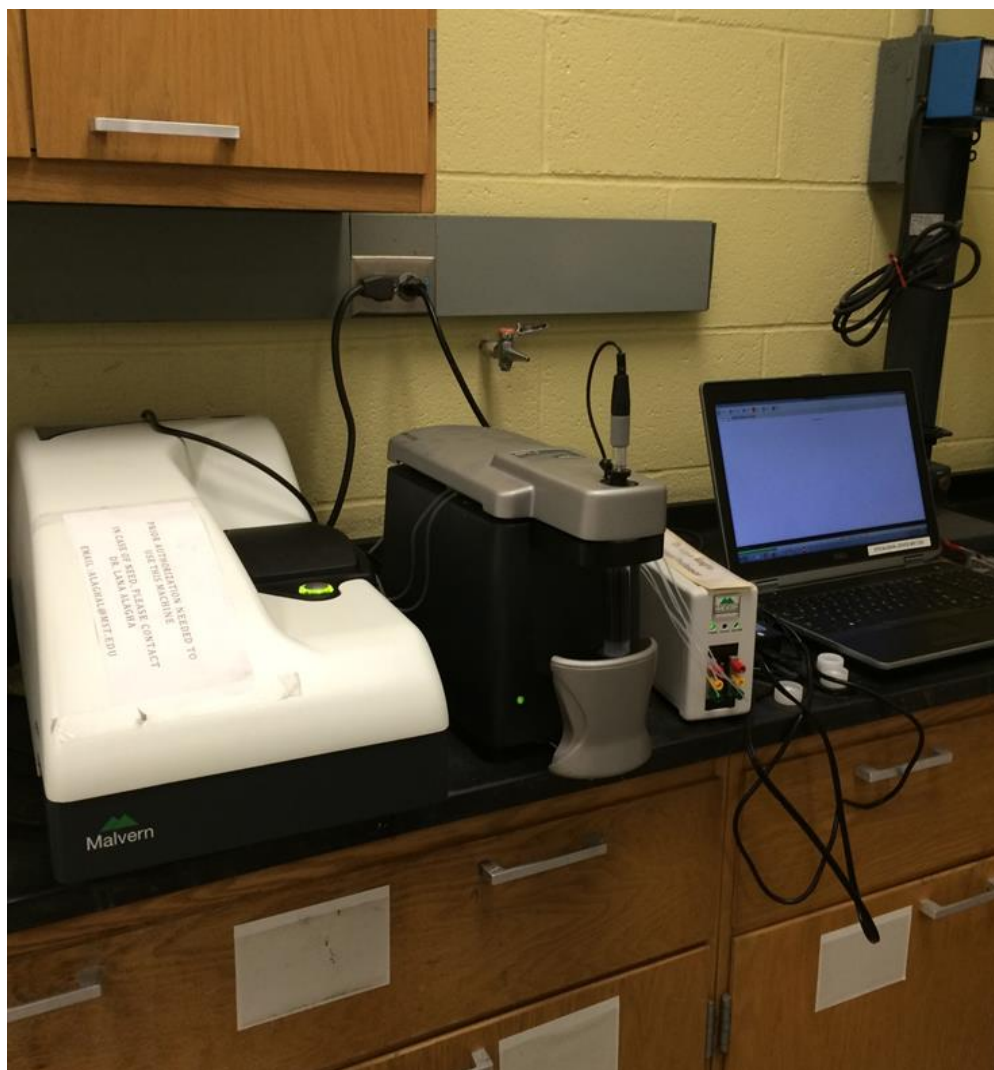
Figure 3.7. Zetasizer nano ZS (Malvern Instruments Inc)

To determine the zeta potential of clean coal, the first concentrate from the release

analysis was used, while for raw coal the sample prepared for the flotation feed was used.

Fine coal was added to a 100 mL beaker and 0.01 M of KCI solution was then added to

make a 1 %wt of coal suspension in 0.01M KCl the suspension was then agitated using

an IKA RW20 mechanical stirrer for about 30 minutes at a constant agitation rate of 300

rpm. The suspension was then sonicated for 2 hours and allowed to settle for 5 to 10

minutes. The upper portion of the supernatant was taken for zeta potential distribution measurement.

3.5. BATCH FLOTATION EXPERIMENTS

All flotation experiments were conducted with a D12- Denver Flotation laboratory cell which has a capacity of approximately 5 liters, as shown in Figure 3.8. In the study, the operating parameters such as polymer dosage, impeller speed, pH and conditioning time were assessed individually. The air flow rate was kept constant at 6 Lpm in all the experiments.

In a typical flotation test, the pulp was first conditioned for 5 minutes prior to any reagent addition to allow wetting of the coal. Collector (kerosene) was then added at a predetermined dosage and the suspension was conditioned for additional 3 minutes. A desired dosage of Al $(OH)_3$-PAM was added after the slurry was conditioned with the collector, and the pulp was agitated for another 3 minutes. The polymer dosages were expressed in reference to the total volume of the feed slurry (coal + water). The frothing agent (MIBC) was added at a fixed amount of 200 µl/ton on mass basis relative to the dry feed mass. The suspension was further conditioned for 2 minutes before the air was introduced. The froth was collected at 2 minutes time intervals. The concentrate fractions were washed, filtered and dried in an oven overnight at 80 ^{0}C. After drying, the concentrates were analyzed for ash content according to the ASTM D3174-73. An example of the experimental conditions and different parameters investigated are shown in Table 3.4.

Table 3.4. Summary of flotation experimental conditions and different parameters investigated.

Experimental Conditions	Parameters Investigated
Feed size = -75 + 38 µm	Polymer dosage
Feed volume = 4800 mL	Polymer conditioning time
Feed solids = 5 %	Polymer addition method
Aeration = 6 lpm	Dual use of polymer - dispersant effect
Impeller speed = 1800 rpm	Dispersant effect
Collector dosage = 200 µL	pH
Collector conditioning time = 3 mins	Impeller speed
Frother dosage = 300 µL	
Frother conditioning time = 2 mins	

3.6. POLYMERS

The polymers used in this study are listed below:

A. Commercially available Polyacrylamide (PAM), a water soluble white to off- white powder with a molecular weight of about 5×10^6 Dalton and a charge density of 0.75 g/cm^3. The polymer's other commercial name is PAA; 2-Propenamide homopolymer and the chemical formula of the polymer is $(C_3H_5NO)n$. This polymer is manufactured and distributed by Pfaltz & Bauer Rare and Fine Chemical Company.

This polymer is widely used in the petrochemical, metallurgical, coal, mineral processing, and textile industries as precipitation flocculants, thickeners oilfield water injection, drilling mud additives, textile pulp, paper reinforcer, fiber modifier, soil improvers, soil stability agents, thickeners fiber, resin processing agent, synthetic resin coatings, adhesives, and dispersion agent.

Figure 3.8. D12- Denver Flotation laboratory cell.

B. Aluminum Hydroxide- Polyacrylamide (Al-PAM)**,** an in-house synthesized organic-inorganic hybrid polymer with a star-like structure. The chemical formula for this hybrid polymer is $Al(OH)_3$-PAM and it has an ionic bond between $Al(OH)_3$ colloids and polyacrylamide chains. Three main steps were followed to prepare the polymer: preparing the aluminum hydroxide colloidal nanoparticles, polymerizing of acrylamide in Al-$(OH)3$ colloid to produce Al-PAM, and purifying and drying of the Al-PAM. The polymer is anticipated to have a star-like structure. The star-like structure of this polymer is due to the monomer acrylamide being initiated on the surface of the positively charged $Al(OH)_3$ colloid particles. The anticipated structure of Al-PAM is shown in Figure 3.9.
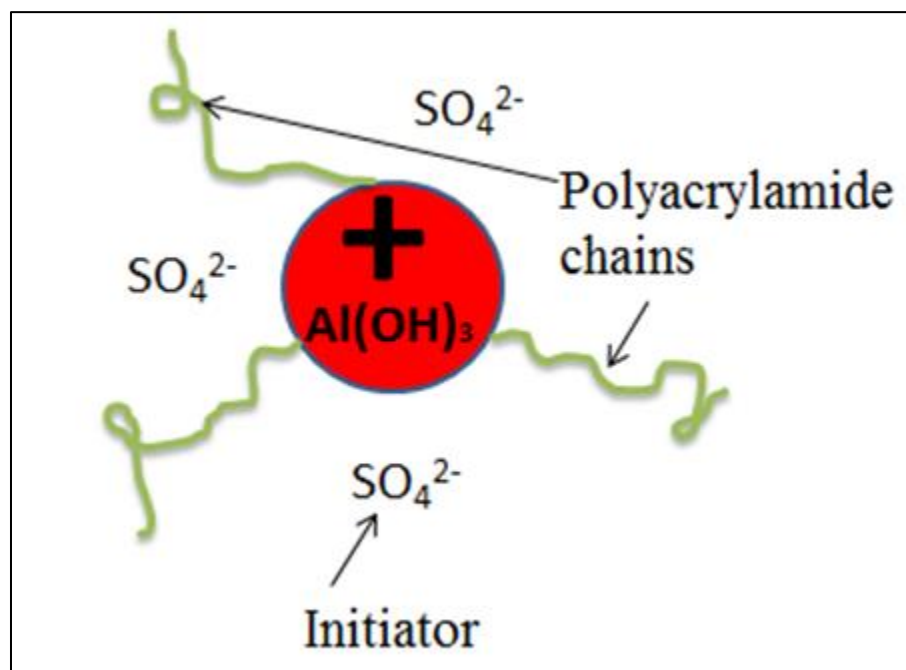
Figure 3.9. The structure of Al-AM with organic polyacrylamide arms grafted on the aluminum hydroxide nanoparticles cores

3.6.1.   Colloid Preparation. The colloid preparation, synthesis and characterization of Al-PAM have been discussed in detail in the work of Alagha et al. (2011), Gou et al. (2012) and Yang et al. (2004) but will be mentioned briefly here. The chemical reaction involved in the synthesis of Al(OH)3 colloid is:

$$2 \text{ AlCl}_3 +_3 (\text{NH}_4)2\text{CO}_3 + 3 \text{ H2O }_2 \rightarrow \text{Al(OH)}_{3 \text{ (s)}} + 6 \text{ NH}_4\text{Cl} + 3 \text{ CO}_{2 \text{ (g)}}$$
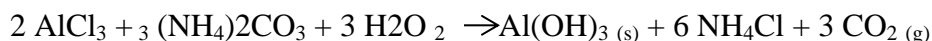
3.6.2.   Procedure for Colloid Preparation. About 0.33 g of aluminum chloride anhydrous (>99%) (AlCl$_3$) was dissolved in distilled water to make 25 g of 0.01M (AlCl$_3$) solution. About 0.48 g of ammonium carbonate (NH$_4$)2CO$_3$ was dissolved in distilled water in a different to make 50 g of 0.1M (NH4)2CO3. After the two solutions were prepared, the Master FLEX mini pump was then used to add the (NH$_4$)2CO$_3$ solution to AlCl$_3$ solution at a rate of 0.5 g/min. The addition rate of the (NH$_4$)2CO$_3$ solution to AlCl3 solution was controlled by an electronic balance. An IKA RW20 mechanical stirrer was used to mix the two solutions at an initial constant rate of 500 rpm. After adding about 36- 37g of the (NH$_4$)2CO$_3$ solution into 25g of AlCl$_3$ solution the pump was stopped and the solution was gently stirred at a rate of 300 rpm for about 30 minutes to complete the reaction. The experimental set up for colloid preparation is shown in Figure 3.10. The measured particle size and zeta potential value of the prepared Al(OH)$_3$ colloidal suspension were 50 nm and +30 mV, respectively

3.6.3.   Synthesis of AL-PAM. The proposed mechanism for Al- PAM synthesis is shown in Figure 3.11.
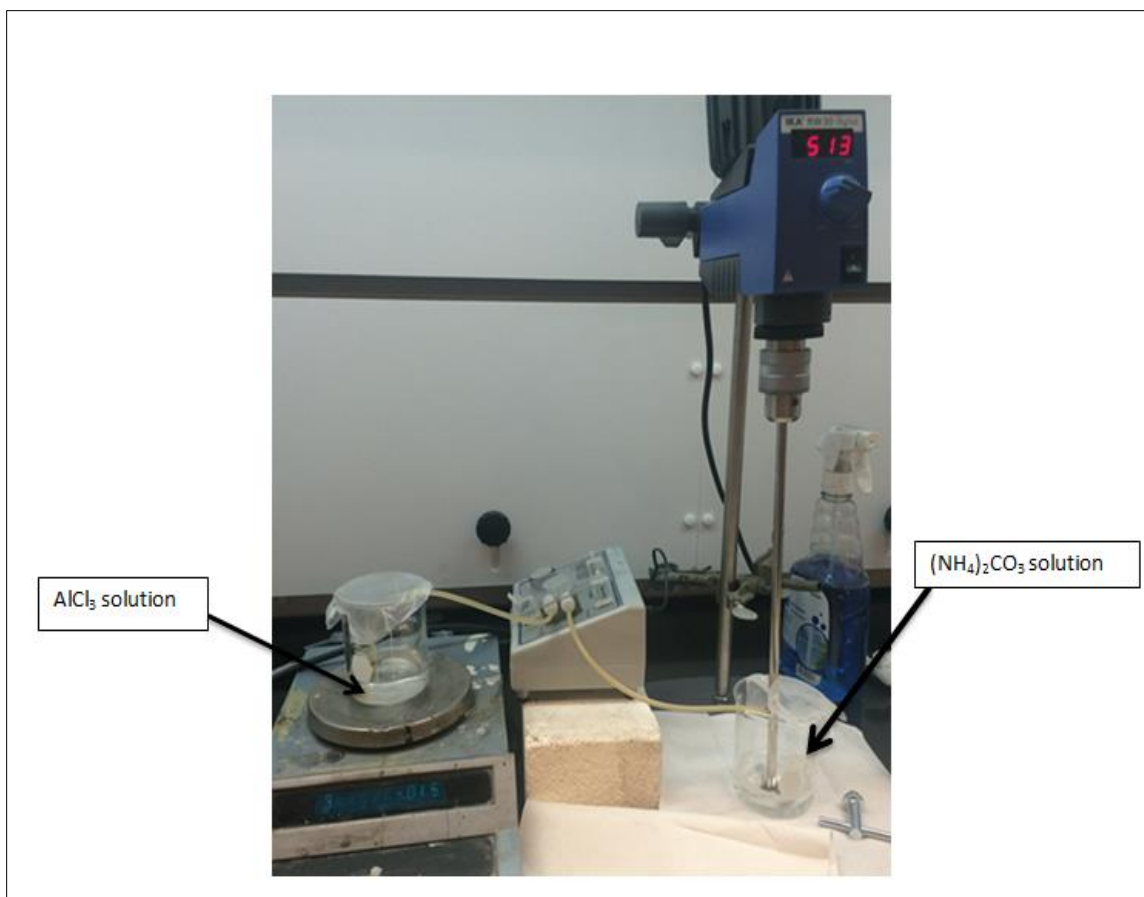
Figure 3.10. Experimental set up for colloid preparation
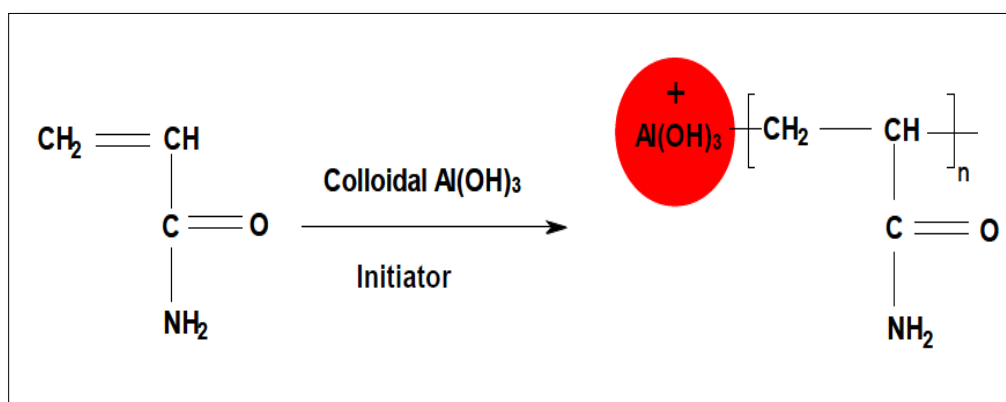
Figure 3.11. Schematics of Al-PAM synthesis(Yang et al., 2004)

