University of Alberta

A Novel Flocculant for Enhanced Dewatering of Oil Sands Tailings

by

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Abstract

A cationic temperature sensitive polymer, poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] (CP) of different molar ratios, known as CP05 and CP10 was synthesized in-house. By doping aluminum hydroxide ($Al(OH)_3$) colloids into CP during the polymerization process, a novel hybrid polymer flocculant, Al-CP05, was synthesized. All flocculants showed a temperature and pH dependent coil-globule transition, and could alter the surface charge of fine kaolinite particles. For comparison, a coagulant and flocculant mixture was prepared by blending CP05 and $Al(OH)_3$, which was called {CP05+Al}.

The synthesized flocculants or blends were applied to kaolinite suspensions and laboratory oil sands extraction tailings to evaluate their settling and filtration performances. Al-CP05 was shown to provide the most effective flocculation on both kaolinite suspensions and tailings while its temperature sensitivity was partially lost in filtration of tailings. CP05 and CP10 showed similar flocculation performance on both kaolinite suspensions and tailings which was less effective than {CP05+Al} blends.

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Chapter 1 Introduction

1.1 Oil Sands

Oil sands exist naturally as a mixture of bitumen, sand, clay and water. Bitumen can be extracted to crude oil which is the main natural resource for energy. Canadian oil sands are mainly located in the Athabasca region in Alberta, with the rest in Peace River and Cold Lake [1]. Thanks to Alberta heavy oil resources, Canada becomes a growing contributor to the oil supply worldwide [2]. Being proven to have 171.3 billion barrels of oil reserves, Alberta is the second largest oil reserve in the world while Saudi Arabia is the first [2]. In 2009, about 1.9 million barrels of cruel oil, of which 1.5 million from oil sands, were produced daily [2]. As of January 2009, 1352 km^2 out of 4800 km^2 mineable area has been approved for surface mining [2].

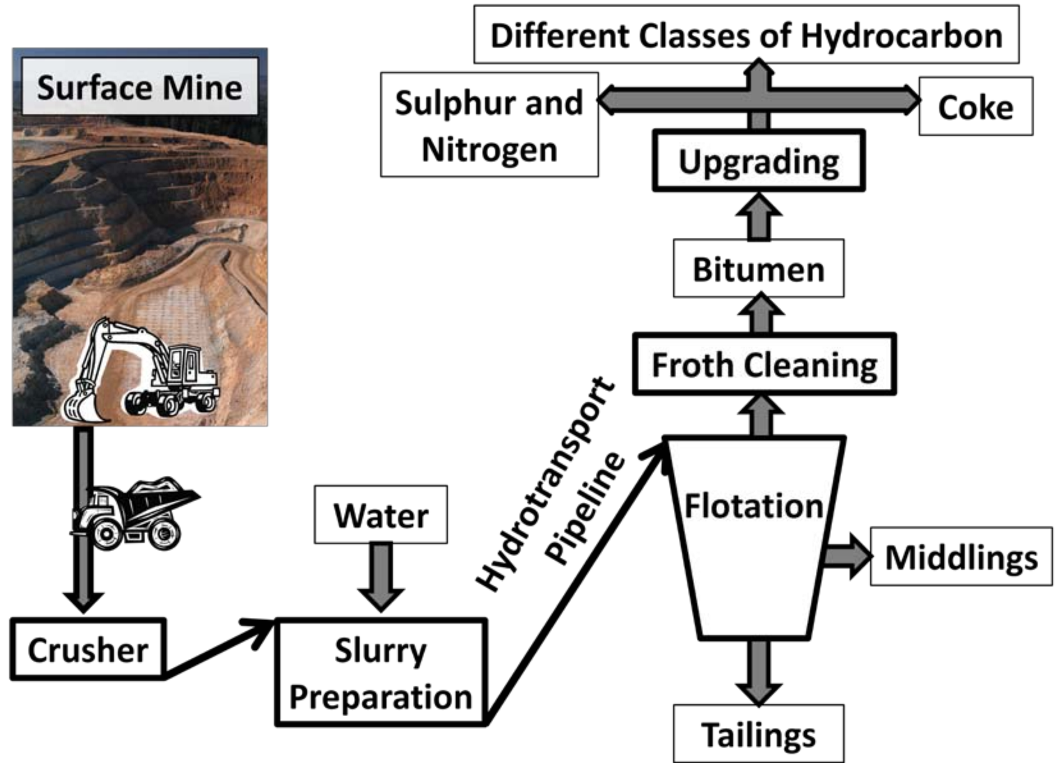

Figure 1-1-1 Schematic Flowchart of Bitumen Production [3]

Figure 1-1-1 shows a typical flowchart of bitumen extraction from a surface mine [3]. Oil sands, which are mined and crushed into smaller pieces, are mixed with warm water and additives to make slurry for hydrotransport pipeline [3]. With the heat and mechanical shear, the bitumen is liberated from the sands and separated by flotation in a separation vessel to produce bitumen froth [3]. Water and solids are removed from bitumen froth in a froth treatment process, and bitumen is upgraded into different streams of hydrocarbons after the removal of sulphur and nitrogen [3]. To produce an upgraded barrel of bitumen, on average 2 tonnes of oil sands are needed [3].

The development of oil sands industry is governed by three major factors. The first factor is the market condition [3]. The demand and supply of oil and labour are two possible factors affecting the profit of bitumen production [3]. As the extraction of bitumen from oil sands requires natural gas as the heating energy for water used in extraction and hydrogen supply, the price of bitumen and natural gas is critical on the bitumen extraction [3]. Another factor is the geography issue. The mineability of the ore, the distance between the mine, the facilities and the water source, and the length of and the pressure in the pipeline for hydrotransport of oil sands slurry are the three major geographic limitations [3]. Last but not least, the third factor is the environmental issue. The flue gas emission, the usage of clean water, and the tailings waste issue are the three most important environmental concerns needed to be addressed [3]. In addition to the existing government policies, the Government of Alberta also released a 20-year strategic plan for the oil sands industry in February 2009 [2]. Furthermore, a number of organizations (including the Alberta Environment, the Alberta Sustainable Resource Development (SRD), the Energy Resources Conservation Board (ERCB), and others) have been formed to monitor the environmental impacts and to ensure an efficient development of oil sands resources [4,5]. It is expected to develop the most efficient way to utilize the limited resource of oil sands and at the same time to protect the environment for our next generations. This work focuses on the accumulating tailings waste produced from the oil sands extraction process.

1.2 Separation Processes

There are two main industrial processes for bitumen extraction: the Clark Hot Water Extraction (CHWE) and the Steam-Assisted Gravity-Drainage (SAGD). CHWE is the original extraction process and is used by the majority of the oil sands industry as the standard extraction process from open pit mining. SAGD is the most commonly used in in-situ operations [2]. Cyclic Steam Stimulation (CSS) is another in-situ extraction process used in the industry in cold lake area.

1.2.1 Clark Hot Water Extraction (CHWE)

The Clark Hot Water Extraction (CHWE) was developed by Dr. Karl Clark with Alberta Research Council in the 1920s. The basic idea is to mix hot water to open-pit mined oil sands, and the bitumen floats to the top of the mixture [3].

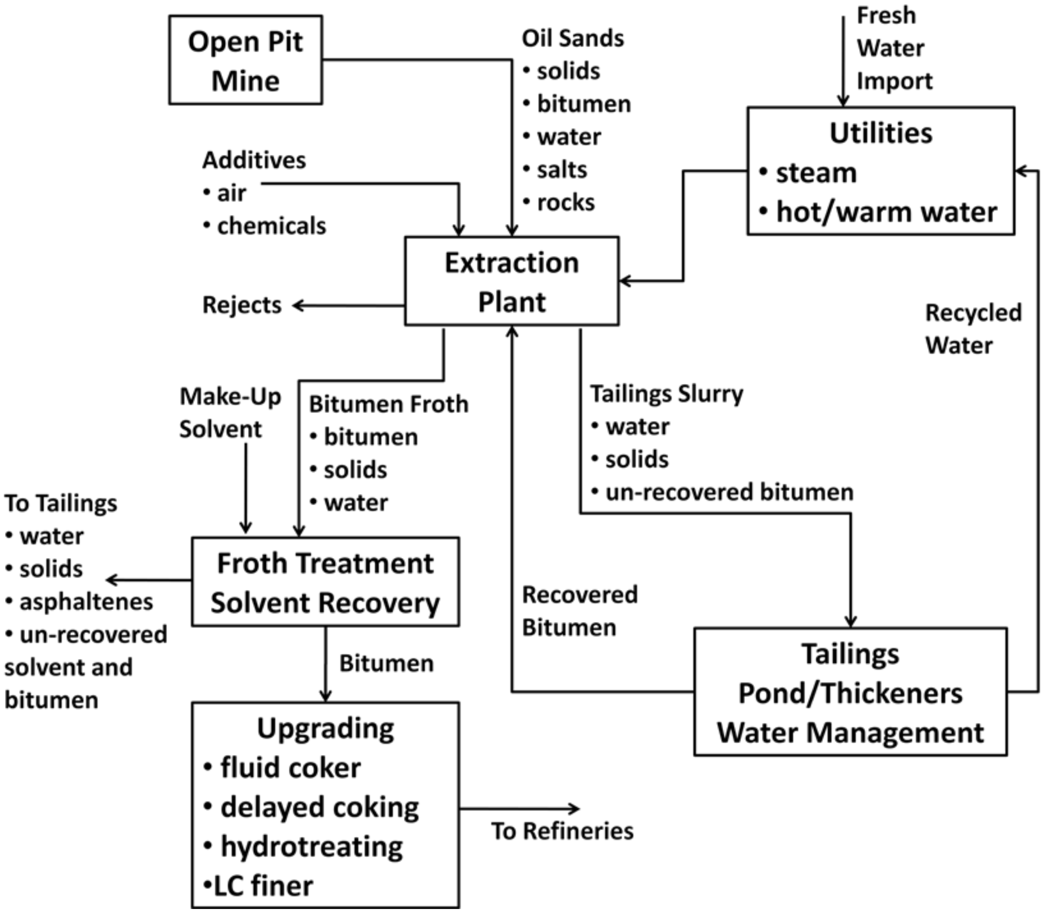

Figure 1-2-1 Generalized Flow Diagram for CHWE Process [3]

Figure 1-2-1 shows a flow diagram of CHWE process from mining to upgrading. There are three major processes in the “Extraction Plant”. After mining and crushing, the oil sands are delivered through hydrotransport pipelines with warm recycled process water and little amount of air [3]. The heat from process water reduces the viscosity of the bitumen, and the mechanical shear helps to liberate bitumen from the sands [3]. Aeration of bitumen favours the next process. The slurry mixture with liberated and aerated bitumen is pumped to gravity separation vessels [3]. The aerated bitumen aggregates are less dense than the slurry and float to the top as froth, while the heavier solids settle to the bottom as tailings [3]. The middlings with unrecovered bitumen goes to flotation cells or hydrocyclones for further bitumen recovery by induced air flotation [3]. In some cases, the tailings from gravity separation vessels are reprocessed with middlings to minimize bitumen loss to the tailings [3].

Chemicals, such as naphtha or paraffinic diluents, are used to reduce viscosity of bitumen in the bitumen froth for the removal of solids and water using inclined plate settlers, cyclones, and centrifuges [3]. Finally, the tailings waste goes to tailings pond or thickeners for further water management.

1.2.2 Steam-Assisted Gravity-Drainage (SAGD)

As about 85% of the oil sands resource is located underground in depth that is not feasible for open pit mining, Roger Butler and his colleagues at Imperial Oil developed the Steam-Assisted Gravity-Drainage (SAGD) for bitumen recovery from oil sands in the late 1970s [3]. This technology was first employed in Cold Lake [3].

In SAGD, a pair of wells, with a separation of 5 m to each other, runs parallel from the surface into the oil sands formation horizontally as illustrated in Figure 1-2-2 [3]. The upper well injects steam while the lower well is the oil producer [3]. The producer wellbores are equipped with mesh screen of very fine slots of 0.1-0.3 mm to prevent fine solids from entering the wellbores [3]. The steam is injected continuously to reduce the viscosity of the bitumen [3]. Hot bitumen and steam condensate are drained through the steam envelope and are pumped to the surface though the producer wellbore [3]. The bitumen and condensed water are transported to the above ground processing plant [3].