3.6.4. Procedure for Synthesis of AL-PAM. In a 100 mL flask, about 4.5 grams of acrylamide monomer were added to 25 grams of colloid suspension. The addition was done under magnetic stirring at 20 rpm. To avoid oxidation during the reaction, nitrogen gas was introduced to the mixture from the beginning to the end of the experiment. A constant temperature of 40 degrees Celsius was maintained throughout the experiment using oil bath. The flask was also covered with aluminum foil to protect from exposure to light. After 0.5 hours of stirring under nitrogen, 1 mL of 2 g/l $(NH_4)2S_2O_8$ and 1 mL of 1 g/l $NaHSO_3$ were added within 30 minutes through a 10mL glass funnel. The reaction was kept for 4 - 8 hours until of a transparent gel formed. The experimental set up for Al-PAM synthesis is shown in Figure 3.12**.**

3.6.5. Purification. Purification of the Al-PAM was done mainly to remove unreacted monomer and initiators from the product gel. The transparent 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 added drop-wise to acetone. Finally the purified polymer was transferred to a Teflon dish, and the dish was placed at 60 ^{0}C in a vacuum oven overnight.
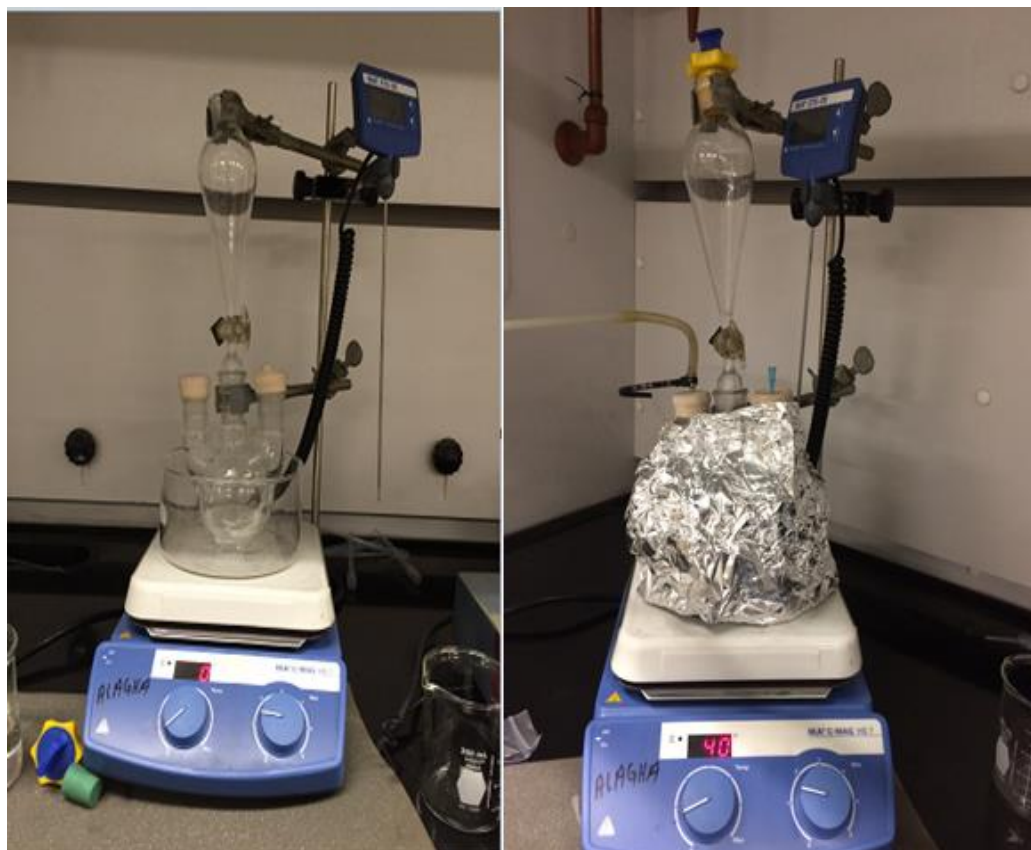
Figure 3.12. Experimental setup for Al-PAM synthesis (A) Setup before aluminum foil was put on for protection from exposure to light; (B) setup with aluminum foil for protection from exposure to light.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1. SAMPLE CHARACTERIZATION

      4.1.1. Particle Size and Ash Distribution. Particle size analysis and ash distribution results of the raw coal samples obtained from ball milling discharge are shown in Table 4.1. and Figure 4.1. It can be seen from Figure 4.1. That the median (D50) of the distribution is corresponding to grain size (78 µm), which means 50% of the sample are smaller than or equal to 78 µm. Also it can be seen that 80% of the sample is less than 114 µm and 20% of the sample is less than 35 µm. from Table 4.1 it can be clearly seen that the overall ash content of the gross sample was 30.85%. The ash distribution of the sample also increases with decreasing particle size which is consistent with what have been previously reported in literature about the concentration of ash in fine fractions of coal. Particle size distribution analysis of the flotation feed (75µm +38 µm) was also analyzed. The size distribution results are shown in Figure 4.2. and Table 4.2.

      4.1.2. Proximate Analysis. The results for proximate analysis of the flotation feed sample are shown in table 4.3.

4.2. RELEASE ANALYSIS

      For the efficient separation of ash forming minerals (mainly clay minerals which is the major cause of slime coating) from coal particles using physiochemical process

such as froth flotation, it is necessary that the ash forming minerals be present in liberated state. To determine the liberation characteristics of coal, flotation timed release analysis was used.

Table 4.1. Particle size analysis data for raw coal (ball mill discharge)

Size		Wt. (%)	Ash (%)	Cum Wt. (%)	Cum Ash (%)	Cum Wt. (%)	Cum Ash (%)
Mesh Number	Size Range (μm)						
-35	500	0.16	18.35	0.16	18.35	100.00	21.53
-35+100	150	6.51	19.47	6.67	19.44	99.84	21.54
- 100+200	75	45.27	18.03	51.93	18.21	93.33	21.68
- 200+400	38	37.56	23.52	89.50	20.44	48.07	25.12
-400	-38	10.50	30.85	100.00	21.53	10.50	30.85
	Totals:	100					
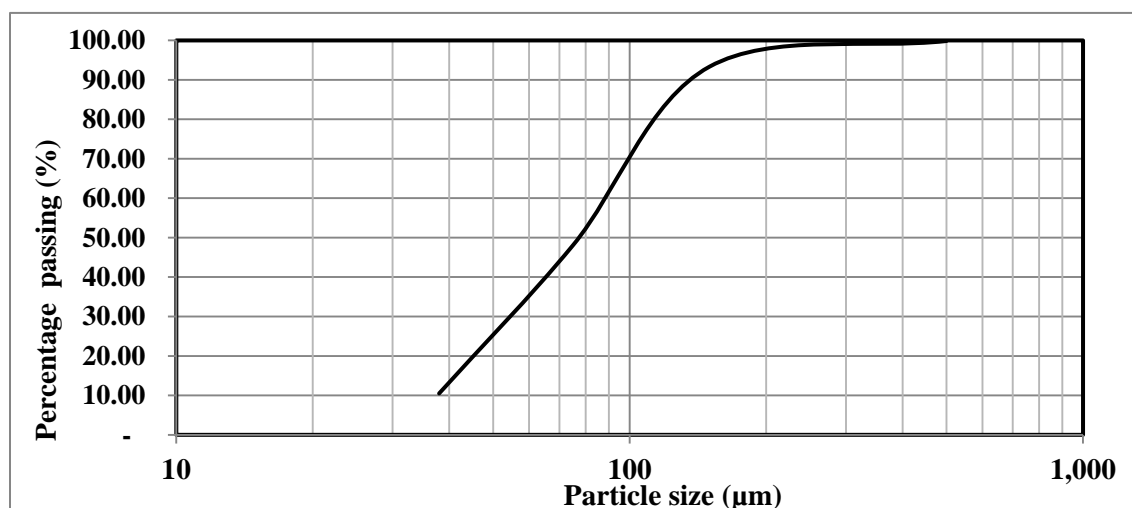
Figure 4.1. Particle size distribution curve for raw coal (ball mill discharge)

Table 4.2.Particle size analysis for coal flotation feed sample (-75+38µm)

	Size					
Mesh Number	**Size Range (mm)**	**retained wt.**	**Retained (%)**	**cumulative wt.**	**cumulative percentage**	**Passing (%)**
200	75	0	0	0	0	100.00
230	63	7	3.51	7	3.51	96.48
270	53	11	5.53	18	9.05	90.95
325	45	58	29.15	76	38.19	61.81
400	38	111	55.78	187	93.97	6.03
pan		12	6.03	199	100	-
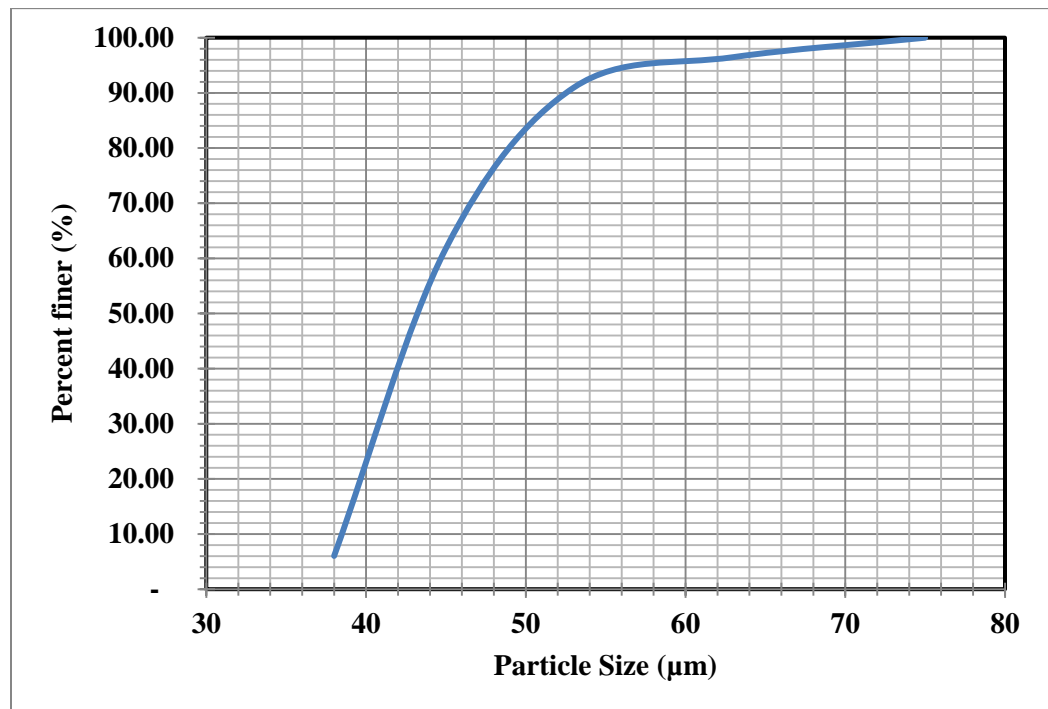
Figure 4.2.Particle size distribution curve for coal flotation feed sample (-75+38µm)

Table 4.3. Proximate analysis for flotation feed sample (-75+38µm)

	As determined
Moisture	10.05
Ash	25.12
Fixed carbon	44.86
Volatile matter	37.65

Timed release analysis provides a practical boundary line conditions for best possible separation performance achievable by any froth flotation process (Dell, 1964) The timed release analysis data provide a better understanding of the floatability of the coal sample and the data also provide the best possible flotation performance and the actual flotation separation. Figure 4.3 shows timed release analysis result for coal flotation feed sample: combustible recovery vs product ash. It can be clearly seen that at the product ash of 8.2 % and the combustible recovery of coal is around 58 -59%. The release analysis data also indicates that further cleaning of this coal sample to produce product ash of 5-6 % is much more difficult. This is shown by the behavior of the curve, since the combustible recovery of coal sharply drops down with lowering ash product to less than 6%. During the tests it was observed that little froth was generated and recovery was very slow which revealed a poor floatability of this coal sample.
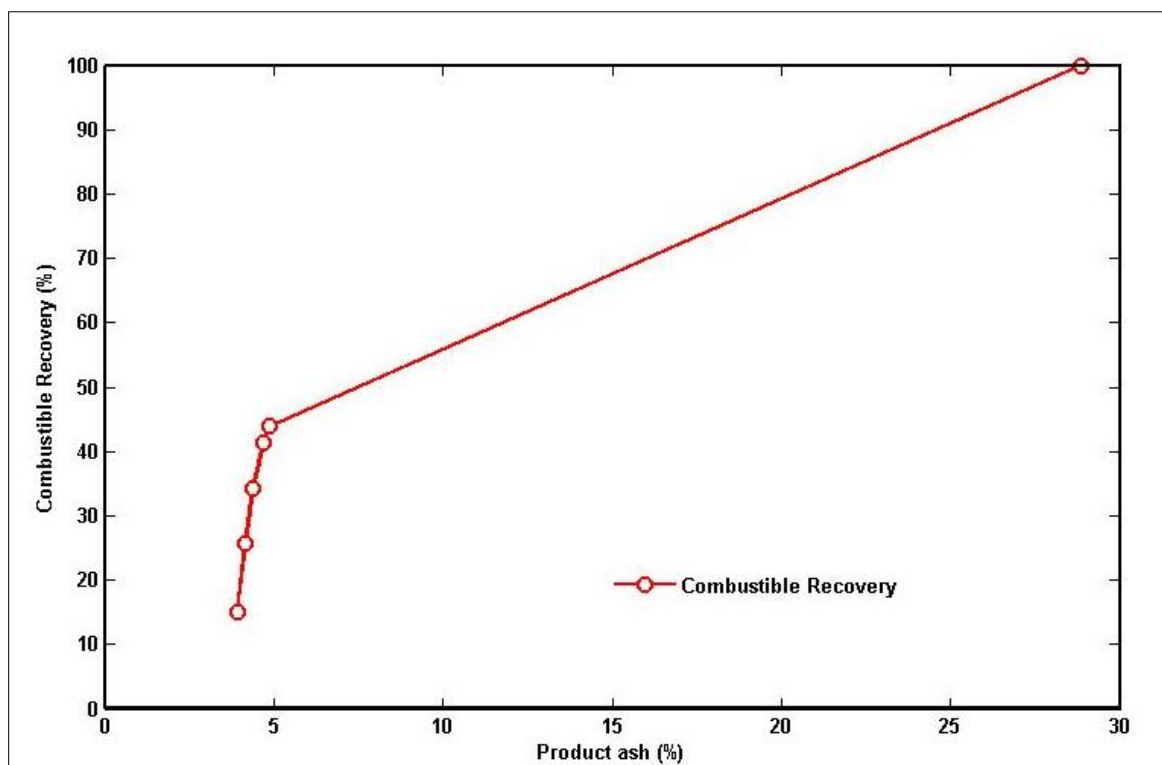
Figure 4.3. Timed release analysis result for coal flotation feed sample

4.3. X-RAY DIFFRACTION ANALYSIS

Coal is a sedimentary rock composed of complex heterogeneous mixture of organic matter and inorganic matter. These inorganic matter composed within the coal matrix are said to affect utilization of coal during cleaning and combustion. In order to understand the effects of these materials, the minerology of the coal must be characterized. X-ray diffraction is the most practical used technique for mineralogical characterization. It used to identify minerals (mineral matter) present in coal, as well as determine the proportion of the amorphous material to the crystalline material in the coal

To evaluate the effects of Al $(OH)_3$-PAM on removal of ash forming minerals to produce clean coal product during froth flotation the flotation feed sample (raw coal sample) was first characterized using XRD analysis to determine the ash forming minerals (mineral matter) present in raw coal samples. For comparison purpose, the froth (clean coal) produced from froth flotation experiments in the presence and absence of Al $(OH)_3$-PAM was also analyzed using XRD to evaluate the effectiveness of Al $(OH)_3$-PAM on reducing the ash forming mineral in raw coal. Froth products obtained at optimum conditions during coal flotation were analyzed. This includes the froth obtained by using the collector and frother only, froth of Al $(OH)_3$-PAM alone, froth of Al $(OH)_3$-PAM with dispersant and the froth of PAM. The proportion of the amorphous material to the crystalline material for each froth sample was determined.

Figure 4.4. and Table 4.4. show both the quantitative and qualitative results of mineral matter composition in raw coal samples obtained using XRD analysis. The proportion of the amorphous material to the crystalline material in the coal sample was found to be 76.2% by weight, while the major crystalline phases observed were FeS_2 (Pyrite), Quartz, Kaolinite $Al_2(Si_2O_5)(OH)_4$, corundum Al_2O_3 and small amounts of calcite $Ca(CO_3)$. The quantitative results of mineral matter composition in the froth for collector and frother alone, Al $(OH)_3$-PAM alone, Al $(OH)_3$-PAM and dispersant, dispersant alone and PAM from XRD analysis are presented in Table 4.5, 4.6, 4.7, 4.8 and 4.9 respectively. It can be seen from proportion of the amorphous material to the crystalline material in the froth obtained from froth flotation experiment using collector and frother alone, Al $(OH)_3$-PAM, Al $(OH)_3$-PAM and dispersant, dispersant alone and PAM was found to be 92.9%, 93.6%, 94%,92.6% and 89.5% respectively.

Table 4.4. Quantitative results scaled to the internal standard for raw coal sample used as flotation feed (-75+38μm). The values (No std.*) are calculated excluding the internal standard. Internal standard phase

Raw Coal (-75+38μm)		
CONTENT	Wt. (%)	No std.
Amorphous	76.2	84.9
FeS_2 (Pyrite)	1.0	1.0
Quartz	5.9	6.6
Kaolinite $Al_2(Si_2O_5)(OH)_4$	4.6	5.2
Corundum, Al_2O_3	10.2	0.0
Calcite, $Ca(CO_3)$	2.1	2.3
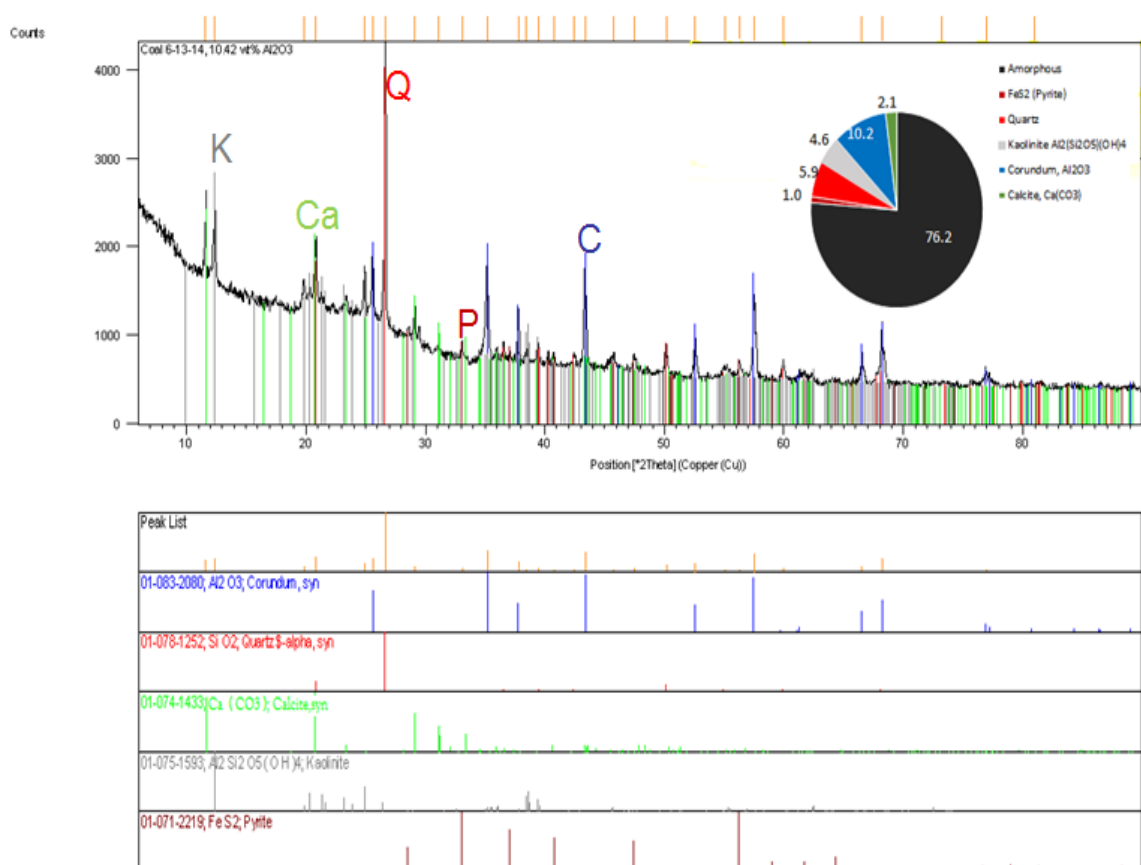
Figure 4.4. XRD analysis spectrums for raw coal sample (-75+38μm)

The major crystalline phases observed in each froth were FeS_2 (Pyrite), Quartz, Kaolinite $Al_2(Si_2O_5)(OH)_4$, and Aluminum Oxide Al_2O_3. The results also shows that the small amounts of calcite $Ca(CO_3)$ that was observed in the raw coal was not identified in the froths obtained from each system tested in this study.

From the results it can be clearly seen that the use of $Al(OH)_3$-PAM together with the dispersant during coal froth flotation produced a more clean coal product with least amount of ash forming minerals than the rest of systems tested in this study while the use of PAM produced a clean product with the highest amount of ash forming minerals. The amount of pyrite, quartz, kaolinite and corundum in the raw coal was found 1.0, 5.9, 4.6, 10.2 % by wt. and concentrate obtained from using $Al(OH)_3$-PAM together with the dispersant was 0.5, 1.9, 0.9 and 2.8 % by w.t respectively. These indicates that pyrite, quartz, corundum and kaolinite were effectively removed from the carbon constituents by the use $Al(OH)_3$-PAM together with the dispersant during coal flotation. The small amount of quartz and pyrite reported in the froth is expected as locked particles in the coal matrix. (Amold and Aplan, 1986) reported that kaolinite and corundum do not affect the floatability of coal more significantly like other clay minerals and it may float along with coal particles during froth flotation.

Table 4.5. Quantitative results scaled to the internal standard for Froth for collector and frother only. The values (No std.*) are calculated excluding the internal standard

Froth for collector and frother only		
CONTENT	Wt. (%)	No std.
Amorphous	92.9	95.5
FeS_2 (Pyrite)	0.6	0.6
Quartz	2.3	2.4
Kaolinite $Al_2(Si_2O_5)(OH)_4$	1.4	1.5
Corundum Al_2O_3	2.8	0.0

Table 4.6. Quantitative results scaled to the internal standard for Froth Al (OH)$_3$-PAM alone. The values (No std.*) are calculated excluding the internal standard

Froth for Al (OH)$_3$-PAM alone		
CONTENT	Wt. (%)	No std.
Amorphous	93.6	96.4
FeS$_2$ (Pyrite)	0.5	0.5
Quartz	2.1	2.1
Kaolinite Al$_2$(Si$_2$O$_5$)(OH)$_4$	1.0	1.0
Corundum Al$_2$O$_3$	2.8	0.0

Table 4.7. Quantitative results scaled to the internal standard for Froth of Al (OH)$_3$-PAM and dispersant The values (No std.*) are calculated excluding the internal standard.

Froth for Al (OH)$_3$-PAM and dispersant		
CONTENT	Wt. (%)	No std.
Amorphous	94	96.7
FeS$_2$ (Pyrite)	0.5	0.5
Quartz	1.9	1.9
Kaolinite Al$_2$(Si$_2$O$_5$)(OH)$_4$	0.9	0.9
Corundum Al$_2$O$_3$	2.7	0.0

Table 4.8. Quantitative results scaled to the internal standard for Froth of dispersant alone. The values (No std.*) are calculated excluding the internal standard.

Froth for dispersant alone		
CONTENT	Wt. (%)	No std.
Amorphous	92.6	94.9
FeS$_2$ (Pyrite)	0.7	0.7
Quartz	2.5	2.6
Kaolinite Al$_2$(Si$_2$O$_5$)(OH)$_4$	1.7	1.8
Corundum Al$_2$O$_3$	2.5	0.0

Table 4.9. Quantitative results scaled to the internal standard for Froth for PAM. the values (No std.*) are calculated excluding the internal standard.

Froth for PAM		
CONTENT	Wt. (%)	No std.
Amorphous	89.5	91.9
FeS$_2$ (Pyrite)	0.7	0.6
Quartz	4.7	4.8
Kaolinite Al$_2$(Si$_2$O$_5$)(OH)$_4$	2.6	2.7
Corundum Al$_2$O$_3$	2.5	0.0

4.4. ZETA POTENTIAL MEASUREMENTS

The role of Al $(OH)_3$-PAM in fine coal flotation was fundamentally explored by examining the surface properties of raw coal and froth after polymer-assisted flotation. Zeta potential measurements were conducted for both clean coal (4% ash), raw coal and concentrate from froth flotation experiments in the absence and presence of Al $(OH)_3$-PAM. Zeta potential of clean coal (4 %ash) and raw coal as a function of increasing and decreasing pH mode was tested as shown in figure 4.5. It can be clearly seen from figure 4.5 that clean coal (4 % ash) exhibits a positive charge at pH range below pH 3 while raw coal has a negative charge over the entire pH range of 2- 11. As the pH was increased from pH 3 to pH 11 the zeta potential of clean coal (4 %ash) becomes more negative. The isoelectric point of clean coal was approximately at pH 3.5. This shows that as pH is decreased below pH 3, the increased amount of hydronium (H^+) ions adsorb on the surface of the coal, causing the surface of the coal to be positively charged. Conversely, increasing the pH above pH 3 the amount of hydroxyl (OH^-) ions increases and they will adsorb on the surface of coal particles replacing the hydronium ions and hence rendering the surface of the coal to be negatively charged. This indicates that changing concentration of hydronium and hydroxyl ions does not only change the magnitude of zeta potential, but also the sign as well. It can also be seen that under the increasing pH value of 2 to 11, the zeta potential of clean coal (4 %ash) possess the most negative charge while that of raw coal is the least negative. The less negative surface charge of raw coal under increasing pH is attributed to the coating of positively charged metal ions such as Mg, Ca and Fe species on negatively charged surface of raw coal particles as compared to clean coal.