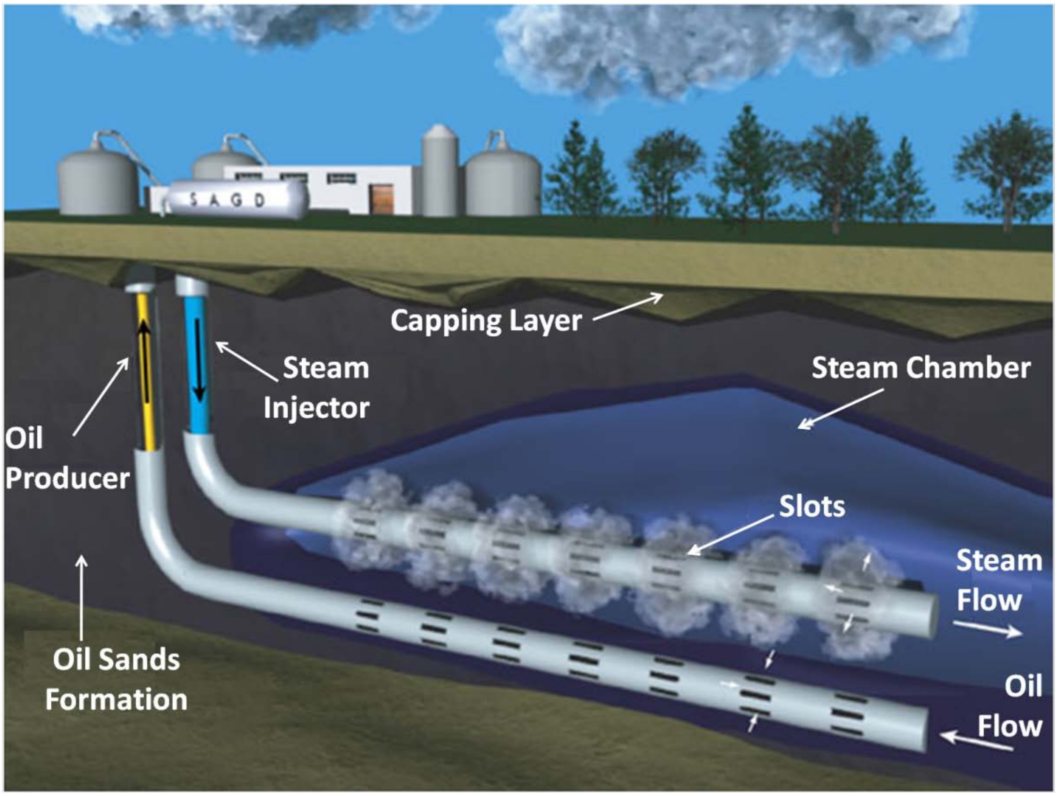

Figure 1-2-2 Schematic Diagram of SAGD Process [6]

The SAGD process reduces the volume of tailings waste and causes less disturbances on the landscape [3]. However, one should be cautious on the SAGD operation. The poor design of the Joslyn Creek thermal bitumen project in 2006 led to a stream explosion through a capping layer [7]. The steam pressure should be carefully chosen according to the cap rock property of the overburden [3].

1.2.3 Other Extraction Processes

Cyclic Steam Stimulation (CSS) consists of three stages: injection of steam, soaking of steam and production of bitumen all from the same well [8]. CSS is a discontinuous production process and is limited by the geography of the reservoirs

[8]. CSS is more effective in deeper reservoirs and with a layer of Grand Rapids formation that can withstand the high steam injection pressure [8].

Vapour Extraction Process (VAPEX), Toe to Heel Air Injection (THAI) and Supercritical Fluid Extraction (SFE) are three additional experimental extraction methods for oil sands. VAPEX shares similar idea as SAGD but using hydrocarbon solvents instead of steam [9, 10]. This provides higher energy efficiency as it is a non-thermal process, but it leads to a lower ultimate oil recovery and a much lower upgrading [9, 11]. THAI is similar to SAGD, but uses a vertical air injection well and a horizontal production well [11]. It is claimed that this method uses less freshwater and produce less greenhouse gases [11]. SFE extracts bitumen from oil sands using supercritical fluid of carbon dioxide, and eliminates the use of freshwater [12].

1.3 Tailings and Water Treatment

Tailings are by-products from mineral processing operations. The oil sands tailings slurry is an alkaline aqueous suspension which contains un-recovered bitumen, salts, soluble organic compounds, sands and clays [13]. The tailings are discharged to tailings ponds for storage. The tailings ponds are closely regulated by the government [13]. Two to four barrels of fresh water are required per barrel of oil produced from the surface mining method [14]. Currently in Alberta, there are more than 170 km^2 of tailings ponds [13]. Fresh water intake is limited by strict legislation, and recycling of water from tailings is essential in the bitumen extraction process [3].

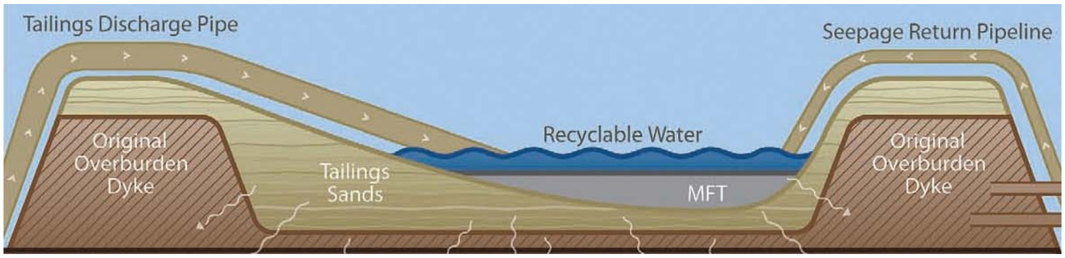

Figure 1-3-1 Schematic Diagram of a Tailings Pond [15]

After the tailings slurry is discharged to the tailings ponds, the coarse solids segregate as the dykes while most of the water and fine solids stay as suspensions in the tailings pond as illustrated in Figure 1-3-1 [3]. A layer of mature fine tails (MFT) develops after two to three years. MFT consolidates very slowly [3]. The completion of the settling process is predicted to take almost a century [3]. As a result, various attempts were made in the past decades to increase the settling rate of the tailings for efficient water recycling and to reduce volume of tailings ponds [3]. The major physical treatments include centrifugation, filtration, electrophoresis and electro-coagulation [3]. On the other hand, chemical methods are emerging by adding chemicals such as sodium silicate, organic flocculants, inorganic coagulants, oxidizing and reducing agents and most recently carbon dioxide [3].

Water treatment and softening processes are required to maintain the buffering capacity of the recycle water from the tailings ponds [3]. As the bitumen recovery is sensitive to the chemistry of the process water, accumulation of salt should be prevented from the water recycling stream [3]. For extraction process, calcium and magnesium levels of 30-40 ppm are considered to be harmful to bitumen recovery [3]. Sodium hydroxide (caustic soda) is often used to soften the recycle water [3]. Carbon dioxide exists naturally in air and slowly diffuses to the clear water phase of the tailings pond [16]. Carbon dioxide dissolves in water as bicarbonate ions which form sodium bicarbonates with sodium ions from caustic soda or lime [16]. The sodium bicarbonates precipitate calcium ions as calcium carbonates, and hence, soften the water [16]. The governing reactions are listed as follows.

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{1-1}$$

$$Ca^{2+} + 2OH^- + 2NaHCO_3 \leftrightarrow CaCO_3 \downarrow + H^+ + 2H_2O \tag{1-2}$$

1.3.1 Current Tailings Treatment Technologies

Treatment of fine tails with calcium sulphate (gypsum) is used by oil producers, such as Syncrude, Suncor and CNRL [3, 17]. The added calcium ions from gypsum destabilize the tailings suspension and lead to a much quicker solids settling [3, 18]. The MFT is combined with the coarse sands in the final tailings from the extraction process and is treated with gypsum[3]. The mixture is pumped to a settling basin, where clear water is released and ready to be recycled after a few days settling instead of decades [3]. After about a month, the sediment would be consolidated to be like “solid earth” and is referred as composite tailings (CT) by Syncrude, consolidated tailings (CT) by Suncor and non-segregated tailings (NST) by CNRL [3]. However, the recycle water contained a considerable amount of calcium ions which is harmful to the extraction process.

Paste technology is a possible solution for treating MFT without putting divalent ions to the water recycle stream [3]. A commercial flocculant, Percol 727, is a high molecular weight, anionic co-polymer of acrylamide and acrylates [3, 19, 20]. Its use increases settling rate but leads to a turbid supernatant [3, 19, 20]. A series of Percol are produced to achieve a clearer supernatant and a more consolidated sediment by enhanced settling of fine tails [3]. The sediment is referred as thickened tailings (TT) [3]. Performance of flocculants becomes critical to the paste technology. Moreover, the effect of flocculant residue on bitumen extraction process should be considered.

Ongoing researches are focussing on various kinds of polymeric flocculants as polymers are widely used in water treatment [21]. Cationic hybrid polymer was found to be more effective than the corresponding organic flocculant [22]. Some of the polymers exhibit a phase change from water-soluble coils to water-insoluble globules at a lower critical solution temperature (LCST). This type of polymers is known as the thermal sensitive polymers [23-26]. The thermal sensitive polymers are hydrophilic (water-like) below the LCST, and are hydrophobic (water-dislike) above the LCST [23]. Using thermal sensitive polymeric flocculants can avoid flocculant residue from entering the water recycle stream [27]. A proposed process is to add flocculant to the bitumen-free tailings cooled below the LCST [27]. When the recycle water is heated up to conduct the oil sands extraction process, the thermal sensitive flocculant will precipitate out and avoid any potential negative impacts of recycle water on bitumen extraction [27].

1.4 Objectives of Present Work

This research was focused on developing an efficient way of recycling water from tailings waste produced from the CHWE oil sands extraction process. The objectives of this project are to

1. synthesize a pH and temperature sensitive polymer for flocculation of kaolinite suspensions,
2. demonstrate the feasibility of the temperature sensitive polymer in settling and filtration of kaolinite suspensions,
3. synthesize a pH and temperature sensitive inorganic-organic hybrid polymer for better flocculation performance on kaolinite suspensions,
4. explore the effect of flocculants on settling and filtration processes of oil sands extraction tailings.

1.5 Organization of Thesis

The body of this thesis consists of 9 chapters. This chapter provides background information of oil sands, bitumen extraction processes, tailings issue and temperature sensitive polymers. Chapter 2 presents an overview of the fundamentals of colloid dispersion and surface chemistry, and reviews the relevant literature of the present work. Chapter 3 introduces the experimental setup for the settling and filtration tests. Chapter 4 illustrates the synthesis and characterization of the flocculants used. Chapter 5 presents the results and discussion on the effect of the temperature sensitive polymer on settling and filtration of kaolinite suspensions. Chapter 6 presents the results and discussions on the effect of the aluminum hydroxide-polymer hybrid on settling and filtration of kaolinite suspensions. The results are compared with those using a coagulant/flocculant mixture (aluminum hydroxide colloid with temperature sensitive polymer). Chapter 7 discusses the effect of all interested flocculants on settling and filtration of laboratory extraction tailings. Conclusions are drawn in Chapter 8 and recommendations for further study are suggested in Chapter 9.

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Chapter 2 Literature Review

2.1 Surface Phenomena and Properties of Clays

As mentioned in Chapter 1, complete settling of fine tailings solids without any treatment would take decades [1]. The long sedimentation process arises from the ultra-fine particles. The ultra-fines refer to the aluminosilicate clay particles which have sizes less than 0.3 μm [2]. A colloidal system is formed when placing the ultra-fines into an aqueous solution. These ultra-fines strongly enhance the stability of the oil sands tailings, and hinder settling. Therefore, some information of clay mineralogy and colloidal dispersion will be provided in this section.

2.1.1 Colloidal Dispersion

Colloidal dispersions are systems of finely dispersed particles, which compose of one or more components and have at least one dimension with 1 nm to 1 μm [3]. Freundlich classified colloidal dispersions into two types, lyophilic (solvent-loving) and lyophobic (solvent-hating) [3, 4]. Kruyt later used the terms reversible and irreversible systems respectively for the same classification [3, 5]. A system is called lyophilic or reversible if the colloids disperse spontaneously when added into the solvent [3]. A system is called lyophobic or irreversible if the solvent is expelled by the colloids [3]. The aqueous system of fine clay particles (<2 μm) falls into the class of lyophobic colloidal dispersion [3]. As the oil sands tailings contain a significant amount of clay particles, the properties of clay and the interactions between lyophobic colloids are provided briefly as follows.

2.1.2 Clay Minerals

Clay particles are composed of sheets of silicon-oxygen tetrahedrons and sheets of aluminum-or magnesium-oxygen octahedrons [3]. Different types of clays have different arrangements of these sheets as their unit layer [3]. A perfect clay crystal is built by laying this unit layer one on top of other as illustrated in Figure 2-1-1 [3]. Typical structure of clays is of hexagonal sheets with length to thickness ratio of 10:1 [3].