Results for zeta potential distribution peaks for clean coal, raw coal, concentrate obtained from froth flotation experiment using, Al (OH)$_3$-PAM and dispersant Al (OH)$_3$-PAM, collector and frother alone dispersant alone and PAM are shown in Figure 4.6, 4.7, 4.8, 4.9, 4.10, 4.11 and 4.12 respectively. The zeta potential distribution peaks for clean coal, raw coal and froth concentrate obtained from collector and frother alone, Al (OH)$_3$-PAM, Al (OH)$_3$-PAM and dispersant, dispersant alone and PAM were centered at -3.6, -46.59,-10.04, -28.1, -32.9, -40.3 and -46.9, respectively. The shift of the peak to a more positive zeta potential value after flotation indicates a significant removal of ash-forming minerals from coal surface by Al(OH)$_3$-PAM.
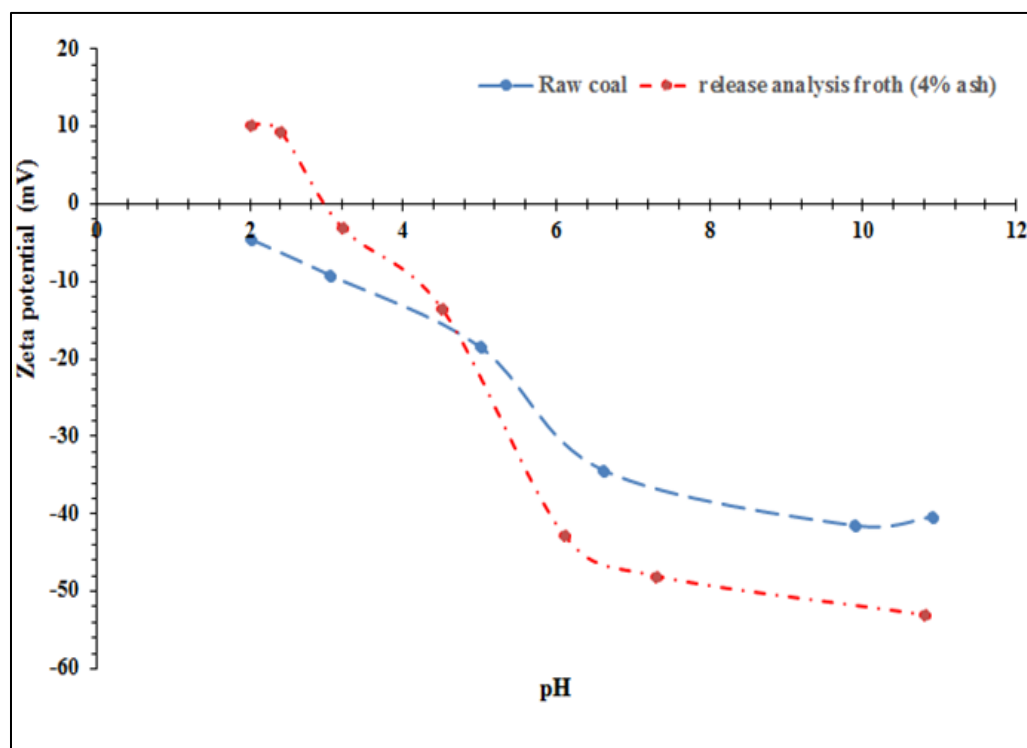
Figure 4.5. Zeta potential Vs pH curve for clean coal (4% ash) and raw coal.
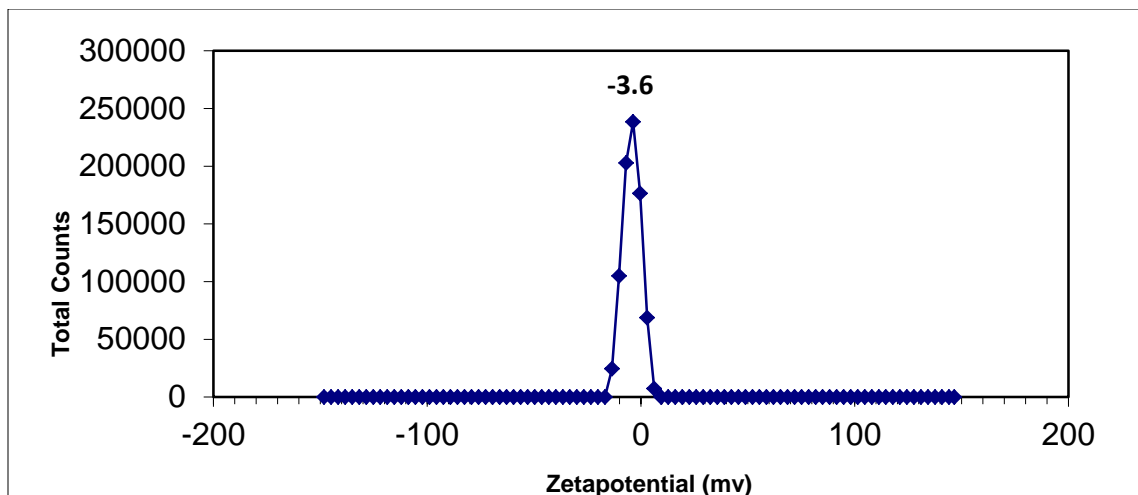
Figure 4.6. Zeta potential measurements for clean coal (4%) at natural pH
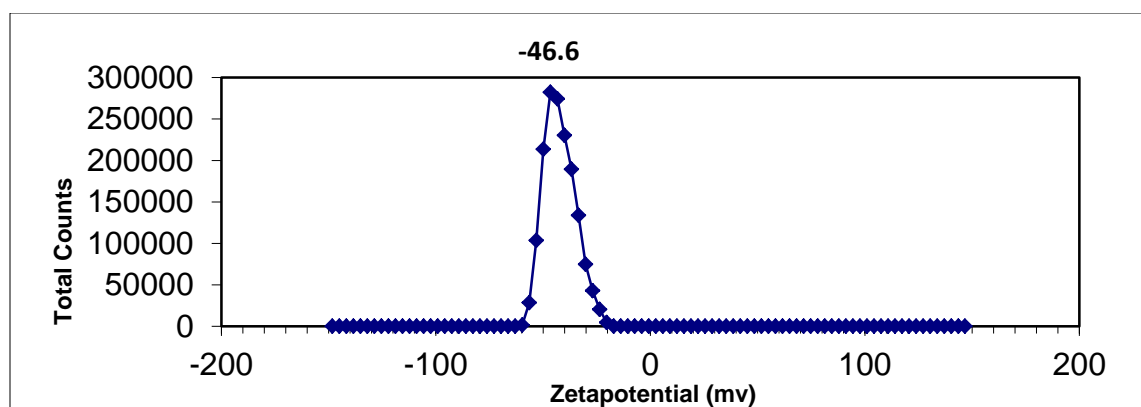
Figure 4.7. Zeta potential measurements for raw coal at natural pH
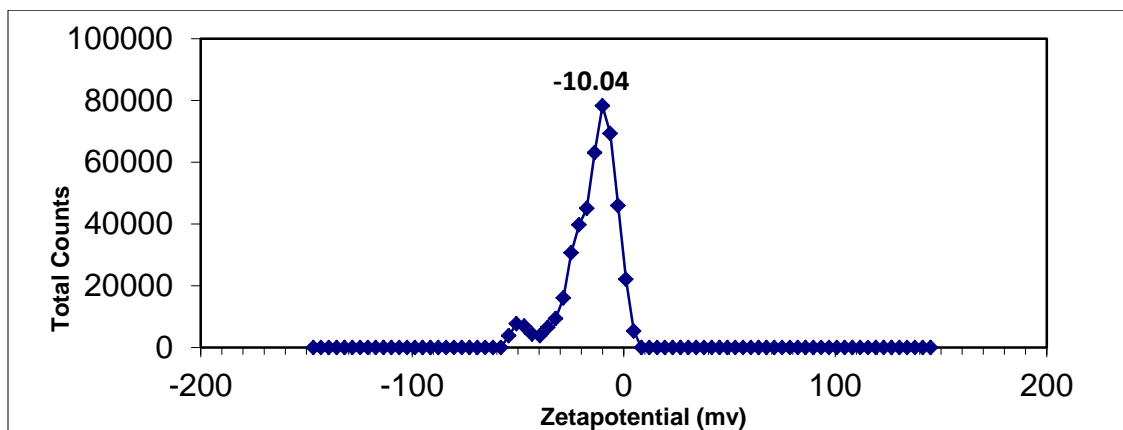
Figure 4.8. Zeta potential measurements for froth of Al-PAM with Dispersant
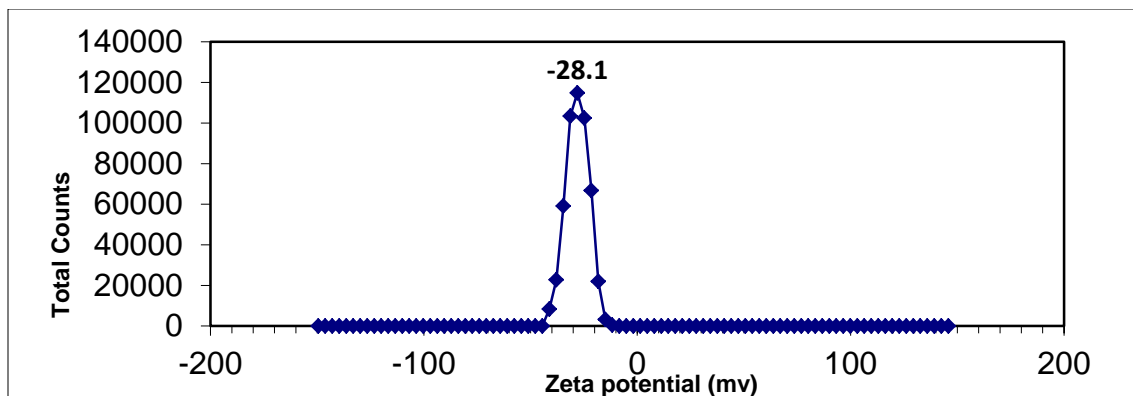
Figure 4.9. Zeta potential measurements for froth of AL-PAM alone
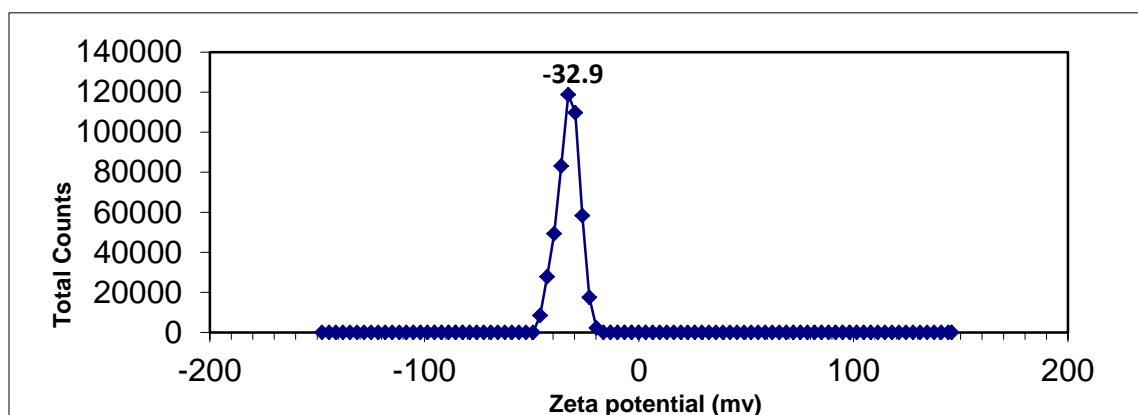
Figure 4.10. Zeta potential measurements for froth of collector and frother only
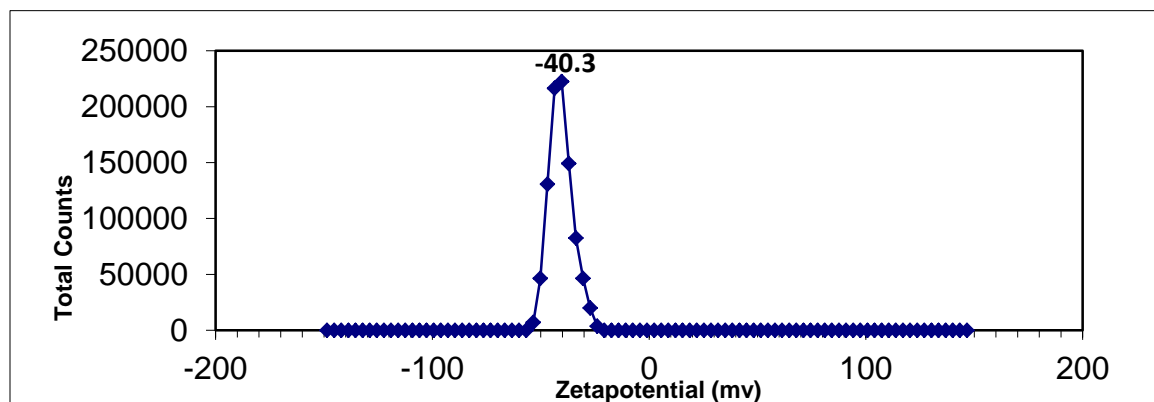
Figure 4.11. Zeta potential measurements for forth of dispersant only
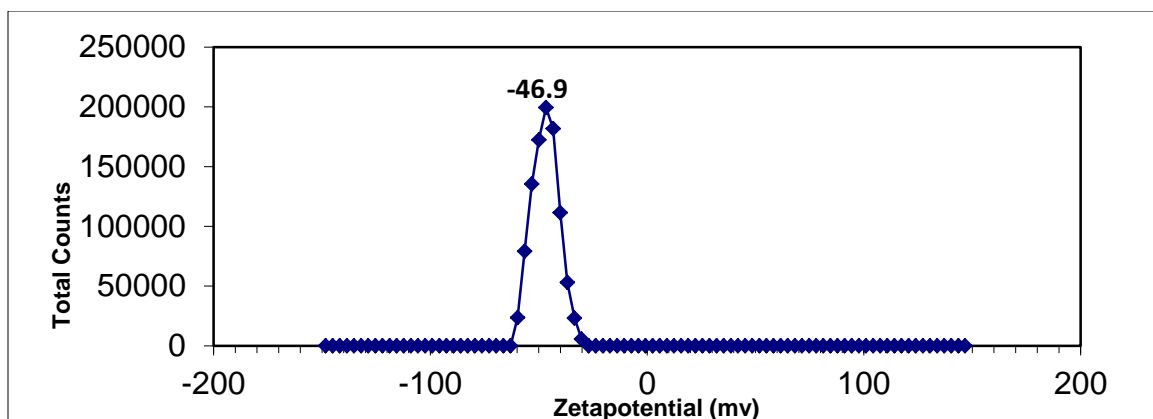
Figure 4.12. Zeta potential measurements for froth of PAM

4.5. BATCH FLOTATION EXPERIMENT

A detailed evaluation of the effect of organic/inorganic (hybrid) polyacrylamide polymer in enhancing combustible recovery and ash depression in fine coal flotation was investigated under various operating conditions. The study was conducted using a D12 Denver batch flotation cell shown in Figure 3.8. The evaluation encompassed varying operating parameters; including organic/inorganic (hybrid) polyacrylamide polymer dosage, polymer conditioning time, impeller speed, dual use of polymer-dispersant system, and lastly, the pH.

After each flotation experiment the float products were dried, weighed and analyzed for ash content. Using these data, the combustible recovery of coal was calculated as follows (Akdemir & Sonmez, 2002).

$$\% \ Combustible \ Recovery \ (coal) = \frac{C(100-c)}{F(100-f)} * 100$$

Where:

C = Weight of concentrate (g)

F = Weight of feed (g)

c = Ash percentage of concentrate

f = Ash percentage of feed

4.5.1. Effects of AL-PAM Dosage. A series of flotation experiments were

conducted to determine the effects of Al-PAM at varying dosages (0.04, 0.08, 0.16, 0.25, 0.5, 1, 2, 3 ppm) on the combustible recovery of coal and ash product. For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes; using an agitation of 1800 rpm. Flotation was carried out at the natural pH of coal, which was measured to be 7.8. The procedure for reagent addition and conditioning can be summarized as follows:

1. Add collector (200 µL).

2. Condition for 3 minutes.

3. Add Al-PAM = (0.04, 0.08, 0.16, 0.25, 0.5, 1, 2, 3 ppm).

4. Condition for 3 minutes.

5. Add frother (300 µL).

6. Condition for 2 minutes.

7. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions.

The baseline experiments (coal flotation with the collector and frother only) results are shown in Figure 4.13 by a 0 ppm dosage of Al-PAM. Experiments were completed periodically throughout the study to define a base recovery/ product ash- dosage relationship and to ensure the reproducibility of the results and congruity of experiment

parameters. Figure 4.13 show that Al-PAM increased the overall combustible recovery of coal by 7.2%. This increase in combustible recovery was observed when a polymer dosage range of 0.04 ppm to 0.25 ppm was used. The combustible recovery of coal at 0.25 ppm dosage of Al-PAM was 66.65% as compared to 59.5% when no Al-PAM was added to the flotation pulp. However, increasing dosage of Al-PAM from 0.04 to 0.08 ppm produced a slight increase in the combustible recovery and the maximum recovery was obtained at 0.25 ppm. The increase in the combustible recovery was due to the adsorption of $Al(OH)_3$ on the surface of slimes by electrostatic attractive forces due to the cationic nature of the polymer. The adsorption of $Al(OH)_3$-PAM led to the reduction of electrostatic repulsion among the mineral particles in the flotation pulp by a partial or complete charge neutralization. The arms (branches) of PAM helped to bridge the particles and flocculate them, which resulted in their settling in the tailing stream. The results also showed that the percentage of ash content in the product ash was slightly decreased by 0.21% at 0.25 ppm of $Al(OH)_3$-PAM. The optimum dosage of Al-PAM was found to be 0.25 ppm.

Increasing the dosage of Al-PAM from 0.5 to 3 ppm resulted in a decrease in the overall combustible recovery of coal from 66.65% to 43.3%. This reduction could have been due to the homo or hetero coagulation of coal particles by polymer molecules if excess polymer were added. The coagulation of coal by Al-PAM was driven by the physical adsorption of the polymer molecules on the surface of coal particles. This physical adsorption could have been due to short range electrostatic attractive forces or hydrogen bonding, or both. Coagulation would result in the settling of coal particles which would eventually decrease the recovery. In addition, the product ash was also

increased as the dosage of Al-PAM was increased from 0.5 to 3 ppm. (heterocoagulation of ash and coal)
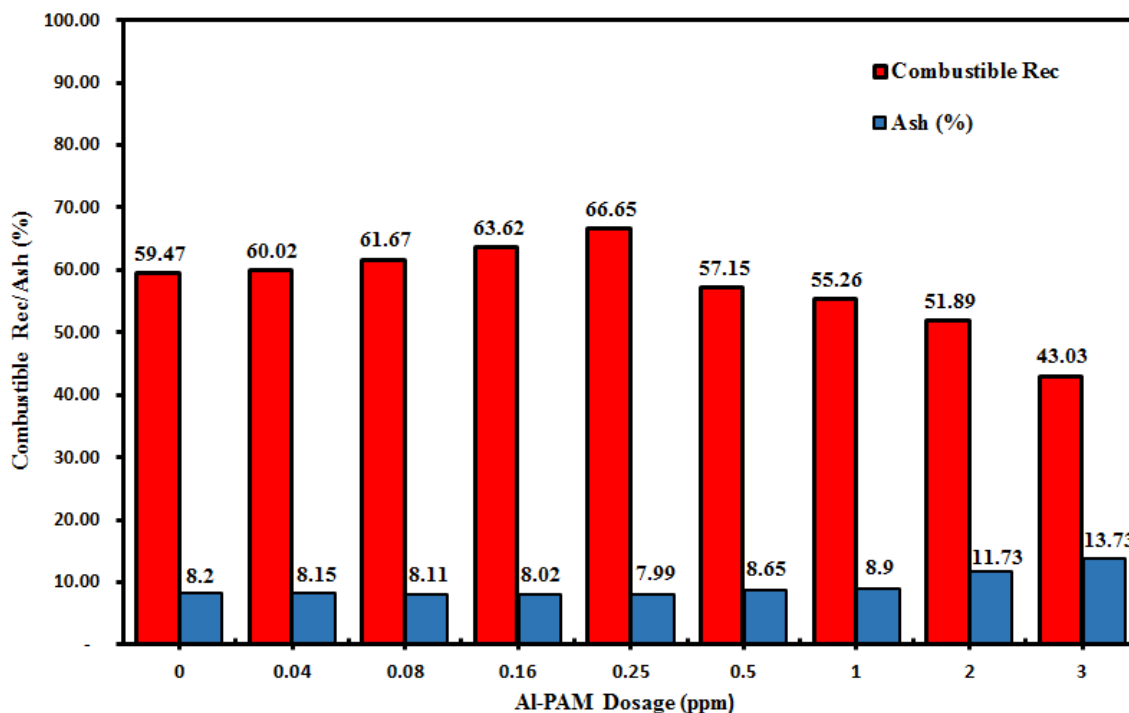
Figure 4.13. Effect of Al-PAM dosage on the combustible recovery of coal and the product ash

4.5.2. Effects of Using Dispesant Alone. Coal flotation was conducted in the presence of ash dispersant in order to investigate the possibilty to optimize the flotation performane. Sodium metasilicate was the dispersant used in this study, and it was selected because it was reported in the litereture to be one of the most effective dispersants for coal flotation (Raleigh and Aplan, 1993). A set of flotation experiments was conducted to evaluate the effects of the dispersant (sodium metasilicate) on the combustible recovery of coal and product ash. The results are shown Figure 4.14. For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12

Denver cell and conditioned for 5 minutes; using an agitation of 1800 rpm. Flotation was carried out at the natural pH of coal, which was measured to be 7.8. The procedure for reagent addition and conditioning can be summarized as follows:

1. Add a dispersant = 0.2, 0.5, 0.8, 1.2, 1.5 ppm

2. Condition for 3 minutes

3. Add collector (200 μL)

4. Condition for 3 minutes

5. Add frother (300 μL)

6. Condition for 2 minutes

7. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

A control experiment was performed for background (coal flotation with collector and frother only) with no dispersant added, as shown in figure 4.14. The combustible recovery of coal and product ash for the background test were 59.58% and 8.2 %, respectively. As seen from Figure 4.14, addition of dispersant (sodium metasilicate) during the froth flotation from 0.2 up to 0.8 ppm improved the overall combustible recovery of coal from 59.58 % to 64.80%. In general, adding dispersant in the coal flotation incresed the combustible recovery of coal more in the float product than it did in the background tests. Therefore, it can be deduced that a dosage of 0.2 to 0.8 ppm of sodium metasilicate could disperse clay slimes and eliminates slime coating. This would prevent the floating of high ash-forming particles. Bulatovic et al., proposed that sodium metasilicate disperses clay slimes by two mechanisms. One mechanism is the dispersion of clay particles due to electrostatic repulsion. This repulsion is due to the presence of free polysilic acid, which

is ionized partially. The consequent adsorption of these ions on the surface of clay particles increases the density of the negative charge and lead to repulsion. The other mechanism is that sodium metaslicate adsorbs on the clay particle surface which forms a hydrated layer on the surface leading to an increased negative charge (Bulatovic, 2007). The increased combustible recovery of coal at a dosage of 0.2 to 0.8 ppm is likely due to the dispersive effect, which allows hydrophobic coal particles to freely float. The increase in the combustible recovery of coal in the presence of the dispersant alone was smaller compared to the case when floation was carried out using Al-PAM alone as shown in Figure 4.13. Adding Al-PAM to coal the flotation pulp increased the combustible recovery of coal by 7.2% while the dispersant increased the recovery by 5 %. The froth quality of Al-PAM was better than that of the dispersant alone, which was 8.02% for Al-PAM and 8.11% for the dispersant.