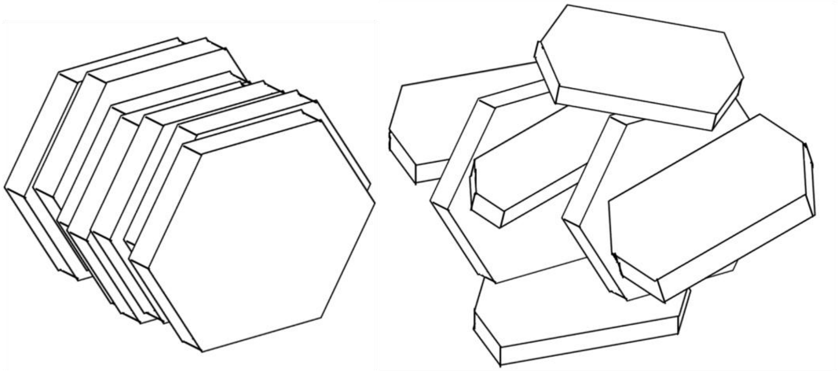

Figure 2-1-1 Two Different Structures of Clay Particles: Stacking Structure of a Perfect Crystal (left) and “House of Cards” Structure (right)

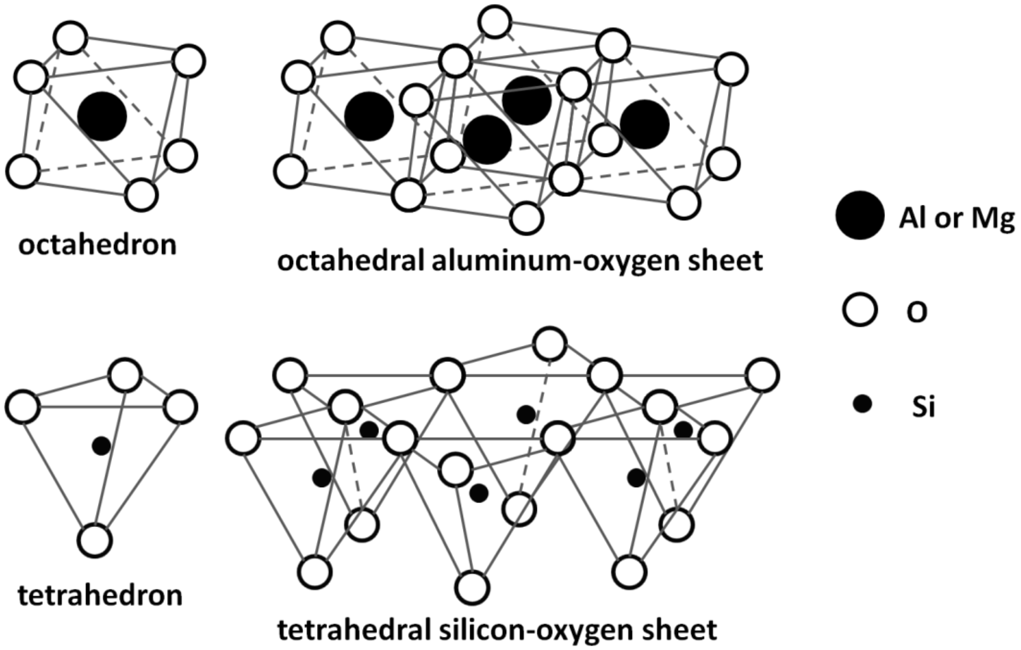

Figure 2-1-2 Schematic Diagram of the Building Units of Clay

Clay minerals can be divided into two main types by the structure of their unit layer. Two-layered clay particles, such as kaolinite, have unit layer of one tetrahedral silicon-oxygen sheet attached to one octahedral aluminum-oxide sheet as illustrated in Figure 2-1-2 [3]. The structure of two-layered clays is stacking of unit layers which hold partly by van der Waals force and partly by hydrogen bonds from the hydroxyl groups of the octahedral sheet [3]. Three-layered clay particles, such as illite or smectite, have unit layer of one octahedral sheet in between two tetrahedral sheets [3]. The structure of two-layered clay crystal is stacking of unit layers which hold only by van der Waals force [3].

Unlike kaolinite that does not swell under normal conditions, smectite swells by absorbing water in between its unit layer, increasing the distance between the sheets of the unit layer [3]. The swelling of smectite is presumably associated with the electrostatic repulsion between the particles [3].

Another important phenomenon of clays is the process of cation exchange. Clay particles obtain electric charge by substitution of cations in the unit layers [3]. A negative charge is left to the structure when a tetravalent silicon ion is replaced by a trivalent aluminum ion because of the similar morphology of the ions [3]. This charging mechanism is known as isomorphous substitution of ions. The charges on basal plane are considered as permanent charge, independent of pH. The primary alumina and silica bonds are broken at the edge, leading to a pH dependent charge. For kaolinite crystal, the edge is positively charged in acidic condition and negatively charged in alkaline condition [3]. In an acidic suspension, the positively charged edges of the unit layer may attach to the negatively charged basal plane, giving rise to a space-filling “house of cards” structure as shown in Figure 2-1-1 [1].

2.1.3 Electrical Double Layer

Various types of interactions between particles are closely related to the surface properties of particles in a colloidal system. The surface phenomena of particles in clay-aqueous system affect the stability of the colloidal dispersion. Interaction of charged species in an electrolyte solution is usually explained by the formation of electrical double layer. In such a system, the charged surface attracts oppositely charged ions in the solution and an electrical double layer is formed near the charged surface with the whole system being electrically neutral [6]. A Stern model is usually used to describe the profile of electrical potential distribution near the charged surface as shown in Figure 2-1-3 [7, 8].

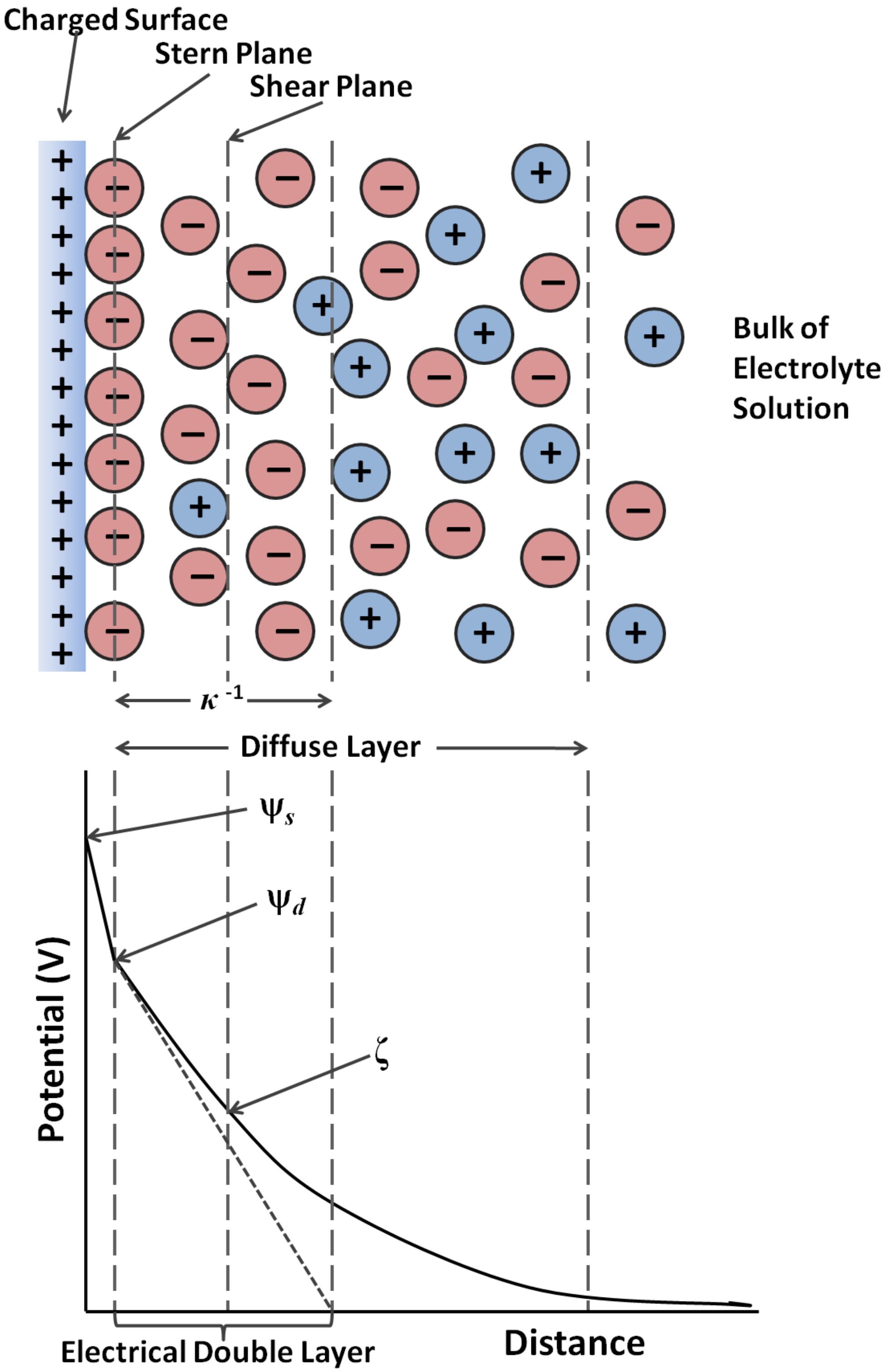

Figure 2-1-3 Schematic Illustration of the Electrical Double Layer according to Stern Model (top) and Corresponding Electrical Potential Profile Showing the Debye Length (κ^{-1}) and the Diffuse Layer (bottom) [8]

Stern layer is the region between the particle surface and the Stern plane [8]. The potential in Stern layer decreases linearly from the particle surface due to the presence of counter ions [8]. The potential at the Stern plane is called the Stern potential (ψ_s), beyond which the potential decreases exponentially away from the Stern plane [8]. The ions in the Stern layer are believed to be bounded to the particle surface [8]. Shear plane refers to the plane that the ions and the ion bearing solution move around the particle [8]. The slipping condition applies at the shear plane and the potential at the shear plane is known as the zeta potential (ζ) [8]. The potential within the double layer region, including the zeta potential, depends on the type of electrolytes and their concentrations [8].

2.1.4 DLVO Theory

The DLVO theory, which is named after Derjaguin and Landau in the ex-USSR, and Verwey and Overbeek in the Netherlands, describes the force between particles in a suspension [1]. In the DLVO theory, only van der Waals and electrostatic double layer forces are considered. Other forces, such as hydrodynamic forces, are ignored [1, 8]. Therefore, the stability of the system depends on the net interaction resulting from the attraction and repulsion between the particles [8]. If the net interaction between the particles is repulsive, the system is stable and stays as dispersion. On the other hand, if the net interaction between the particles is attractive, the system is unstable and the particles will coagulate. The repulsion between particles comes from the presence of electrical double layer while the attraction is due to van der Waals forces [8]. Although some limitations hold, the DLVO theory provides a better understanding of complicated colloidal dispersion systems [3, 8]. For example, one can consider increasing overall attraction between clay particles by compressing the electrical double layer, which favours sedimentation of oil sands tailings.

2.2 Coagulation and Flocculation

Different definitions of coagulation and flocculation can be found in literature. Some use the terms interchangeably. In this study, the definitions are modified from the definitions used by Crittenden et al. and Hunter, R.J. [3, 9]. Coagulation process is defined as the addition of an organic “chemical coagulant… for the purpose of conditioning the suspended” particles [9]. Coagulation destabilizes particles by reducing particle charges and/or compressing electrical double layers, forming doublets, triplets, etc., upon collision driven by Brownian motion [3]. Flocculation process refers to the macroscopic aggregation of suspended particles into loosely packed flocs by addition of polymeric flocculant [3, 9]. The flocs settle quite rapidly with relatively clear supernatant if the flocs have a density higher than the surrounding medium [3]. Otherwise, with an upward water flow, the flocs float as froth and accumulate on top on the medium.

Coagulants are usually inorganic salts such as potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$), aluminum sulphate ($Al_2(SO_4)_3 \cdot 14H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$) [9]. In oil sands tailings, for example, the electrical double layer of the negatively charged kaolinite clay particle is compressed when divalent calcium ions in gypsum are added to the tailings. The compression of electrical double layer reduces the energy barrier, and eventually makes the net interaction between the kaolinite particles is attractive for aggregation of kaolinite particles. When two particles come together due to the random collision of Brownian motion, they form doublet because of a net attractive force. According to DLVO theory, the critical coagulation concentration is inversely proportional to the sixth power of the charge on the electrolyte ions [9]. Therefore, trivalent ions can compress electrical double layer more effectively than monovanlent and divalent ions.

Polymers are often used as flocculation aids to produce large and stable flocs [9]. The adsorption of polymer chains on suspended particle at one or more sites is mainly by electrostatic interactions and hydrogen bonding [9]. For a dispersion system with negatively charged particles, using non-ionic and anionic polymers will be more efficient after destabilization of suspended particles by addition of coagulants [9]. Cationic polymer can be used without the primary coagulation because the electrostatic interaction increases the chance of polymer adsorption on particle surfaces. In other words, the positive charges on the polymer chain are attracted to and neutralize the negatively charged particles, enhancing particle flocculation. Mixing condition and dosage are found to be critical for the bridging process of particles by polymers. Insufficient mixing may cause local overdosed, and hence, poor inter-particle bridging by secondary adsorption on one particle [9]. Poor inter-particle bridging produces poor flocculation while secondary adsorption stabilizes the dispersion. Excessive mixing ruptures the flocs by extensive shear [9]. Some particles will remain non-flocculated when insufficient polymer is added, while excessive dosage of polymer causes enmeshment of particles in polymer matrix, which stabilizes the dispersion (steric stabilization) [9].

A suitable flocculant for the alkaline oil sands tailings needs to be carefully chosen as the polymeric flocculants are usually quite specific to a dispersion system. The goal is to find a flocculant that is effective on the oil sands tailings and not harmful to the bitumen recovery process. Two types of polymers, the inorganic-organic hybrid polymer and the temperature sensitive polymer, are introduced in the following sections in order to find a suitable polymeric flocculant for the oil sands tailings treatment.

2.2.1 Inorganic-Organic Hybrid Polymers

Inorganic-organic hybrid is firstly used in different disciplines other than flocculation. A wide variety of applications of inorganic-organic hybrids ranges over composite materials [10, 11, 12], selective membranes [13], coatings, lenses and non-linear optics [14, 15], electroconductive materials [14], sensors [16], and biomimetic materials [17]. Inorganic-organic hybrids consisting polymeric acrylamides and inorganic substances such as silica [18, 19], silicate [20], zirconium (IV) arsenate [21], tungstophosphate acid [22], copper chloride and cadmium chloride [23] were studied by different researchers. The large scope of application of these materials drew Yang and his/her colleagues' attention [24]. They synthesized hybrid aluminum hydroxide-polyacrylamide (Al-PAM) flocculant which leads to more effective flocculation than both the organic polymer, polyacrylamide (PAM), and the PAM/aluminum chloride blend [24]. Sun et al. studied the interactions between an Al-PAM molecule and a silica surface and the morphology of the flocs formed from kaolinite suspension by Al-PAM addition [25]. They concluded that Al-PAM has a star-like structure as shown in Figure 2-2-1 [25]. Li et al. claimed that Al-PAM is also useful for oil sands processing from low grade ore of high fines content [26]. Their work showed a decrease in bitumen recovery with increasing Al-PAM dosage up to 20 ppm, above which, Al-PAM addition has negligible effect on further decreasing bitumen recovery [26]. Addition of Al-PAM is shown to reduce solids content of the bitumen froth from flotation, but increases the water content of bitumen froth [26]. Improvement in settling of the produced tailings without further addition of Al-PAM is shown [26].

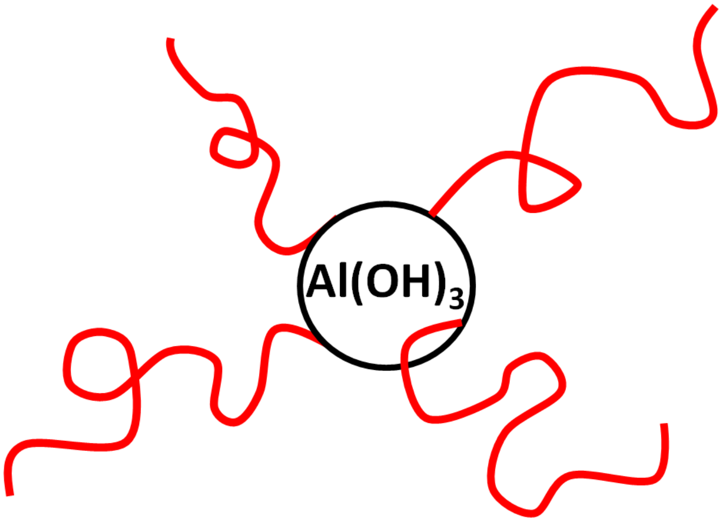

Figure 2-2-1 Schematic Diagram of the Proposed Structure of an Inorganic-Organic Hybrid Polymer Molecule

Wang et al. studied the flocculation of Al-PAM on oil sands tailings which was compared with a commercial, partially hydrolyzed polyacrylamide flocculant, Magnafloc 1011 (Percol 727) [27]. They concluded that Al-PAM is more efficient to flocculate fine particles, and hence Al-PAM is a better filtration aid than Magnafloc 1011 [27]. In recent study, calcium chloride-polyacrylamide and ferric chloride-polyacrylamide were synthesized and are claimed to be effective flocculants of low-concentrated acidic kaolinite suspension [28, 29]. However, the bitumen recovery in the oil sands extraction process is sensitive to the ion concentration in the recycle process water as mentioned in Chapter 1. As the residue of polymer hybrid from the tailings treatment process would go to the recycle stream, the effect of the residue on the bitumen recovery, therefore, should be studied in detail.

2.2.2 Temperature Sensitive Polymers

Temperature sensitive polymers are polymers that when temperature increases the dissolved polymer molecules are separated from the solvent in a specific polymer-solvent system. In other word, the temperature sensitive polymers, in contrast to most of the aqueous systems, become less soluble in water upon heating [30]. The Flory-Huggins solution theory is used to explain this phase separation phenomenon of temperature sensitive polymers as follows.

The Flory-Huggins solution theory, which is named after Paul Flory and Maurice Huggins in the United States, is a mathematical model to describe the thermodynamics of polymer solution. It is derived from the equation of Gibbs free energy of mixing (ΔG_m) [31].

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2-1}$$

ΔH_m is the change of enthalpy of mixing, ΔS_m is the change of entropy of mixing and T is the absolute temperature. The Flory-Huggins theory takes into account of "(i) the large differences in size between solvent and polymer molecules, and (ii) intermolecular interactions" [31]. The Flory-Huggins equation for the Gibbs free energy of mixing is given by,

$$\Delta G_m = RT[n_1 ln\phi_1 + n_2 ln\phi_2 + n_1\phi_2\chi] \tag{2-2}$$

where R is the universal gas constant, n_1 and n_2 are the numbers of moles of the solvent and the polymer respectively while ϕ_1 and ϕ_2 are the volume fractions of the solvent and the polymer respectively [31]. χ is the Flory-Huggins polymer-solvent interaction parameter and is defined as

$$\chi = (z-2)\frac{\Delta g_{12}}{kT} \tag{2-3}$$

where z is the lattice parameter, Δg_{12} is the Gibbs free energy change, and k is the Boltzmann constant [31].

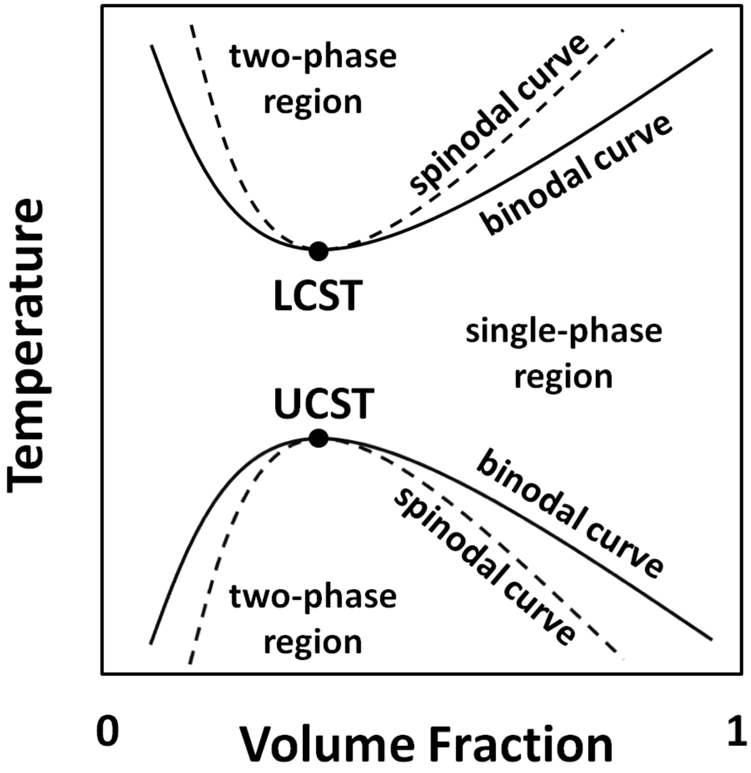

Figure 2-2-2 Schematic Phase Diagram for Polymer Solution Showing UCST and LCST Behaviours [31]

The effect of temperature on phase changes of non-crystallizing polymer solutions can be analyzed theoretically based on the Flory-Huggins theory [31]. The Flory-Huggins theory and its extensions predict that all polymer-solvent systems should have a phase diagram showing the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST) as illustrated in Figure 2-2-2 [31]. The UCST is the temperature above which the polymer and the solvent are miscible for all concentrations, while the LCST is the temperature below which the polymer and the solvent are miscible for all concentrations [31]. The LCST behaviour can be observed if there exists (i) favourable polymer-solvent interaction such as hydrogen bonding, or (ii) volume contraction upon mixing [31]. The LCST behaviour is observed in temperature sensitive polymers which exhibit a ***coil-globule transition***.

A coil-globule transition is a reversible process that polymer molecules collapse from expanded coils to shrunk globules as the temperature of the solution passes LCST, or vice versa when temperature drops below LCST [30, 32]. Poly(*N*-isopropylacrylamide) (pNIPAM) is an prominent example of polymers which have a coil-globule transition in aqueous system at 32^{o}C. More examples of temperature sensitive polymers are tabulated in Table 2-2-1 [33]. PNIPAM, like other amphiphilic polymers, is appropriately balanced with its hydrophilic and hydrophobic moieties. PNIPAM is soluble in water at temperature below its LCST because of hydrogen bonding [30-32]. Hydrogen bonding is disrupted when the solution is heated to above the LCST at which the coils shrink into globules due to the hydrophobic moiety of the polymer molecules as illustrated in Figure 2-2-3 [30, 32].

Table 2-2-1 List of Homopolymers with Coil-Globule Transition in Aqueous System and Corresponding Lower Critical Solution Temperatures [33]

Homopolymers	**LCST of 1wt% Aqueous Solution (^{o}C)**
Poly(*N*-ethylacrylamide)	74
Poly(*N*-isopropylacrylamide)	32
Poly(*N*,*N*-diethylacrylamide)	25
Poly(*N*-ethylmethacrylamide)	58
Poly(*N*-cyclopropylacrylamide)	57
Poly(*N*-(3'-methoxypropyl)acrylamide)	10
Poly(2-ethyl-*N*-vinylimidazole)	38

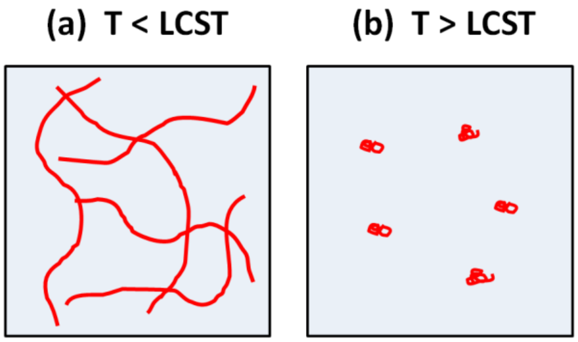

Figure 2-2-3 Schematics of the Coil-Globule Transition of Temperature Sensitive Polymers

Fujishige et al. illustrated that the coil-globule transition of pNIPAM in water is independent of molecular weight from 5×10^4Da to 840×10^4Da and concentration of the solution lower than 1 wt% [32]. Carter et al. showed that the branched pNIPAM has a lower LCST than the linear pNIPAM [34]. Meewes et al. and Walter et al. showed that the LCST increases with increasing concentration of sodium *n*-dodecyl sulphate [35, 36]. Homopolymer and copolymers of NIPAM are shown to be good flocculants of suspensions [37, 38]. Li et al. showed that pNIPAM shrinks above LCST and produces compact flocs [39]. A flocculation mechanism is proposed in their work as shown in Figure 2-2-4 [39].

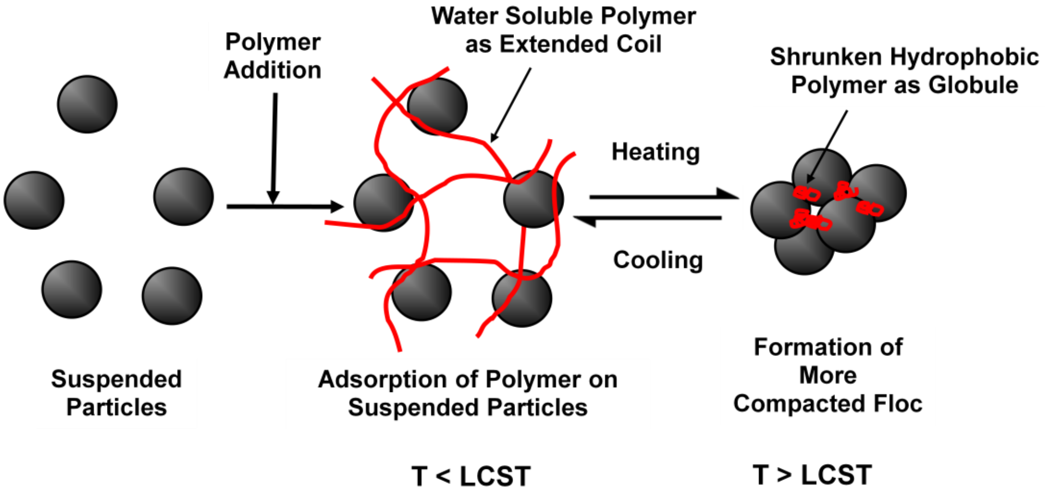

Figure 2-2-4 Proposed Flocculation Mechanism of Temperature Sensitive Polymers [39]

The clay minerals in the oil sands tailings contain mainly kaolinite which carries a negative charge. Cationic polymers, therefore, are believed to be more effective to flocculate the kaolinite suspensions. Guillet et al. studied a number of temperature sensitive flocculants [37]. They showed that cationic flocculants of copolymers of NIPAM are more effective to flocculate an aqueous mixture of titanium oxide (TiO_2), clay and paper fibres than pNIPAM [37]. The two specific flocculants are copolymers of (i) 85.3 mole% NIPAM and 14.7 mole% methacrylamidopropyltrimethylammonium chloride (MAPTAC) and (ii) 92.8 mole% NIPAM and 7.2 mole% dimethylaminopropylmethacrylamide (DMAPMA) [37]. Deng et al. showed that poly(NIPAM-co-MAPTAC) is a good flocculant for TiO_2 which is negatively charged above pH 5.5 [40]. Sakohara and Nishikawa [41] used *N*, *N*-dimethylaminopropylacrylamide (DMAPAA), which has a methyl group less than DMAPMA, to copolymerize with NIPAM as a good flocculant of TiO_2. They showed that the coil-globule transition of the flocculant is affected by pH, temperature, and the DMAPAA content [41]. Sakohara et al. demonstrated the dewaterability of poly(NIPAM-co-DMAPAA) on activated sludge by filtration [42]. Nichifor and Zhu used *N*-alkylacrylamide and styrene copolymer to flocculate 5wt% kaolinite suspension at 65^{o}C [43]. Their study showed little settling is produced with high polymer dosage [43].