The results also showed when the dosage of sodium metasilicate (dispersant) increased from 1.2 to 1.5 ppm, the combustible recovery of coal dreceased but the product ash content increased. These findings were not suprising since most of the limited literature available about fine coal flotation indicated that moderate to high levels of coal depression could be expected when sodium metasilicate is added in excess. However, more recent studies have proven that the depression of coal during flotation in the presence of sodium metasilicate can be minimized by adding relatively low dosages of the dispersing agents.

The product ash was slightly contaminated in the presence of sodium metasilicate (dispersant). Similar results were obtained in literatue. Zolghadri et al., ,2012 concluded that the froth contamination was likely because of the dispersion of coagulates that

consisted of high ash non-hydrophobic particles and low ash hydrophobic particles. Due to the presence of low ash hydrophobic parts on coagulates, high ash particles could be transferred to froth through adhession of coagulates to bubbles. The optimum dosage of dispersant with the highest combustible recovery of coal (64.80%) was found to be 0.8 ppm.

The product ash was slightly contaminated in the presence of sodium metasilicate (dispersant). Similar results were obtined in literatue. Zolghadri et al., ,2012 concluded that the froth contamination was likely because of the dispersion of coagulates that consisted of high ash non-hydrophobic particles and low ash hydrophobic particles. Due to the presence of low ash hydrophobic parts on coagulates, high ash particles could be transferred to froth through adhession of coagulates to bubbles(Zolghadri, 2012). The optimum dosage of dispersant with the highest combustible recovery of coal (64.80%) was found to be 0.8 ppm.

4.5.3. Effect of Dual Use of Al-PAM and Dispersant System. Baseline experiments were first conducted to evaluate the potential use of a dual dispersant- Al-PAM system to improve the combustible recovery of coal and ash depression during coal flotation. First, floatation experiments were conducted using Al-PAM alone at various dosage levels. This was done mainly to obtain the optimum dosage of Al-PAM. The second step was to conduct a flotation experiment at the optimum dosage Al-PAM with varying dosages of the dispersant (sodium metasilicate). The dosage of Al-PAM was kept constant throughout the experiments. The dosage of Al-PAM was 0.25 ppm, which was found to be the optimum dosage from Figure 4.13.
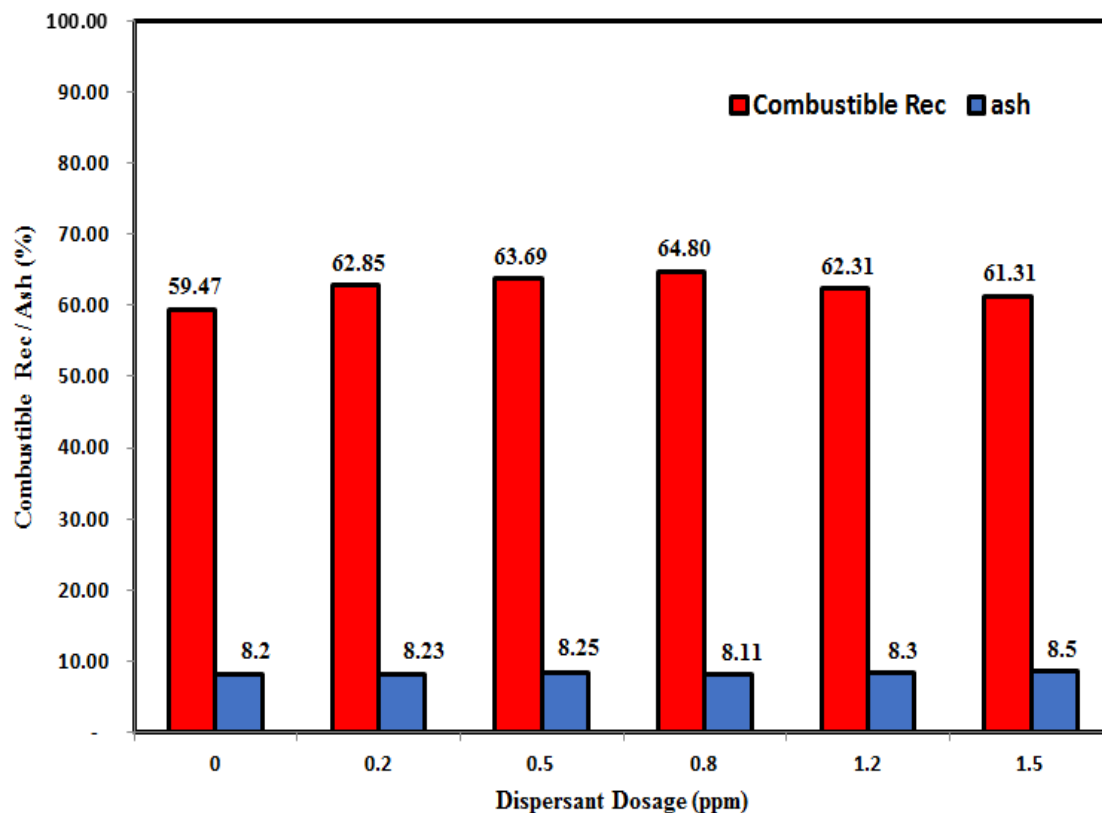
Figure 4.14. Effects of dispersant dosage on the combustible recovery of coal and product ash

Additional floatation experiments were conducted to compare the effects of using a dual dispersant-Al-PAM system to those of using a dispersant alone. For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes using an agitation of 1800 rpm. Flotation was carried out at the natural pH of coal, which was measured to be 7.8. The procedure for reagent addition and conditioning can be summarized as follows:

1. Add a dispersant = 0.2, 0.5, 0.8, 1.2, 1.5 ppm

2. Condition for 3 minutes

3. Add collector (200 μL)

4. Condition for 3 minutes

5. Add Al-PAM = 0.25 ppm

6. Condition for 3 minutes

7. Add frother (300 μL)

8. Condition for 2 minutes

9. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

Figure 4.15 shows the results of coal froth flotation in the presence of a dual Al-PAM with sodium metasilicate (dispersant) system. As shown in Figure 4.15, the overall combustible recovery of coal was improved using the dual dispersant- depressant system. The combustible recovery of coal was improved from 59.47% to 64.39% using the dual dispersant–Al-PAM system at dosages between 0.2 and 0.8 ppm. A similar trend was observed between dosages of 0.2 and 0.8 ppm when these results were compared to the results obtained when the dispersant was used alone. However, the combustible recovery of coal from the dispersant was alone increased from 57% to 64.80%, which was slightly higher than that of the dual dispersant-depressant system. It is believed that the use of the dual dispersant- Al-PAM system causes slight coal depression. The reason for this may be that, since the sodium metasilicate was added into the suspension before Al-PAM, it might have caused coal depression by adsorbing the coal surfaces. Further slight coal depression was due to Al-PAM. The optimum combustible recoveries of coal for the baseline test (with the collector and frother only), Al-PAM alone, dispersant alone and the dual Al-PAM-dispersant system are 59.47%, 64.80%, 66.35% and 64.39% respectively.

Unlike the findings about the combustible recovery, the overall product ash was greatly improved when the dual dispersant- Al-PAM system was used (compared to the cases in which the dispersant alone or Al-PAM alone were used). The product ash with 7.74% ash content was obtained when dual dispersant- Al-PAM system was used while it was 8.11% for the dispersant alone. The reason for this behavior is that, when adding sodium metasilicate in the suspension prior to adding Al-PAM, it will dissociates to produce highly electronegative anionic species, and these anions electrostically adsorb strongly on ash-forming minerals and to a lesser extent, on coal particles, and causes the charge density in the electrical double layer around the coal and ash-forming mineral particles to increase. This results in an increase in elecrical repulsion which makes the coal and ash forming mineral particles well dispersed in the suspension. The dispersion effect of sodium metasilicate allows Al-PAM to easily adsorb on the surface of high ash forming minerals (slimes) and flocculates them. This will eventually decrease the entrainment of ash particles in the froth layer.

4.5.4. Effects of Impeller Speed. Impeller rotation speed is one of the main parameters in froth flotation that provides the energy necessary for successful flotation of a hydrophobic coal particle within the flotation cell. Therefore it is considered to be the heart of the flotation cell. Controlling of the impeller speed is said to be significant for improving the overall flotation performance. To better understand the effect of hydrodynamics on the flotation performance, coal flotation experiments was carried out at various impeller speeds of 1200, 1500, 1800 and 2100 rpm in the presence and absence of inorganic-organic hybrid polymers so as to obtain the optimum rotational speed for

improved flotation performance. First, a set of baseline froth flotation experiments was conducted in the absence of Al-PAM at various impeller rotational speeds.
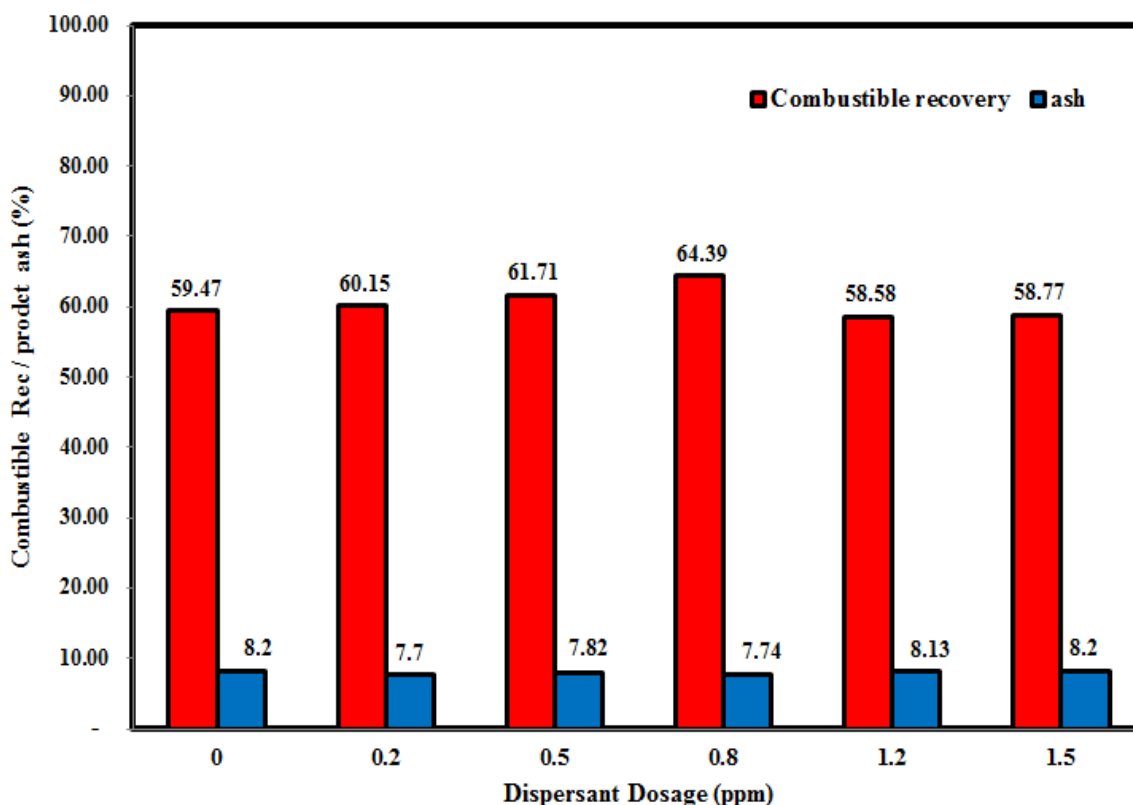
Figure 4.15. Effects of dual Al-PAM- dispersant system on the combustible recovery of coal and product ash.

The baseline flotation experiments were carried out using kerosene (as a collector) and MIBC (as a frother) alone with varying impeller rotation speed. It should be noted that the collector and the frother dosages were kept constant throughout the experiments at 200 μL and 300 μL respectively. Flotation tests in the presence of Al-PAM alone, Al-PAM -dispersant system at optimum dosages was also established at various impeller speeds and compared to the baseline at various impeller speeds.

4.5.4.1. Baseline tests (collector and frother only). Figure 4.16 depicts the

effects of impeller speed on the combustible recovery of coal and the product ash in the

absence of Al-PAM or a dispersant. For each experiment, 253g of coal and 4800 ml of

tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes; using

an agitation of 1200, 1500, 1800 and 2100 rpm. Flotation was carried out at the natural

pH of coal, which was measured to be 7.8. The procedure for reagent addition and

conditioning can be summarized as follows:

1. Add collector = 200 µL.

2. Condition for 3 minutes

3. Add frother = 300 µL

4. Condition for 2 minutes.

5. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute
   interval. Collect 5 fractions.

Figure 4 .16 shows that the combustible recovery of coal was increased with increasing

impeller speed. The recovery of coal was increased from 47.29 % at 1200 rpm to 64.42%

at 2100 rpm. This increase in combustible recovery was due to the fact that increasing

agitation speed tends to increase the energy in the cell. Hence, the momentum of coal

particles also increases, which improves the probability of collision and attachment to air

bubbles. This result correlated with the results obtained by Smith and Warren, (1989) and

Tao, (2000). They both conducted flotation of coal at various impeller rotational speeds

and found out that higher combustible recoveries of coal were obtained at higher impeller

rotational speed. It can also be seen that at a lower impeller rotation speed of 1200 rpm a

cleaner coal product with ash content of 8.75% can obtained. However, increasing the

impeller speed further to 1800 rpm slightly decreased the product ash content to 8.2%. It was also observed that further increasing of the impeller rotational speed to 2100 rpm has led to the slight increase of froth ash to 8.33%. The slight decrease in the product ash content at impeller speeds between 1500 and 1800 rpm was a result of the increased froth stability and increased flotation recovery of less hydrophobic particles in that range. The literature has shown that only when the impeller is adjusted accordingly with an increasing airflow rate does it result in an increase in coal recovery without increasing the product ash content. This might be the case for the observation in this study when the impeller speed was increased from 1200 to 1800 rpm.(Makdemir & Sonmez, 2002)

The higher product ash content and lower combustible recovery of coal at lower impeller rotation speed were due to the insufficient dispersion of air, poor emulsification and dispersion of reagents, which resulted in inadequate bubble-particle attachment in the slurry and reducing the flotation rates constants. The optimum performance was found to be at 1800 rpm with product ash of 8.2% and combustible recovery of 59.47%.