Considering the wide flexibility of changing the coil-globule transition as shown by Sakohara and Nishikawa, the flocculation behaviour of the temperature sensitive copolymer of NIPAM and DMAPMA was studied in this project due to [41]. Aluminum hydroxide was dosed into the copolymer, and the flocculation behaviour of this inorganic-organic hybrid polymer was studied. The hybrid polymer is believed to have excellent flocculation efficiency on both kaolinite suspension and oil sands tailings, as demonstrated by other hybrid polymer flocculants such as Al-PAM. The motivation of using temperature sensitive polymers in this study is their ability to be filtered out from the recycle stream of the process water at temperature higher than the LCST, and hence minimizing its effect on bitumen extraction.

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Chapter 3 Settling and Filtration Experiments

3.1 Materials

Kaolinite clay (kaolin K2-500, Fisher Scientific) was acid washed powder with less than 2% acid-soluble substances and less than 0.001% lead. Sodium hydroxide (NaOH, Fisher Scientific) was more than 95% pure with less than 3% sodium carbonate. Deionized water (Milli-Q water), with resistivity of 18.2 Ω, was prepared with an Elix 5 followed by a Millipore-UV plus water purification system (Millipore Inc., Canada).

3.1.1 Model Tailings

Model tailings were prepared with 5 wt% kaolinite clay dispersed in deionized water at pH 8.5. The particle size of kaolinite clay in 5 wt% suspension (shaken overnight) at pH 8.5 was measured by Mastersizer (Hydro2000SM, Malven, MA, US.). The notation d_x represents the size for which x volume percent of particles are finer than d_x [1]. The effective size (d_{10}), the median size (d_{50}), and the d_{60} of the clay particles were 0.17 µm, 3.8 µm, and 5.3 µm, respectively, as shown in Figure 3-1-1. The uniformity coefficient, d_{60}/d_{10}, relates to particle size distribution [1]. The d_{60}/d_{10} was 31.5 for the kaolinite clay used. The large uniformity coefficient refers to a wide range of particle size [1]. In addition, according to Figure 3-1-2, the kaolinite clay particles contained two typical sizes of 0.16 µm and 4.4 µm, i.e. ultra-fines and fines, respectively. The existence of ultra-fines represents a better model to the real oil sands tailings slurry.

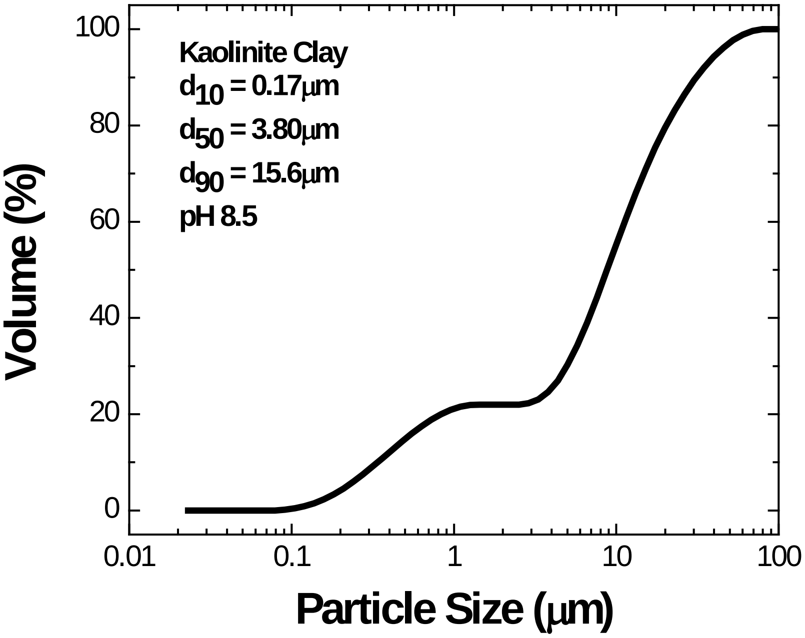

Figure 3-1-1 Cumulative Volume Passing of Kaolinite Clay Particles

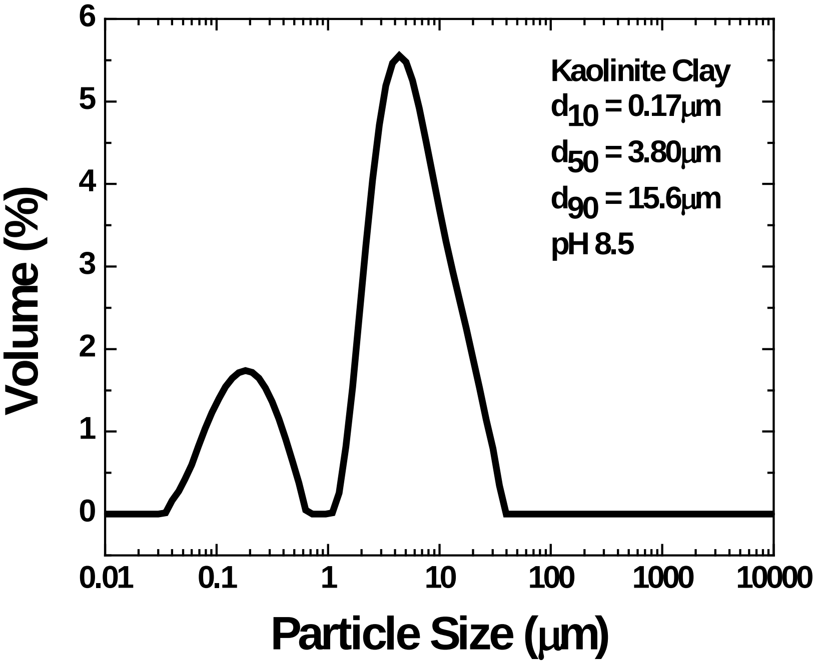

Figure 3-1-2 Size Distribution of Kaolinite Clay Particles

3.1.2 Laboratory Extraction Tailings

The tailings were obtained from oil sands obtained from Aurora mine (SYN704) using Aurora plant process water and a laboratory extraction loop. The tailings were transferred to a 20 L pail after 10 min of settling such that most of the coarse sands were settled out. The composition of Aurora plant process water is given in Table 3-1-1. The water chemistry of the process water was determined using a HPLC (UltiMate 3000, DIONEX, CA, US.). Composition of tailings was determined using a Dean-Stark apparatus with toluene as solvent [2]. Fines are defined as mineral particles smaller than 44 µm. The fines to solids ratio was the weight percent of fines in the whole solid mass, and was measured by Mastersizer (Hydro2000SM, Malven, MA, US.). Composition of laboratory extraction tailings is tabulated in Table 3-1-2.

Table 3-1-1 Composition of Industrial Oil Sands Extraction Process Water

Ions	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	pH
Composition (mg/L)	20	612	16.2	22	405	5.7	114	742	7.8

Table 3-1-2 Composition of Lab Extraction Oil Sands Tailings

Composition (wt%)	Bitumen	Solids	Fines in Solids
Ore	9.6	82.0	25.5
Tailings	0.29	11.6	47.0

3.2 Mixing and Sampling

3.2.1 Mixing Tools

Different mixing tools were used for several systems in this study. Heavy duty shaker (Eberbach heavy-duty shaker, two-speed, Eberbach 6010 Shaker, Eberbach Labtools, USA) was used to provide long term mixing for bottles of volume 4 L or less. Teflon coated magnetic stir bars were used to agitate solution or stable suspension. For polymer synthesis using 100 mL 3-necked reactor flask, octagonal stir bar with dimensions of 5/16” in diameter and 1” in length was used to stir the reaction mixture. For stable kaolinite suspensions in 2000 mL beakers, octagonal stir bar with dimensions of 3/8” in diameter and 2-1/2” in length was used to provide adequate mixing for sampling. Stir bars were also used in solution mixing wherever applicable in this study.

Mechanical stirrers were used to mix suspensions during flocculant addition and sampling of the tailings slurry. A 250 mL beaker was used as a mixing container as illustrated in Figure 3-2-1. The mixing tools were designed to achieve sufficient turbulent mixing conditions according to Tatterson’s theory [3]. An overhead mechanical stirrer (IKA® Digital Stirrer RW20, Fisher Scientific) and an axial flow impeller (blade diameter of 3.8 cm, 45^{o} pitched, and 4-bladed) were used to provide agitation. A tailor-made 316L stainless steel baffle (home made) was inserted into the beaker to prevent solid body rotation. This mixing setup was used in both flocculation of the sample and aluminum colloids preparation.

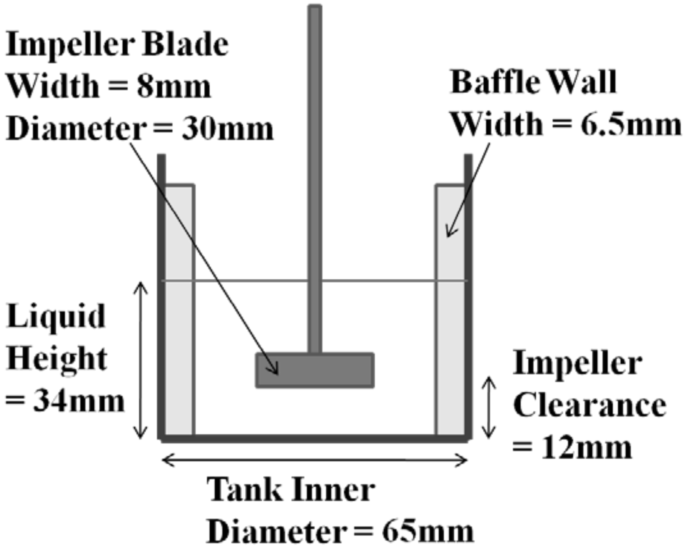

Figure 3-2-1 Schematics and Dimensions of Mixing Container

To agitate tailings slurry in a 4 L bottle, an overhead mechanical stirrer (IKA® Digital Stirrer RW20, Fisher Scientific) and a 3-bladed stainless steel impeller (blade width 6.5 cm, Fisher Scientific) were used. The impeller was tilted in a small angle (about 10^{o}) to avoid central vertex. For tailings stored in a 20 L pail, a high power overhead mechanical stirrer (CANWOOD PRO mechanical stirrer) and a stainless steel cone shape impeller (20cm in diameter) were used to provide agitation. Four steel rods (1/2" in diameter) were fixed up straight inside the pail as baffles to minimize solid body rotation.

3.2.2 Flocculant Stock Solutions

The dry polymer flocculants were stored in sealed glass bottles kept in the dark. To prevent significant decay of polymeric molecules, flocculant stock solutions of 2000 ppm were prepared with Milli-Q water one day prior to their use. The polymer solution was prepared in a 100 mL glass bottle, and was shaken overnight before use.

3.2.3 Model Tailings

Approximately 1 L of 5 wt% koalinite clay suspension at pH 8.5 was prepared and shaken overnight in a 2 L glass bottle. The suspension was then poured into 2000 mL beaker and stirred with the magnetic stir bar (3/8" in diameter; 2-1/2" in length) operating at 500 rpm. A 60 mL syringe was used to distribute 95 g of suspension into 250 mL beakers. The samples were sealed with paraffin film (Parafilm, Pechiney Plastic Packaging Company, Chicago, Illinois, US.) to prevent water loss and entrainment of dust. The samples were mixed in 250 mL beakers at 500 rpm for 5 min before the addition of flocculants with the setup shown in Figure 3-2-1.

3.2.4 Laboratory Extraction Tailings

Tailings were collected into a 20 L pail. The tailings slurry was stirred using the cone shape impeller with a mechanical stirrer (CANWOOD PRO mechanical stirrer) until no sediments was found at the bottom of the pail. Under continuous mixing, a pump (Masterflex® Heavy Duty Pump) was used to pump the tailings slurry into 4 L bottles. Each bottle of tailings slurry was shaken in a shaker overnight before further sampling. Disposable pipettes were used to transfer 95 g tailings slurry from the 4 L bottle to 250 mL beakers under continuous mixing using a 3-bladed stainless steel impeller with mechanical stirrer (IKA® Digital Stirrer RW20) at 900 rpm. Similar to the model tailings samples, the laboratory extraction tailings samples in 250 mL beakers were sealed with paraffin film and were mixed with mechanical stirrer for 5 min at 500 rpm before addition of flocculants using the same setup as shown previously in Figure 3-2-1.

3.2.5 Mixing Speed during Flocculant Addition to Tailings Slurry

The optimum mixing speed of each flocculant was determined according to its settling performance at room temperature. The optimum mixing speeds used during flocculant addition for the settling and filtration tests were summarized in Table 3-2-1. The results in Figures 3-2-2 and 3-2-3 show a noticeable effect of mixing on flocculation of 5 wt% kaolinite suspensions, in particular for flocculant Al-CP05. The optimum mixing speed was calculated by interpolation by a second degree polynomial.

Table 3-2-1 Optimum Mixing Speed of Flocculant Addition to Kaolinite Suspensions

	Mixing Speed (rpm)			
Polymers	CP10	CP05	Al-CP05	CP05+Al
T<LCST	350	350	300	300
T>LCST	400	400	300	300

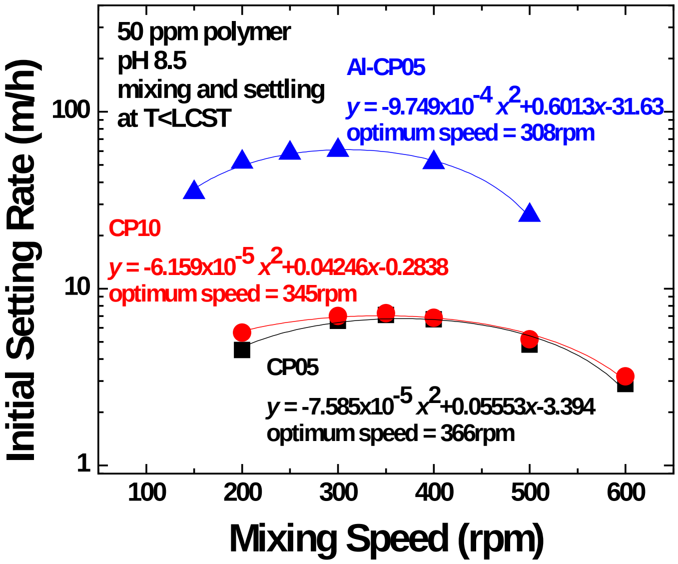

Figure 3-2-2 Mixing Condition of Each Flocculants in 5 wt% Kaolinite Suspensions at Temperatures below LCST

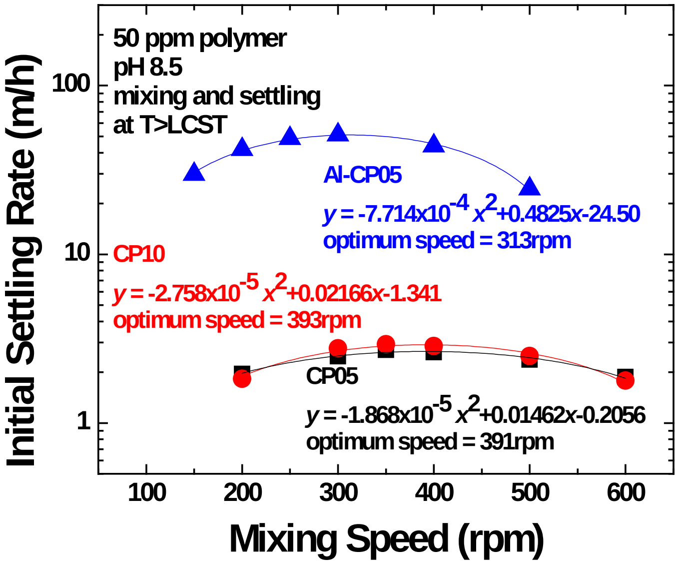

Figure 3-2-3 Mixing Condition of Each Flocculants in 5 wt% Kaolinite Suspensions at Temperatures above LCST

3.3 Procedures of Settling Tests

As the flocculants used are temperature sensitive, the mixing temperature during addition of polymeric flocculants and the settling temperature are the two major factors impacting the settling performance. Different conditions were employed in settling tests as shown in Figure 3-3-1. Although it is expected that adding polymer at temperature higher than its LCST has little effect on settling, two mixing temperatures, below and above the LCST of each flocculants, were used to determine how the addition of hydrophobic polymer (T>LCST) affects settling process. Extended mixing was introduced after addition of polymer to determine the floc strength. The strength refers to the resistance to shear of the flocs. Settling tests were also carried out in various settling temperatures to show the effect of settling temperature on settling of the tailings slurry. Figure 3-3-1 shows the proposed cases that were used in settling tests.

- RMRS (Room temperature Mixing and Room temperature Settling) means mixing polymer with and settling of suspensions both at room temperature;
- RMHS (Room temperature Mixing and Higher temperature Settling) means mixing polymer with suspension at room temperature and settling of suspensions at high temperatures (T>LCST);
- HMHS (High temperature Mixing and High temperature Settling) means mixing polymer with and settling of suspensions both at temperatures above corresponding LCST of each flocculants.

The suffix *–ex* means that extended mixing time was applied to suspensions after completing flocculants addition. The HMHS treatment was used in flocculation tests in this study though O’Shea et al. showed that flocculation of silica suspensions with pNIPAM addition at 50^{o}C shows no effect on settling [4]. The flocculation behaviour of the organic flocculant CP and the hybrid flocculant Al-CP might be different from that of pNIPAM. Treatment of “mixing polymer with suspension at high temperatures and settling of suspensions at room temperature” was not used in this study because the polymer become hydrophilic chains again when the suspension temperature cools down. The flocculation behaviour of flocculants would be similar to RMRS case but with insufficient mixing.

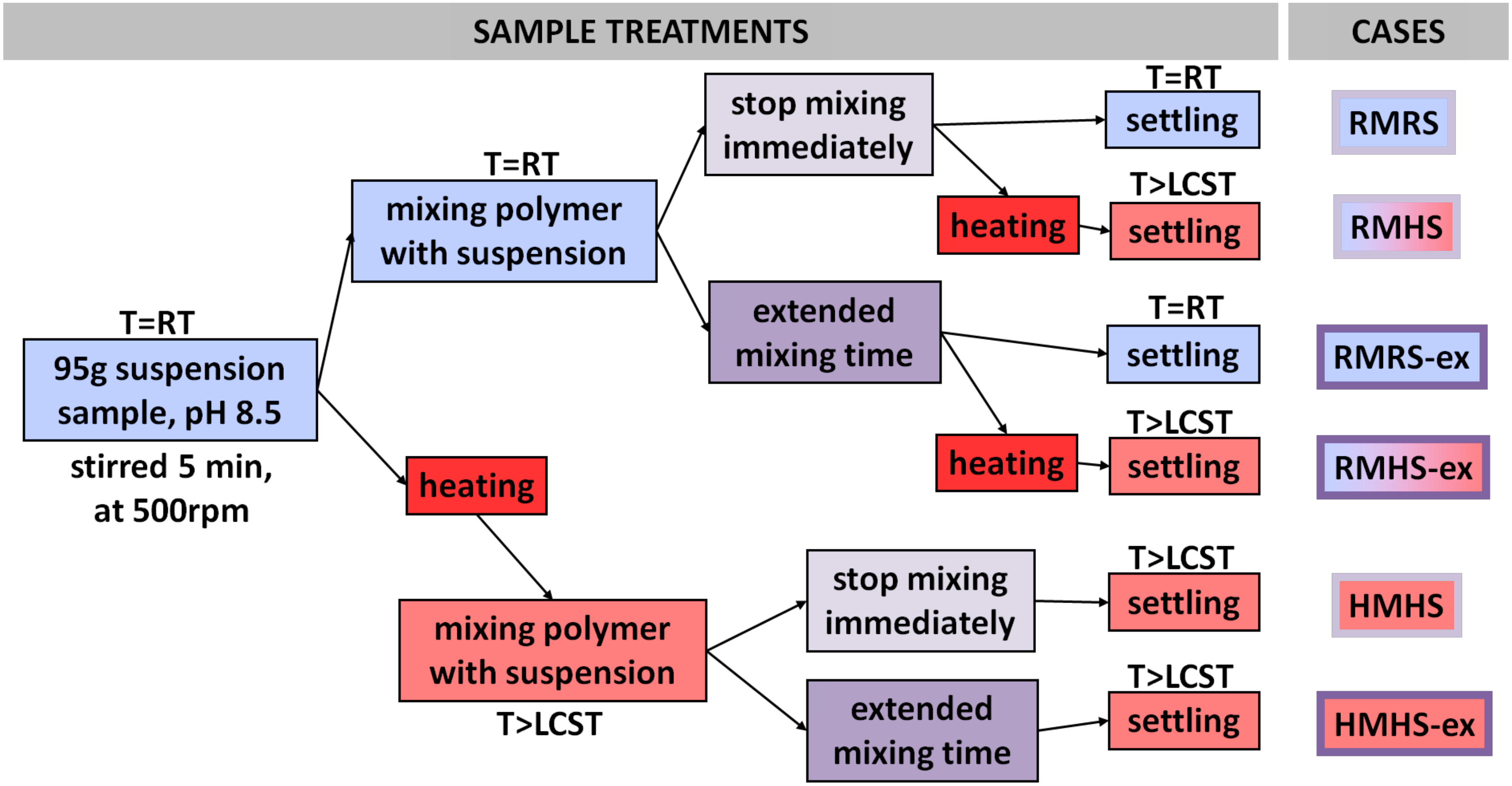

Figure 3-3-1 Proposed Cases Used in Settling Tests

In each settling test, 95 g of tailings sample were stirred at 500 rpm for 5 min at a targeted mixing temperature in a water bath. Before the addition of flocculant, the mixing speed was adjusted to the optimum mixing speed of each flocculant. Flocculant was added into the sample using micropipette (100-1000 µL, Fisher Scientific) at a rate of 0.1 mL/s. After completion of flocculant addition, agitation of sample was stopped immediately. Temperature of sample was adjusted to targeted settling temperature before transferring the sample into a 100 mL capped graduated glass cylinder. The cylinder was inverted up-side-down 5 times before being placed into a water bath at the corresponding settling temperature. Agitation of some samples was extended for 20 min after completion of flocculant addition at the same mixing speed. Temperature of sample was adjusted to targeted settling temperature before performing the settling test. A schematic diagram of the settling setup is shown in Figure 3-3-2.

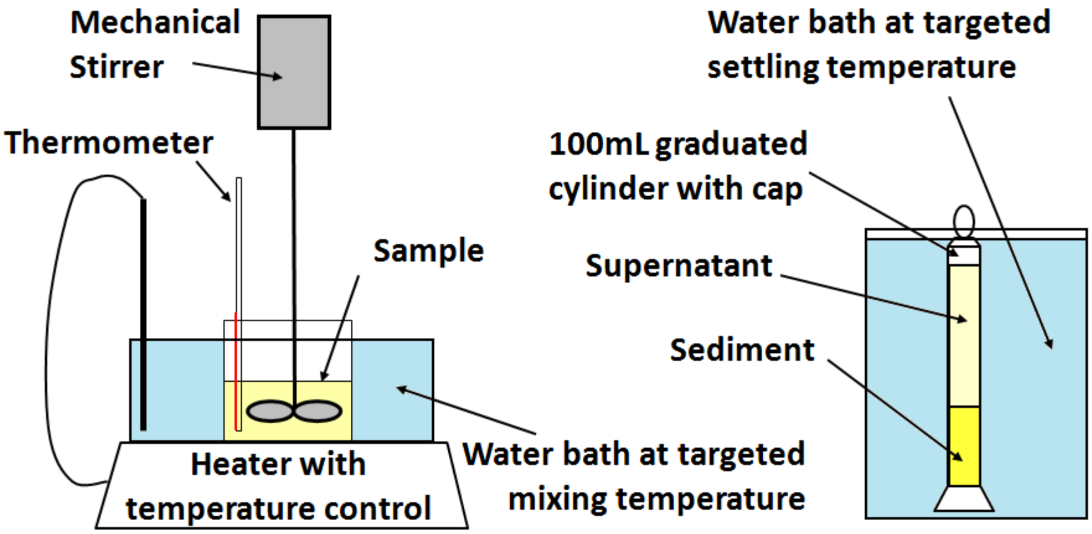

Figure 3-3-2 Schematic Setup of Settling Experiment

During the experiment, the mud-line level, i.e., interface between the supernatant and the concentration suspension, was recorded immediately after the cylinder was placed into the water bath. Some supernatant liquid was collected after 15 min of settling of kaolinite suspensions for turbidity measurement using a turbidimeter (HF Scientific DRT-15CE Portable Turbiditimeters, Fisher

Scientific). Each test was repeated three times and the average data were reported.The turbidity of supernatant was measured after 15 min settling, while the highly turbid supernatant of tailings sample was measured after 1 hour settling.

3.3.1 Data Processing of Settling Tests

A settling curve is the plot of normalized mud-line level as a function of settling time. A schematic diagram of a typical settling curve is shown in Figure 3-3-3. Polymer dosages were represented in ppm (part-per-million, milligrams of polymer flocculant per litre of kaolinite suspension or tailings sample). The initial slopes were taken as initial settling rates for comparison on settling performance. Suspension with no settling yields a normalized mud-line level of unity, i.e., a horizontal line at h/H = 1.0. The viscosity effect on settling was not taken into account [5, 6]. More details can be found in Appendix A.

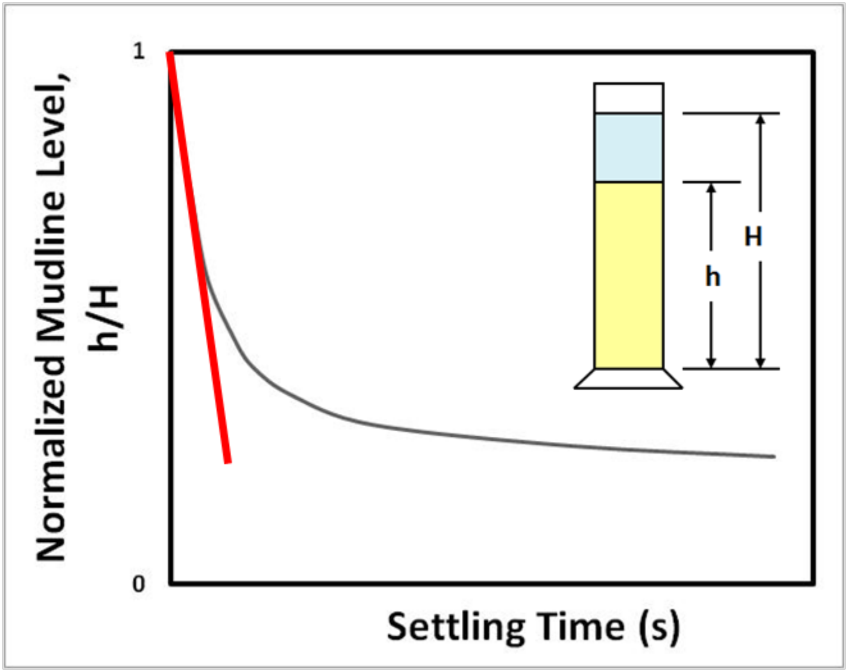

Figure 3-3-3 A Typical Settling Curve

3.4 Procedures of Filtration Tests

Due to the temperature sensitivity of the flocculants used in this work, different cases were set up in the filtration tests, as outlined in Figure 3-4-1, to determine the effect of temperature on the filtration characteristic. Similar to settling tests, two mixing temperatures, below and above the LCST of each flocculant, were used to determine the effect of adding the hydrophobic polymer at T>LCST to suspension on the filtration performance. In addition, two filtration temperatures, below and above the LCST of each flocculant, were used to determine how filtration temperature affects filtration performance of the tailings slurry. Figure 3-4-1 shows the treatments to sample in filtration tests.