4.5.4.2. Effects of impeller speed on flotation in the presence of Al-PAM.

Flotation experiments in the presence of Al-PAM were conducted at various impeller rotation speeds to further investigate the effects Al-PAM on combustible recovery and product ash of coal. It should be noted that the Al-PAM dosage was kept constant at 0.25 ppm throughout the experiments. The impeller rotational speed was varied so as to obtain the optimum speed. Figure 4.17 shows the effects of impeller speed on the combustible recovery and product ash of coal in the presence of Al-PAM at an optimum dosage of 0.25 ppm. The results showed that increasing the impeller rotational speed led to an increase in the combustible recovery of coal.
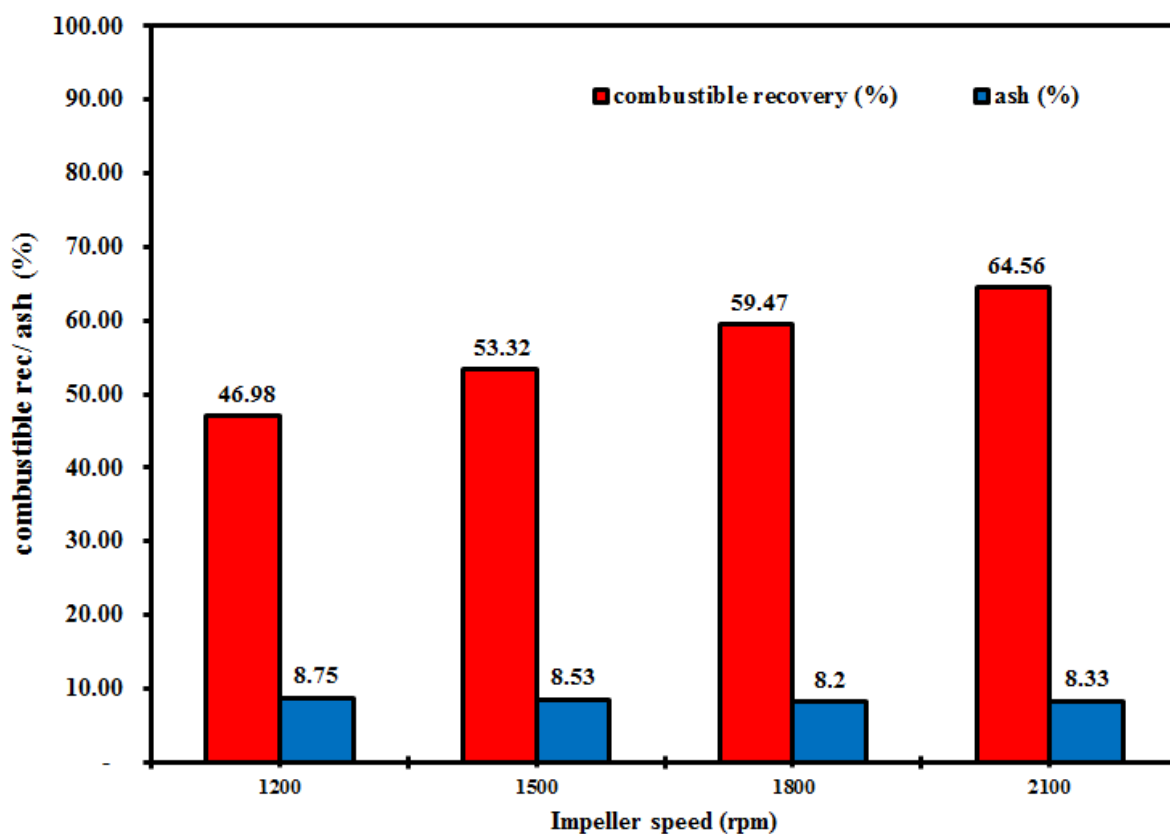
Figure 4.16. Effect of impeller speed on combustible recovery and product ash in the presence of collector and frother only

Comparing these results with the results obtained from baseline tests (flotation in the absence of Al-PAM) shows that the overall combustible recovery and product ash of coal were improved more by adding of Al-PAM in the flotation pulp than in the absence of Al-PAM. The combustible recoveries of coal in the presence of Al-PAM and for baseline tests   were 51.70%, 46.98% at 1200 rpm, 58.49%, 53.32% at 1500 rpm, 66.80%, 59.47% at 1800 rpm and 68.42%, 64.56% at 2100 rpm.

The product ash was also improved more by addition of Al-PAM in the flotation pulp than in the absence of Al-PAM (baseline tests). High products ash content was observed at lower impeller rotational speeds while lower product ash contents was observed at high impeller speed. The optimum impeller rotation speed was found to be at 1800 rpm with the lowest product ash of 7.99 % and combustible recovery of 66.80%.

4.5.4.3. Effects of impeller speed in the presence of dual Al-PAM/ dispersant.

Flotation experiments in the presence of Al-PAM-dispersant dual system were conducted at various impeller rotation speeds to further investigate the effects of Al-PAM on combustible recovery and product ash of coal. For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes; using an agitation of 1200, 1500, 1800 and 2100 rpm. Flotation was carried out at the natural pH of coal, which was measured to be 7.8. The procedure for reagent addition and conditioning can be summarized as follows:

1. Add dispersant = 0.8 ppm
2. Condition for 3 minutes
3. Add collector = 200 μl
4. Condition for 3 mintes
5. Add Al-PAM = 0.25 ppm
6. Condition for 3 minutes
7. Add frother = 300 μl
8. Condition for 2 minutes
9. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

Figure 4.18 shows the effects of dual dispersant- Al-PAM system on combustible recovery and product ash of coal at various impeller rotational speeds. It can be see form the graph that addition of Al-PAM together with the dispersant greatly improved the overall combustible recovery of coal more so than baseline experiments (collector and frother only).
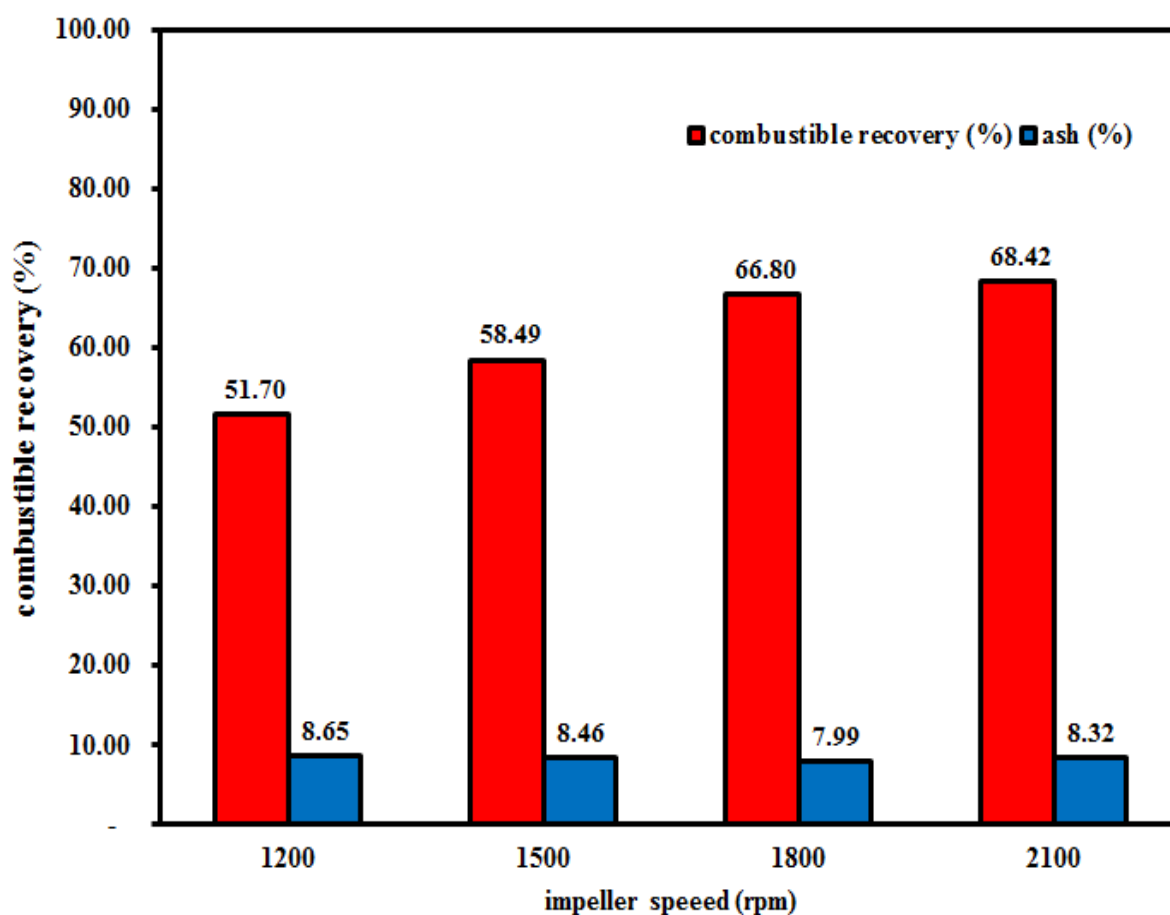

Figure 4.17. Effects of Impeller speed on combustible recovery and product ash the presence of AL-PAM

The overall combustible recovery of coal was increased to 64.56% when the collector and frother were used alone, while, for dual dispersant- Al-PAM system it was increased to 65.41%. However, the overall combustible recovery was greatly improved when Al-PAM was used alone than when Al-PAM was used together with a dispersant and when only the collector and frother were used.

The results also showed that the addition of Al-PAM together with dispersant improved the product ash content more than when Al-PAM was alone and baseline test. The best product ash content of 7.74% was obtained at an impeller speed of 1800 rpm and a dosage 0.25 ppm and 0.8 ppm of Al-PAM and sodium metasilicate respectively.

4.5.5. Polymer Conditioning Time. Reagent conditioning plays a dominant Role in the overall performance of the flotation process, and it has been recognized for some time as an important methodology to improve the performance of the flotation process. Gaudin et al., concluded that reagents conditioning allows regents to be uniformly distributed within the suspension. Hence it will improve the collision and adhesion of distributed reagents with coal particles.

Flotation experiments were performed at optimized conditions of previous tests (polymer dosage, polymer addition method, and dual dispersant-depressant system and impeller speed) at various conditioning time in order to investigate the effects of polymer conditioning time on the combustible recovery and product ash of coal. Previous flotation experiments showed that optimum conditions were found to be at impeller speed of 1800 rpm, adding polymer after collector and using polymer together with a dispersant. It should be noted that all other parameters such as polymer dosage, impeller speed and dispersant dosage were kept constant throughout the experiments except the polymer

conditioning time which was varied at 0, 3 , 6 and 9 minutes. The results of the combustible recovery and product ash of coal as a function of polymer conditioning time are shown in Figure 4.19. The combustible recovery of coal was initially increased with the increase in conditioning time, until it reached a maximum of 3 minutes. The combustible recovery at zero conditioning time is 59.53% and it increased to 64.39% with an increase in polymer conditioning time to 3 minutes. It can also be seen that the combustible recovery was slightly decreased to 63.92% and 61.97% respectively as polymer conditioning time was further increased to 6 and 9 minutes. The results also showed that a cleaner coal product with lower ash content was obtained as the polymer conditioning time was increased. The optimum conditioning time was found to be at 6 minutes with combustible recovery of 63.92% and product ash of 7.5%.

4.5.6. Effects of pH. It was explained that pH is one of the most important factor in controlling slime coating due to electrostatic attraction between the ash forming minerals and coal particles. For this reason, changing the pulp pH to a weakly acidic pulp pH of 5 made the coal surface slightly less negative and the possible electrostatic attraction between coal particles and the polymer become weaker which results in an increase in the combustible recovery. Experiments were conducted at slightly acidic pH of 5 to further investigate the effects of Al-PAM on coal flotation. Flotation parameters that were investigated were the Al-PAM dosage and the use of dual dispersant-depressant system. Other parameters such as impeller speed and polymer conditioning time were kept constant throughout the experiments at 1800 rpm and 6 minutes.

First, baseline flotation experiments (collector and frother only) were conducted at a pH of 5 for comparison. It should be noted that the collector and frother dosages were

kept constant throughout the experiments at 200 and 300 µL, respectively. In addition, baseline experiments where dispersant (sodium metasilicate) was used with the collector and frother were also conducted for comparison with the use of a dual dispersant-depressant system.
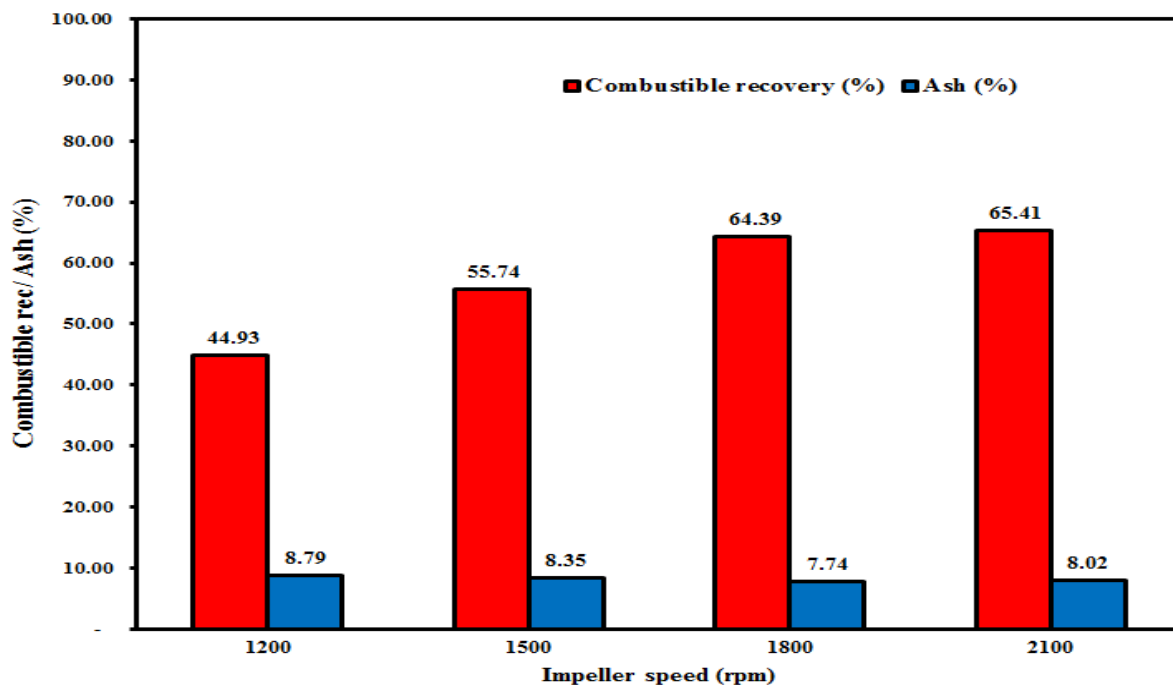
Figure 4.18. Effects of Impeller speed on combustible recovery and product ash in the presence of dual Al-PAM- Dispersant.

4.5.6.1. Effects of AL-PAM dosage at pH 5. The effects of Al-PAM dosage on the combustible recovery coal at a pH of 5 and pH 7.8 are shown in Figure 4.20 while Figure 4.21 shows effects of Al-PAM dosage on product ash at a pH of 5 and pH 7.8. The Combustible recovery and product ash were plotted as a function of Al-PAM dosage. For comparison purpose the results of the effects of Al-PAM on the combustible recovery and product ash at natural pH of 7.8 are plotted on the same graph as shown in Figure 4.20 and 4.21.
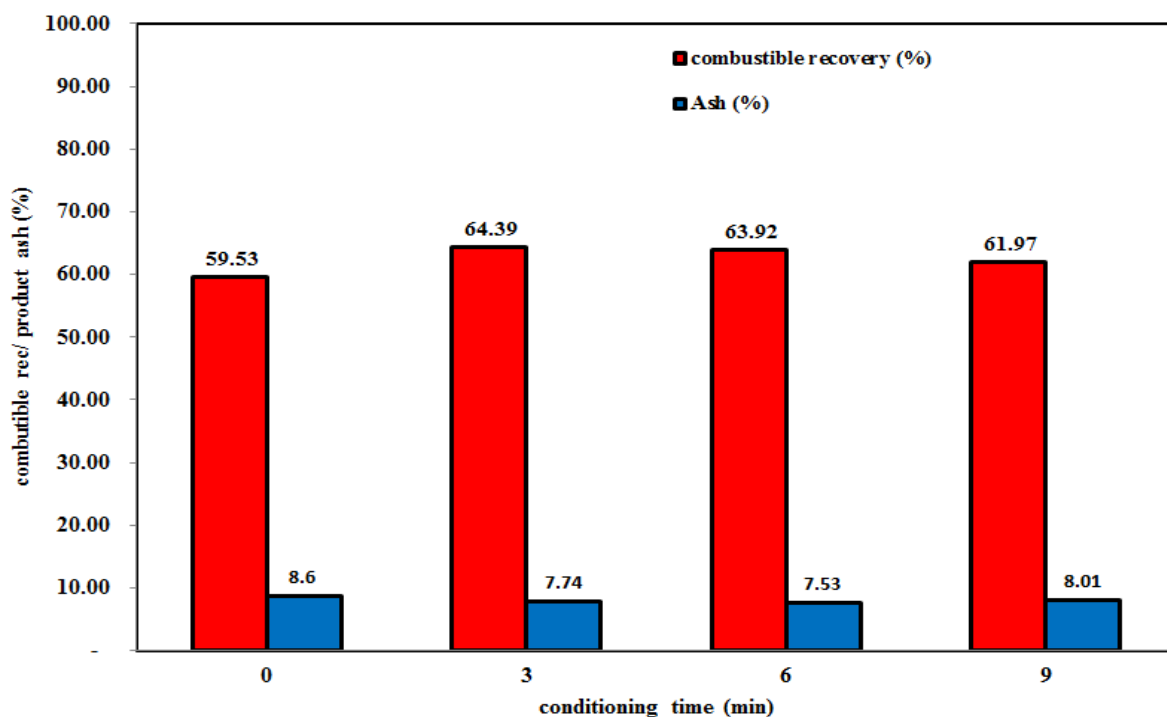
Figure 4.19. Effects Al-PAM conditioning time on combustible recovery of coal and product ash

For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes at an agitation of 1800 rpm. HCL was then added to the pulp to adjust the pulp pH to 5. The procedure for reagent addition and conditioning is summarized as follows

1. Add collector (200 μL).

2. Condition for 3 minutes.

3. Add Al-PAM = (0.04, 0.08, 0.16, 0.25 and 0.5, ppm)

4. Condition for 6 minutes.

5. Add frother (300 μL)

6. Condition for 2 minutes.

7. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

It can be seen from Figure 4.20 that the combustible recovery of coal increased by adding of Al-PAM at a pH of 5. The combustible recovery of coal for baseline tests (collector and frother only) at a pH of 5 was 70.40 % which was much higher than the baseline test (natural pH of 7.8 which was 59.47%). The results also showed that as Al-PAM dosage was increased from 0.04 to 0.16 ppm at a pH of 5, the combustible recovery of coal was also increased from 72.06% to 77.86%. The observed trend at a pH of 5 was much similar to the trend at a natural pH of 7.8. However, the increase in combustible recovery of coal was much higher at a pH of 5 than at natural pH of 7.8. The reason for this was that decreasing pulp pH to a weakly acidic pulp pH of 5 made the coal surface slightly less negative. The possible electrostatic attraction between coal particles and the polymer became weaker, which resulted in an increase in the combustible recovery. Further increasing the dosage of Al-PAM from 0.16 ppm to 0.5 ppm resulted in a decrease in the combustible recovery of coal. Similar effects were observed at a natural pH of 7.8. The reason for the decrease in combustible recovery of coal at both pH values was mainly due to homo or hetero coagulation of the coal particles by polymer molecules when excess polymer was added.