- RMRF (Room temperature Mixing and Room temperature Filtering) means mixing polymer with and filtration of suspensions both at room temperature;
- RMHF (Room temperature Mixing and High temperature Filtering) means mixing polymer with suspension at room temperature and filtration of suspensions at high temperatures (T>LCST);
- HMHF (High temperature Mixing and High temperature Filtering) means mixing polymer with and filtration of suspensions both at temperatures above corresponding LCST of each flocculants.

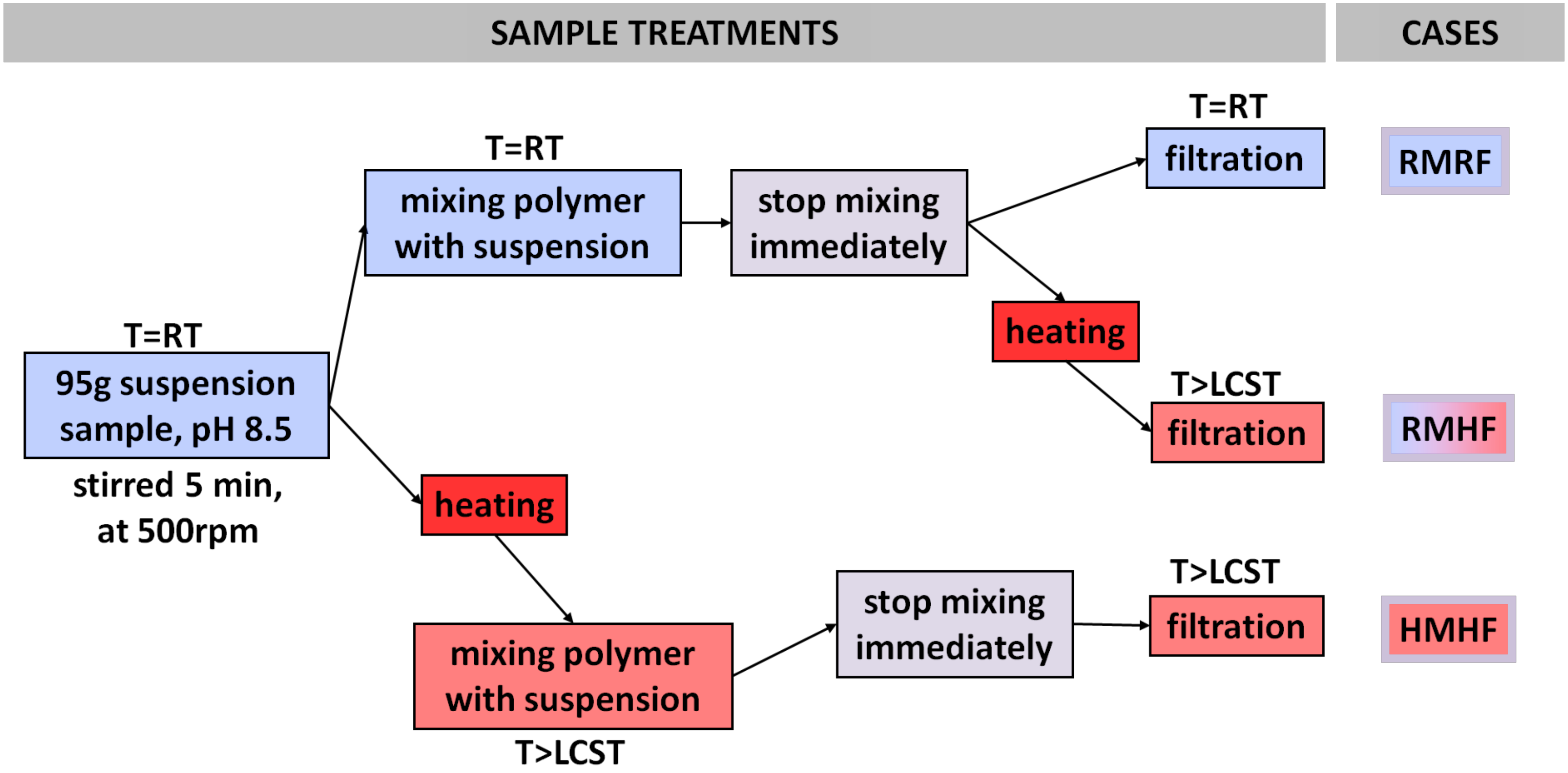

Figure 3-4-1 Proposed Cases Used in Filtration Tests

After 5min stirring at 500 rpm, the sample was adjusted to the optimum stirring speed and flocculant was added with micropipette at a rate of 0.1 mL/s at a targeted mixing temperature. After addition of flocculant, mixing was stopped immediately. The sample was adjusted to the targeted filtration temperature before its transfer into a filter press of 45.8 cm^2 filtration area (LPLT3000, Fann Instrument Company). The filtration test was conducted under 15 psi (103.4 kPa) of compressed air. Special hardened filter paper with wet strength of 75 psi (517.1 kPa) and particle size retention of 2-5 μm (3.5" in diameter, 100% cotton, Fann Instrument Company, Houston, Texas, USA) was used. The filtrate weight as a function of filtration time was determined by an electronic balance interfaced with a computer program. Figure 3-4-2 shows the setup of the filtration experiments.

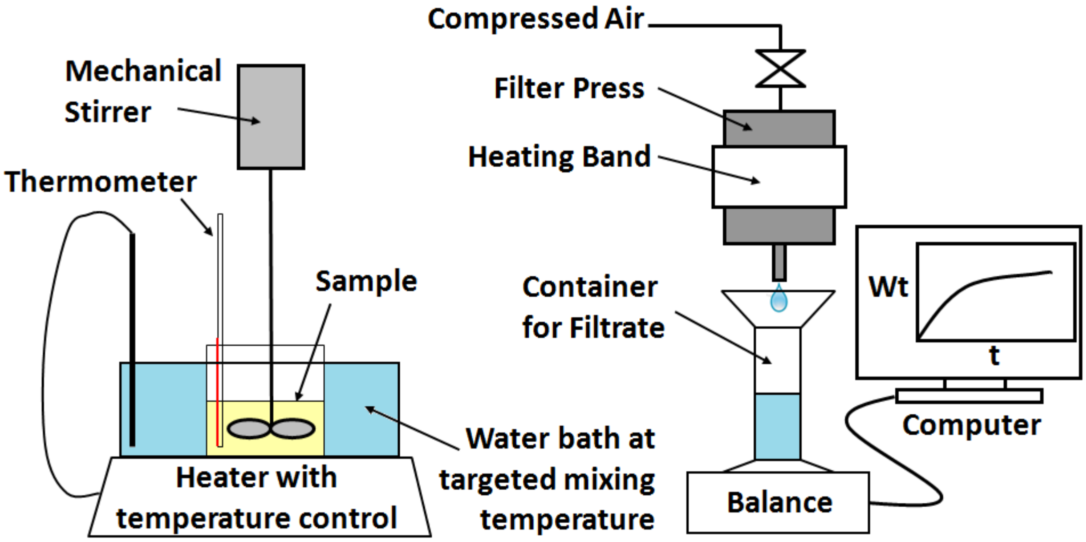

Figure 3-4-2 Schematic Setup of Filtration Experiment

To analyze the filter cake moisture content, the wet cake obtained was dried in an oven at 110°C to a constant weight. Each test was repeated three times and the average data were reported.

3.4.1 Data Processing of Filtration Tests

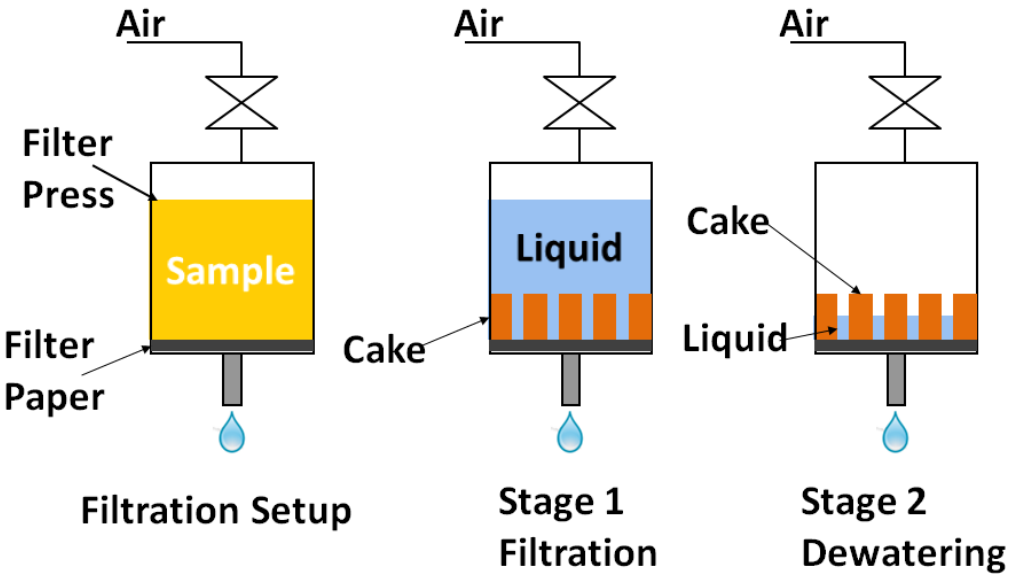

Figure 3-4-3 Schematic Diagram of Filtration Stages

Filtration process can be divided into two stages, filtration and dewatering, as shown in Figure 3-4-3. Filtration usually refers to the flow of the liquid in a suspension through a porous medium, while dewatering refers to the removing of liquid from filter cake by applying desaturating forces as described by Wakeman [7, 8]. Liquids are strained out and solids are left to form filter cake during the filtration stage [8]. This layer of cake acts as a filtration medium that its thickness and filtering resistance increase during filtration [9]. The permeability of the cake depends on the number, size, and shape of the micro-channels of the cake [8]. The micro-channel is a pathway for the filtrate to strain out from the cake. Figure 3-4-4 shows three different cake structures. A uniform slurry mixture of coarse solids or flocs would form a more permeable cake while slurry having a wide particle size distribution would be more likely to form a compact cake [8]. Fouling refers to the deposition of suspended particles at the pore openings of the filter medium or within the pores of the filter medium or cake such that the filtration fails [9]. Fouling usually happens when the suspended particles, especially the ultra-fines, are not fully flocculated.

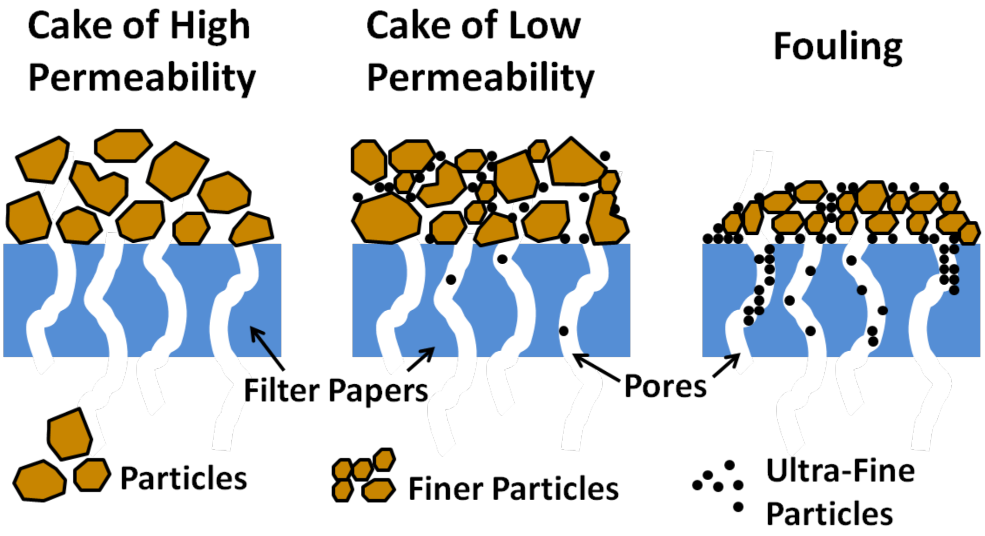

Figure 3-4-4 Schematic Diagram of Different Filter Cake Structures

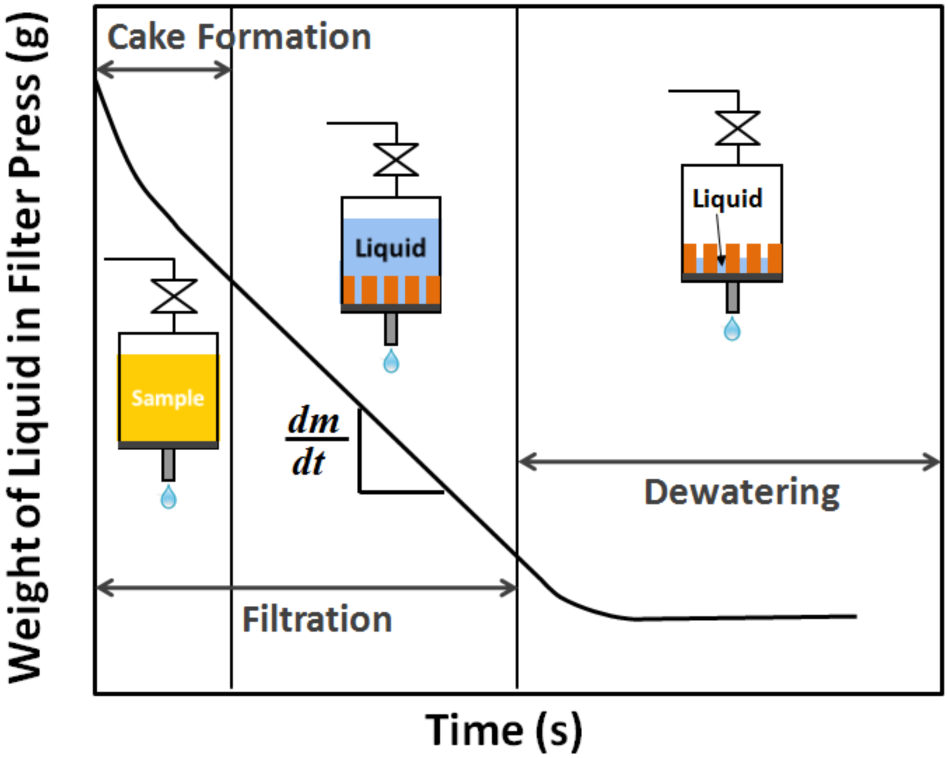

Figure 3-4-5 Filtration Stages in Filtration Curve

The filtration behaviour can be evaluated mathematically by analyzing of filtration rate and/or filter cake moisture content. Darcy proposed an empirical relation of filtration through a bed of sands,