4.5.6.2. Effects of dispersant alone at a pH of 5. To investigate the effects of the dispersant (sodium metasilicate) on the combustible recovery coal and product ash at a pH of 5, flotation experiments were conducted as follows. About 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes at an agitation of 1800 rpm. HCL was added to the pulp to adjust the pulp pH to 5.
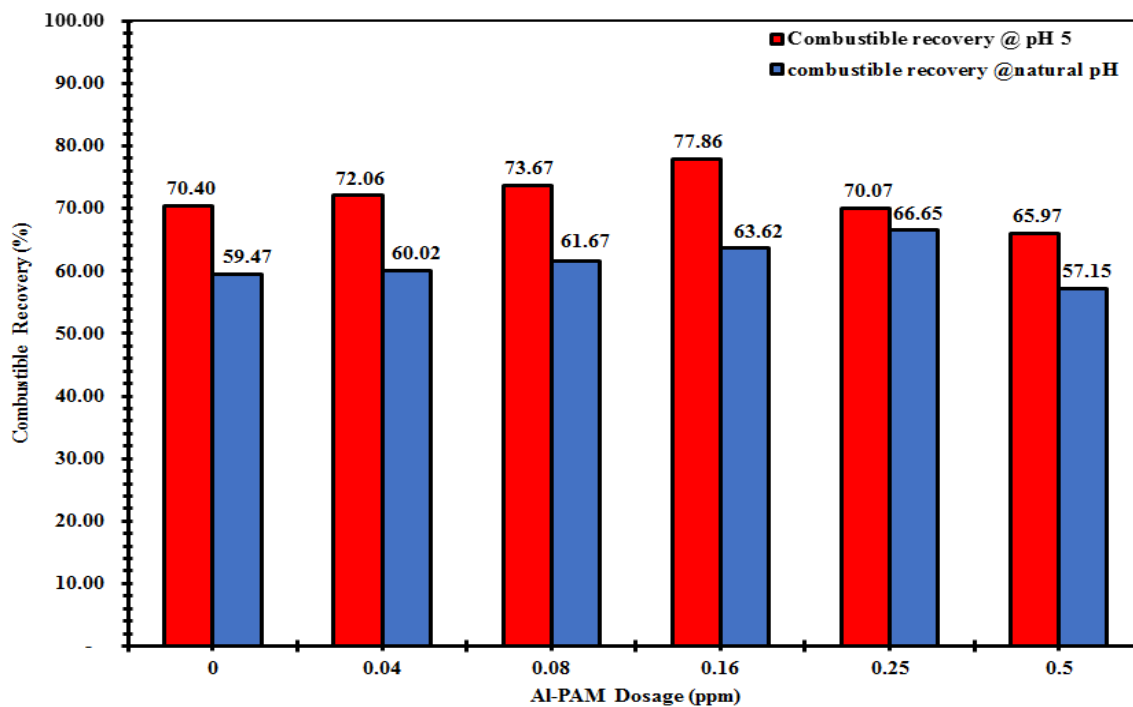
Figure 4.20. Effects of Al-PAM dosage on combustible recovery of coal
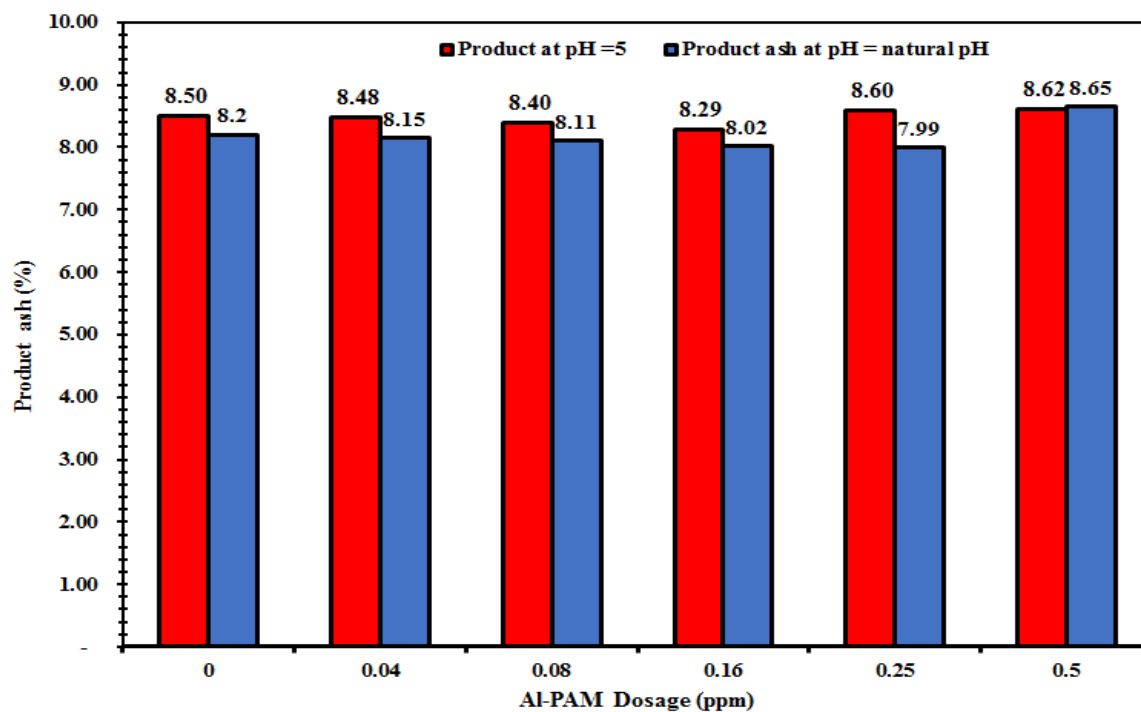at a pH of 5 and pH 7.8

Figure 4.21. Effects of Al-PAM dosage on product ash at a pH of 5 and pH 7.8

The procedure for reagent addition and conditioning can be summarized as follows;

1. Add dispersant = (1, 2.5, 4, 5.5, 7 mL)

2. Condition for 3 minutes

3. Add collector = 200 µl

4. Condition for 3 minutes

5. Add frother = 300 µl

6. Condition for 2 minutes.

7. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

The results of the effect of dispersant alone at pH 5 on combustible recovery of coal are depicted in Figure 4.22. For comparison purpose the results of the effects of dispersant alone at natural pH of 7.8 are plotted on the same graph as shown in Figure 4.22. It can be seen that addition of dispersant to flotation pulp at pH 5 depressed the coal hence decreasing the overall combustible recovery of coal. The combustible recovery of coal for baseline test (collector and frother only) was 70.40% and it was decreased to 57.15% when dispersant was added. Comparing these results to the results obtained when dispersant was added to flotation pulp at natural pH of 7.8 it can be concluded that dispersant at natural was much better than at pH 5. The reason for the observed decrease in combustible recovery of coal at pH 5 in the presence of sodium metasilicate is that at lower pH sodium metasilicate dissociates to form colloidal silica gels. These colloidal silica gels are said to be negatively charged at acidic pH hence they will adsorb on the positively charged coal surfaces rendering them hydrophilic. This is in agreement with the results obtained in literature by (fuerstenau, 1968).

Figure 4.23 shows the effects of dispersant on the product ash at pH 5. For comparison purpose the results of the effects of dispersant alone on product ash at natural pH of 7.8 are plotted on the same graph as shown in figure 4.23. As can be seen form Figure 4.23 product ash with higher amount of ash content was obtained in the presence of sodium metasilicate at pH 5 than at natural pH of 7.8. The reason for this is that at pH 5 sodium metasilicate depressed the coal thus allowing ash forming minerals to float.

4.5.6.3. Effects of dual Al-PAM- dispersant system at pH 5. To investigate

The effectiveness of dual dispersant-depressant system on the combustible recovery and product ash at pH of 5, a set of flotation experiments were conducted as follows. About 253g of coal and 4800 ml of tap water were first placed in a 5 liter D12 Denver cell and conditioned for 5 minutes, using agitation at 1800 rpm. HCL was added to the pulp to adjust the pulp pH to 5. The procedure for reagent addition and conditioning can be summarized as follows;

1. Add dispersant = 0.8 ppm

2. Condition for 3 minutes

3. Add collector = 200 μl

4. Condition for 3 minutes

5. Add Al-PAM = 0.16 ppm

6. Condition for 6 minutes

7. Add a frother = 300 μl

8. Condition for 2 minutes

9. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions.
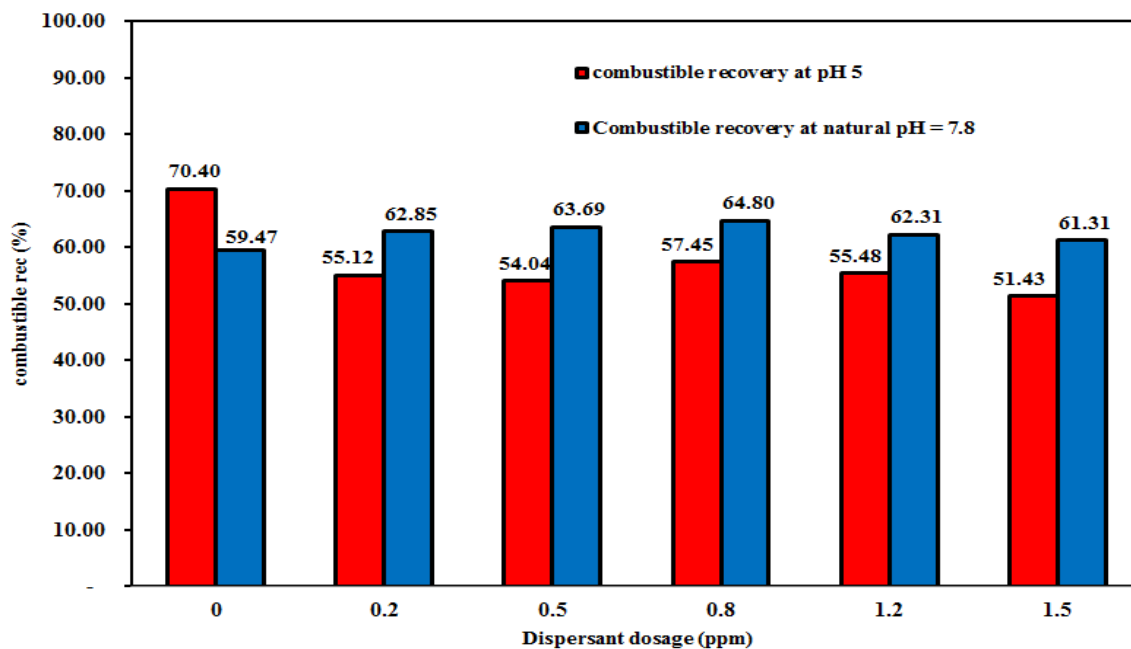
Figure 4.22. Effects of dispersant alone on the combustible recovery of coal at pH 5 and pH 7.8.
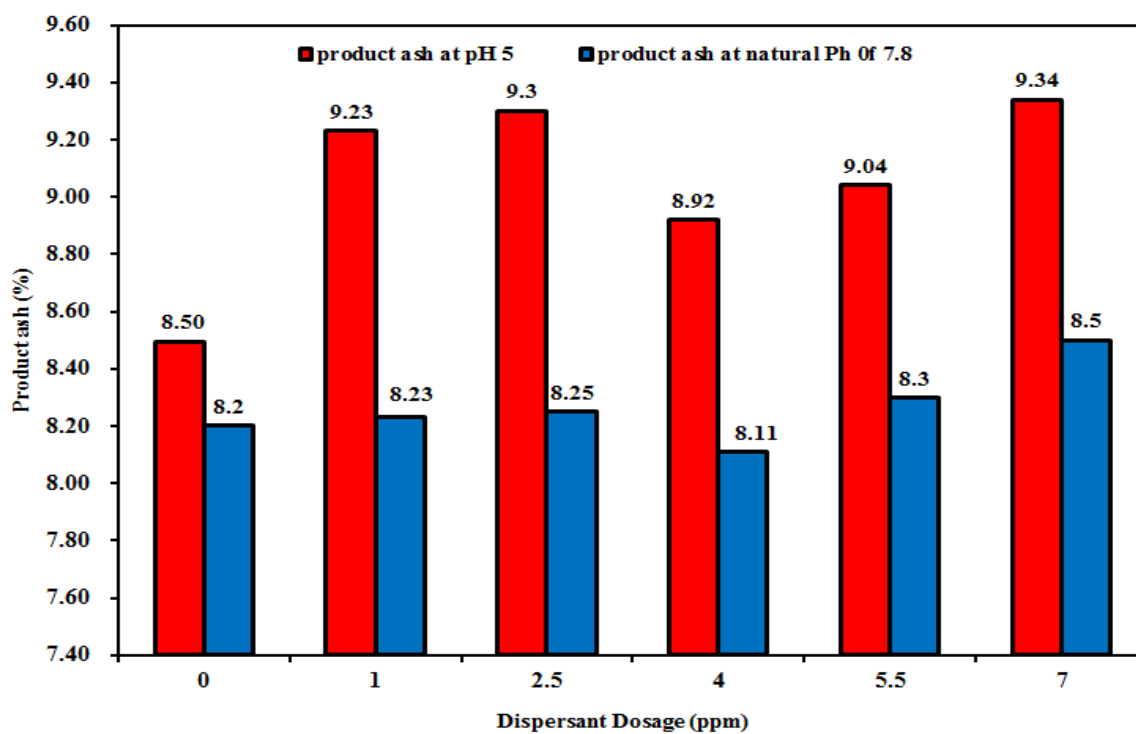

Figure 4.23. Effects of dispersant alone at pH 5 and pH 7.8 on the product ash.

According to the results of Figure 4.24 the addition of Al-PAM with sodium metasilicate on the flotation pulp at a pH of 5 did not improve the combustible recovery of coal. The combustible recovery of coal for baseline tests was 70.40% and addition of Al-PAM together with sodium metasilicate decreased the overall combustible recovery to 53.34%. Similar effects were obtained from previous results when dispersant was alone at a pH of 5 as shown in Figure 4.22. Comparing these results to the results obtained when Al-PAM was added to the flotation pulp with sodium metasilicate at natural pH of 7.8 shows that flotation at a natural pH flotation was much better than at a pH of 5. At natural pH of 7.8 adding of Al-PAM together with sodium metasilicate increased the combustible recovery of coal by 7.2%. The reason for the decrease in combustible recovery at a pH of 5 was due to the depression of coal caused by sodium metasilicate, which inhibited the adsorption of polymer on coal surfaces.

Figure 4.25 also shows that adding Al-PAM together with sodium metasilicate at pH 5 highly increased the amount of ash in the froth, while the adding Al(OH)3-PAM together with sodium metasilicate at pH 7.8 greatly improved the product ash of the froth.

4.5.7. Flotation Experiments Using PAM. For comparison, coal flotation experiments were conducted in the presence of commercially available polyacrylamide (with a molecular weight of about five million) to see its effects on the combustible recovery and product ash. Flotation experiments were first conducted by varying the dosage of PAM at a constant pH of 7.8. Lastly the pH was changed to a pH of 5. For each experiment, 253g of coal and 4800 ml of tap water were placed in a 5 liter D12 Denver cell and conditioned for 5 minutes, at an agitation at 1800 rpm. Flotation was carried out at a natural pH of 7.8 and slightly acidic pH of 5.
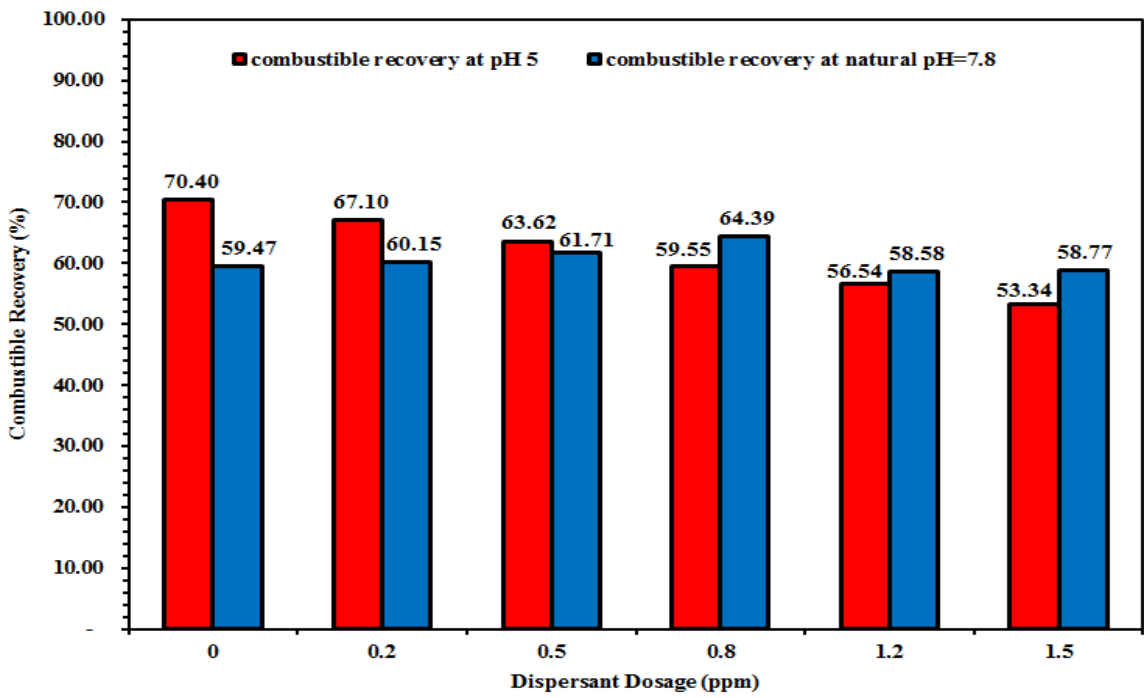
Figure 4.24. Effects of dispersant at pH 5 and ph 7.8 on combustible recovery of coal at a fixed Al-PAM dosage
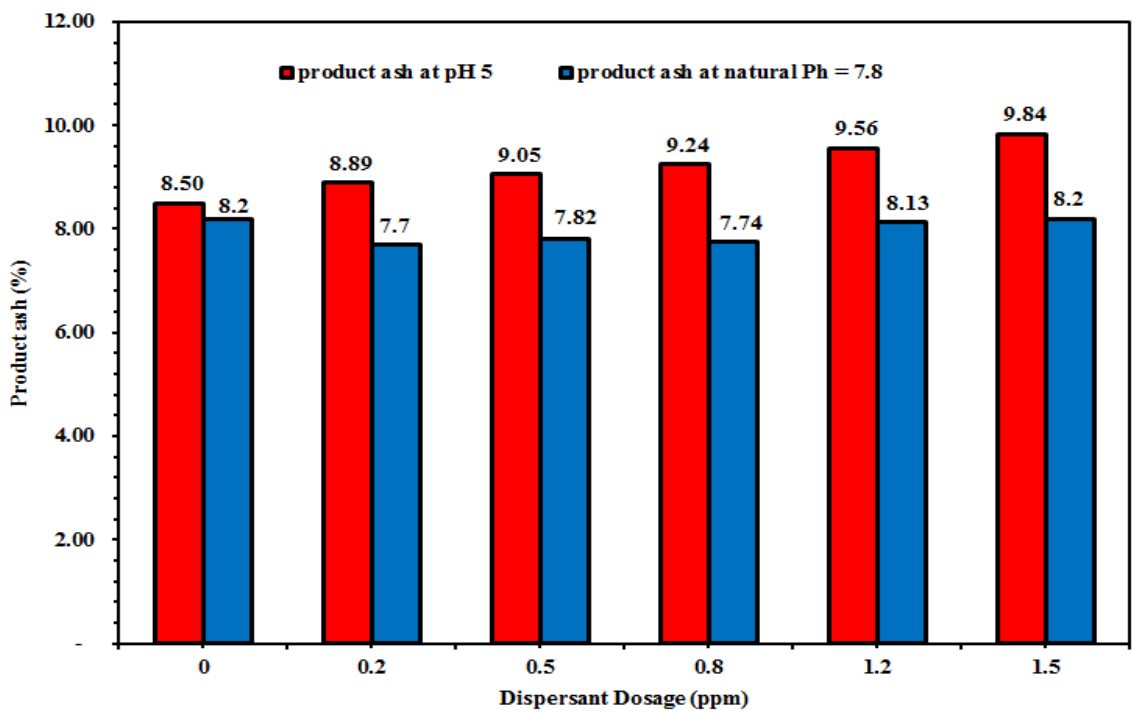

Figure 4.25. Effects of dispersant at pH 5 and pH 7.8 on Product ash at a fixed Al-PAM dosage

The procedure for reagent addition and conditioning can be summarized as follows:

1. Add collector = 200µl

2. Condition for 3 minutes

3. Add PAM (0.08, 0.16, 0.25, 0.5, 1, 2, 3 ppm)

4. Condition for 3 minutes

5. Add frother

6. Condition for 2 minutes.

7. Turned air on at a rate of 6 lpm and collect the froth for 5 minutes at 1 minute interval. Collect 5 fractions

The effects of PAM on the combustible recovery of coal and product ash at natural pH of 7.8 as a function of PAM dosage are shown in Figure 4.26. When no PAM was added to the flotation pulp (flotation with collector and frother only), the combustible recovery of the coal was 59.47% with product ash of 8.2%. However, coal was depressed when PAM was added to the flotation. The depression of coal was observed as PAM dosage increased from 0.08 to 3 ppm. The overall combustible recovery of coal was decreased from 54.47% to 30.54% when PAM was added to the flotation pulp. The results obtained in this study are in line with the results obtained by (Moudgil, 1983). Carried out a study on coal flotation experiments in the presence of PAM to see the effects it had on the combustible recovery of coal. Experimental results showed that coal was completely depressed by the addition of PAM. The depression action of PAM on the coal was due to the adsorption of hydrophilic polymer molecules on coal particles, rendering the surface of the coal particles polar in nature. These could explain the observations made in this study.

It can also be concluded that the addition of PAM increased the amount of ash content in the concentrate. The product ash obtained when no PAM was added was lower with an ash content of 8.2%. However, when PAM was added to the flotation pulp the ash content in the concentrate was highly increased. The overall ash content in the product ash was increased from 8.2% to 19.62%.

To further investigate the effects of PAM on combustible recovery of coal and product ash, flotation experiments were conducted in the presence of PAM at slightly acidic pH of 5. The results are shown in Figure 4.27. The overall flotation of coal was decreased at pH 5 when PAM was added to the flotation pulp. The combustible recovery of coal when no PAM was added at a pH of 5 was 70.40 %. However, increasing dosage of PAM from 0.08 to 1 ppm resulted in decrease in combustible recovery of coal. The same trend was observed when flotation was carried out at natural pH of 7.8.
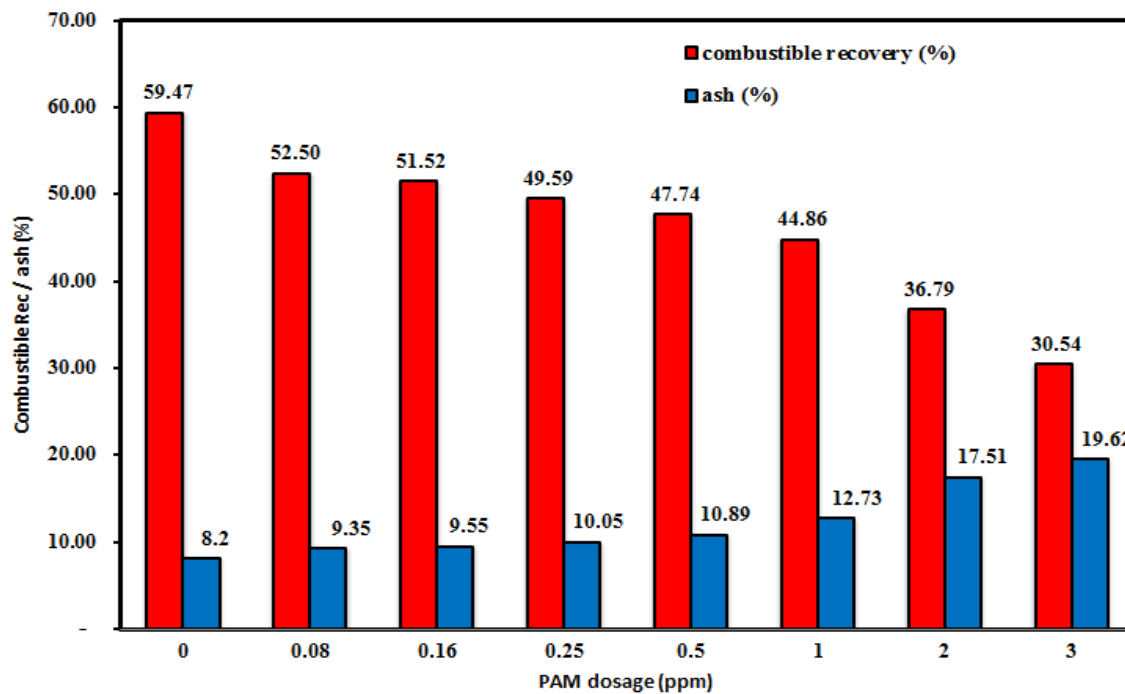
Figure 4.26. Effects of PAM dosage on combustible recovery of coal and product ash at a natural pH of 7.8
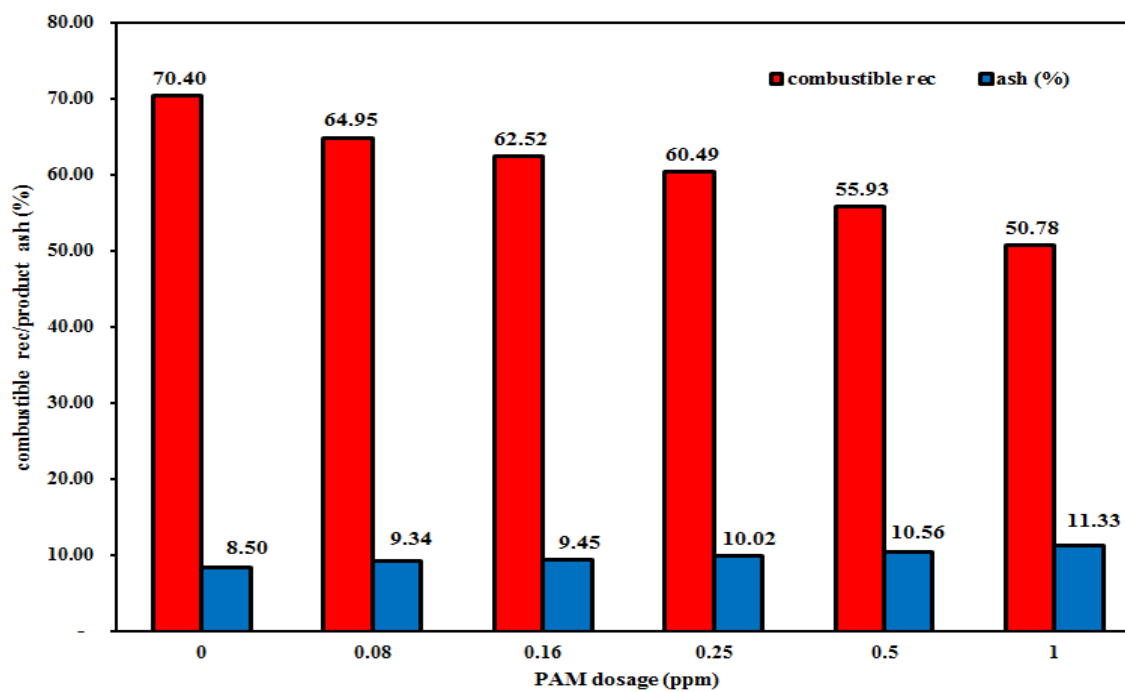

Figure 4.27. Effects of PAM dosage on combustible recovery of coal and product ash at a pH of 5.

5. CONCLUSION, RECOMMENDATIONS AND FUTURE WORK

5.1. CONCLUSION

This study investigated the effect of organic/inorganic (hybrid) polyacrylamide polymer on fine coal flotation. Laboratory batch flotation results obtained from the current study demonstrates that there is positive impact of hybrid polyacrylamides polymer on the combustible recovery of coal and ash reduction in the product. The following conclusions may be drawn from this study:

➤ The combustible recovery of coal for baseline experiments (use of collector and frother alone) at natural pH of 7.8 was 59.54% with product ash content of 8.2% while at slightly acidic pH 5 it was 70.40% with product ash content of 8.5%. These results indicate that flotation was better at slightly acidic pH of 5 than at natural pH of 7.8.

➤ Flotation tests results showed that adding Al-PAM in the flotation pulp at natural pH of 7.8 greatly improved the combustible recovery of coal by 7.2% and the product ash content was reduced to 8.02%. The optimum dosage of Al-PAM was 0.25 ppm.

➤ Addition of sodim metasilicate alone in flotation pulp at natural pH of 7.8 increased combustible recovery of coal by 5.2% with product ash content of 8.11%.

➤ The study has proven that depression of coal during flotation in the presence of sodium metasilicate can be minimized by adding relatively low dosages of the dispersing agents while moderate to high levels of coal depression may be expected when sodium metasilicate is added in excess.

➢ The tests results indicate that the use of dual dispersant- Al-PAM system provides an attractive means of improving the overall flotation performance. The best separation was obtained when 0.25 ppm of Al-PAM with 0.8 ppm of sodium metasilicate were added in the flotation pulp.

➢ Tests results showed that impeller speed has a significant influence on the combustible recovery of coal and product ash. Increasing the level of impeller speed increased the combustible recovery of coal but this accomplished by slight contamination of the product ash at higher impeller speed. Higher product ash content and lower combustible recovery of coal at lower impeller rotation speed was due to the insufficient dispersion of air, poor emulsification and dispersion of reagents which results in inadequate bubble-particle attachment in the slurry.

➢ Polymer conditioning time plays a dominant role in reducing the ash content of clean coal froth. The best clean product ash content of 7.5% was achieved when polymer was conditioned for 6 minutes.

➢ Flotation experiments in the presence of dispersant alone at slightly acidic pH of 5 did not improve flotation performance as it completely depressed coal. It is believed that at pH 5, sodium metasilicate dissociates to form colloidal silica gels. These colloidal silica gels are said to be negatively charged at acidic pH hence they will adsorb on the positively charged coal surfaces rendering them hydrophilic.

➢ The study also demonstrated that the use of dual dispersant-depressant system at slightly acidic pH of 5 did not improve the combustible recovery of coal. The reason for this is due to depression of coal caused by sodium metasilicate at slightly acidic pH which inhibits the adsorption of polymer on coal surfaces.

➤ Addition of commercially available Polyacrylamide (PAM) in the flotation pulp did not enhance flotation performance as the coal was completely depressed.

➤ This study also illustrate that organic/inorganic (hybrid) polyacrylamide polymer is a better than ash forming depressant than commercially available Polyacrylamide (PAM)

5.2. RECOMMENDATIONS AND FUTURE WORK

Findings obtained from this study show that using hybrid polyacrylamide polymer (Al-PAM) in fine coal flotation has a positive impact on the both the combustible recovery and the ash rejection. However, more studies are needed to further investigate the effects of such polymers on fine coal flotation process. The following studies are recommended for future work:

➤ Fundamental studies to investigate the selectivity of Al-PAMs adsorption on coal and mineral particles as well as quantitative measurements of the amount adsorbed.

➤ Study the flotation performance at different feed solids percentage and further optimization of other parameters accordingly.

➤ Pilot scale testing should be conducted using the results obtained from the laboratory batch tests.

➤ Flotation in the presence of hybrid polyacrylamides should be tested in other types of coal with different ash contents.

➤ Flotation in the presence of hybrid polyacrylamide polymers should be tested using other flotation machines such as column flotation cell.

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