$$\frac{1}{A}\frac{dV}{dt} = k'\frac{\Delta p}{\mathrm{L}} \tag{3-1}$$

where the left term is the overall fluid velocity, *k'* is a constant, Δp is the pressure drop, and *L* is the bed diameter [8, 9]. Poiseuille equation, on the other hand, is given by

$$\frac{dV}{dt} = \frac{\Delta p \cdot \pi \cdot r^4}{8 \cdot \eta \cdot L} \tag{3-2}$$

where *r* is the radius of filter medium and/or cake, η is the viscosity of fluid. Combining the Darcy equation with the Poiseuille equation leads to,

$$U = \frac{1}{\rho A}\frac{dm}{dt} = \frac{k \cdot \Delta p}{\eta \cdot L} \tag{3-3}$$

where *U* is the filtration rate, ρ is the density of filtrate, *A* is the apparent filtration area, *dm/dt* is the rate of filtrate collected, and *k* is an empirical constant [8, 10]. The term *dm/dt* is determined experimentally from a filtration curve as shown in Figure 3-4-5. Filtration rate U is then calculated using Equation (3-3) and used to compare the filtration performance of flocculants. Suspensions of highly concentrated ultra-fines such as MFT which resist filtration could yield a filtration rate of zero.

The filter cake moisture content is calculated by,

$$Cake\ Moisture = \frac{M_{wet} - M_{dry}}{M_{wet}} \tag{3-4}$$

where, M_{wet} is the mass of filter cake freshly taken out from filter press, and M_{dry} is the mass of filter cake fully dried in oven. Sample filtration data and analysis of filter cake resistance of laboratory extraction tailings are present in Appendices B and C, respectively.

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Chapter 4 Synthesis and Characterization of Temperature Sensitive Polymers

4.1 Materials

N-isopropylacrylamide (99 wt% NIPAM, Fisher Scientific) was stabilized with 500 ppm MEHQ. *N*-[3-(Dimethylamino)propyl]methacrylamide (DMAPMA, Sigma-Aldrich) had purity of 99%. *N*, *N*, *N*', *N*'-tetramethylethylenediamine (>99 wt%, GC, Sigma-Aldrich) had less than 0.02 wt% water as impurity. Ammonium persulphate (>98 wt% APS, ACS reagent, Sigma-Aldrich) had total impurities of less than 0.005 wt% insolubles and less than 0.04 meq/g acid remain from titration test. (According to IUPAC, equivalence (eq) is an "entity corresponding to the transfer of a H^+ ion in a neutralization reaction, of an electron in a redox reaction, or to a magnitude of charge number equal to one in ions.") The APS also contained traced amount of anions Cl^- and ClO_4^- of less than 0.001 wt% and traced amount of cations (<0.001 wt% Fe, <0.5 ppm Mn), and <0.005 wt% heavy metals as Pb. Ammonium carbonate (99 wt% $(NH_4)_2CO_3$, HPLC grade, Sigma-Aldrich) had 30.1% assay of NH_3 and impurities of 4ppm Cl, 1.7ppm heavy metal (as Pb), 1.5 ppm Fe, 0.002 wt% non-volatile matter, 0.001 wt% insoluble matter, and 0.001 wt% sulphur compounds (as sulphate). Aluminum chloride (99 wt% $AlCl_3$, Sigma-Aldrich) was in the form of anhydrous crystals. Deionized water (Milli-Q water) with resistivity of 18.2 Ω, prepared by an Elix 5 followed by a Millipore-UV plus water purification system (Millipore Inc., Canada) was used wherever applicable throughout this study. Dialysis tubing (Seamless Cellulose Dialysis Tubing, Fisher Scientific) had pore size of 4.8 nm in diameter and MWCO (molecular weight cut off) of 12000 Da. The tubing contained glycerine, water, and 1% sulphur, and was washed in boiling Milli-Q water twice before its use. Tetrahydrofuran (>99% THF, Sigma-Aldrich) contained inhibitor less than 0.025% of butylated hydroxytoluene (2,6-di-tert-butyl-p-cresol). Methanol (99.8% MeOH, Sigma-Aldrich) was of anhydrous form with less than 0.002% water. Potassium chloride (>99.0 wt% KCl, Sigma-Aldrich) contained less than 0.0005% phosphorus (P) and less than 0.1% insoluble matter. Sodium Hydroxide

(>95 wt% NaOH, Fisher Scientific) contained less than 3% of sodium carbonate. Kaolinite clay (kaolin K2-500, Fisher Scientific) was acid washed powder with less than 2% acid-soluble substances and less than 0.001% Lead.

4.2 Synthesis of P[NIPAM-co-DMAPMA]

The cationic temperature sensitive polymer p[NIPAM-co-DMAPMA] (CP) was prepared by free radical polymerization by following the procedures used to synthesize a temperature sensitive polymer, p[NIPAM-co-DMAPAA], with similar structure as CP by Sakohara and Nishikawa [1]. Two CPs with different lower critical solution temperatures (LCSTs) were synthesized. CP05 and CP10 contained 5 mole% and 10 mole% DMAPMA, respectively. CP05 was targeted to have LCST below the industrial tailings process temperature, 45^{o}C, while CP10 was made to have LCST above 45^{o}C. The total weight of NIPAM and DMAPMA for synthesis was approximately 5 g. Both monomers were dissolved in 50 mL Milli-Q water in a 100 mL 3-necked glass flask. The mixture was stirred by a magnetic stir bar (octagonal, 5/16" in diameter; 1" in length) at 250 rpm. Nitrogen gas (grade 5.0) was sparged into the mixture vigorously through a stainless steel needle under the liquid surface and 45μL of *N*, *N*, *N*', *N*'-tetramethylethylenediamine was added as an accelerator of the polymerization reaction. The reactor flask was wrapped up with aluminum foils to prevent the exposure of the reactants to light sources. A schematic diagram of the synthesis setup is shown in Figure 4-2-1. After 1 hour purging with N_2 gas, 2.3 mL of APS solution (10 g/L) was added into the mixture at a rate of 1 mL/min. The sparging needle was withdrawn from the liquid surface 10 min after the addition of initiator. The viscosity of the mixture was found by naked eyes to increase during this period. Mixing and purging of N_2 were stopped, and the reactor flask was sealed. The polymerization reaction was allowed to run for 2 hours at room temperature. The obtained polymer was in the form of transparent gels, and it was rubbery.

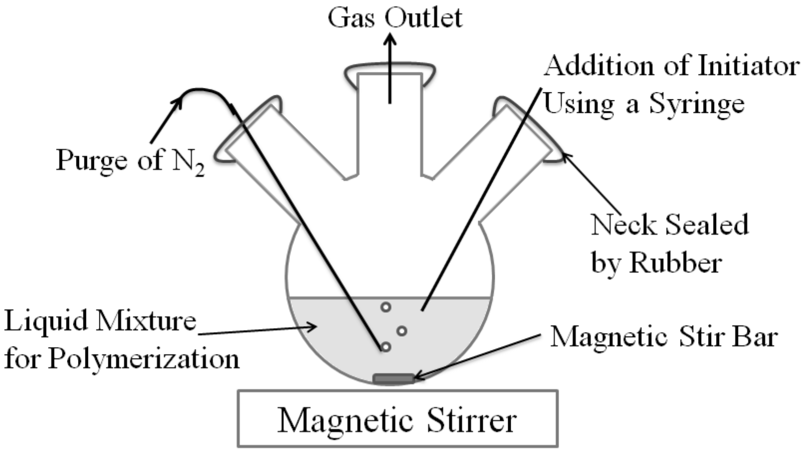

Figure 4-2-1 Apparatus used for Polymerization Reaction

Polymer gel was taken from the reactor flask after reaction, and was dissolved in Milli-Q water as 0.5 g/L aqueous solution. Dialysis tubing was placed in boiling Milli-Q water twice to wash off the preservatives. The aqueous polymer solution was then poured into the dialysis tubing for purification. The purified polymer had molecular weight greater than 12000 Da. The polymer solution was dried by freeze drying. The obtained polymer was in the form of white cottony foam.

4.3 Synthesis of Aluminum Hydroxide-P[NIPAM-co-DMAPMA] Hybrid

4.3.1 Preparation of Aluminum Hydroxide Colloids

Aluminum hydroxide colloids, $Al(OH)_3$, can be prepared by adding ammonium carbonate solutions into excess aluminum chloride solutions under vigorous mixing, causing the production of $Al(OH)_3$ colloids as shown by the reaction below [2]:

$$2AlCl_{3\,(aq)} + 3(NH_4)_2CO_{3\,(aq)} + H_2O_{(l)} \rightarrow 2Al(OH)_{3\,(aq)} + 6NH_4Cl_{(aq)} + 3CO_{2\,(g)} \qquad (4\text{-}1)$$

The $Al(OH)_3$ colloids were prepared one day prior to the synthesis of polymer-colloid hybrid, $Al(OH)_3$-P[NIPAM-co-DMAPMA], (Al-CP).

The preparation of the aluminum hydroxide colloids was accomplished as follows. 25 g of 0.1 M $AlCl_3$ solution and 50 g of 0.1 M $(NH_4)_2CO_3$ solution were prepared separately in two 250 mL beakers. 36 g of $(NH_4)_2CO_3$ solution was added into $AlCl_3$ solution at a rate of 0.5 g/min using a pump (C/L microflex pump, MasterFlex, USA). The amount of $(NH_4)_2CO_3$ added was monitored by a balance (Fisher Scientific). During the addition of $(NH_4)_2CO_3$ solution, the mixture was stirred with an overhead mechanical stirrer (IKA® Digital Stirrer RW20, Fisher Scientific) at 500 rpm in a mixing tank of the same dimensions as shown earlier in Figure 3-2-1. After completion of $(NH_4)_2CO_3$ solution addition, the mixture was stirred at 300 rpm for 1 hour to complete the reaction. The pH, particle size, and ζ-potential of the prepared aluminum hydroxide colloids were measured by pH meter (accumet AP60, Fisher Scientific) and ZetaPALS (Brookhaven Instruments Corporation, NY, USA), respectively. Physical properties of colloids were measured immediately after preparation (Day 1) and before the synthesis of the inorganic-organic hybrid polymer (Day 2) were given in Table 4-3-1. The results in Table 4-3-1 show that the $Al(OH)_3$ colloids are stable, with particles sizes between 30 to 35 nm and zeta potentials between 34-39 mV. The colloid of those physical properties are suitable for synthesis of Al-CP hybrid flocculants.

Table 4-3-1 Physical Properties of Aluminum Hydroxide Colloids

	Day 1†	Day 2††
pH	5.74	5.58
Colloids Size (nm)	31.9	34.2
ζ-potential (mV)	34.25	39.31

† Measured immediately after preparation of colloids
†† Measured before synthesis of polymer-colloid hybrid

4.3.2 Synthesis of Cationic Temperature Sensitive Inorganic-Organic Hybrid Polymer

The temperature sensitive polymer-colloid hybrid (Al-CP) was synthesized using the similar approach mentioned previously and the same setup shown in Figure 4-2-1. The polymerization was conducted in $Al(OH)_3$ colloidal suspension instead of Milli-Q water. Al-CP05 was prepared by polymerizing 4.65 g of NIPAM and 0.368 g of DMAPMA in 50mL of aluminum hydroxide colloid solution in dark at room temperature. *N*, *N*, *N*', *N*'-tetramethylethylenediamine was added at the beginning to the reaction mixture as an accelerator while mixing all the chemicals with a magnetic stir bar rotating at 250 rpm. After sparging N_2 gas for 1 hour, 2.3 mL of 10 g/L APS stock solution was added to the mixture at a rate of 1 mL/min. The reaction was allowed to run for 2 hours. The obtained polymer hybrid was in slightly milky gel form, and it was rubbery as in the case of p[NIPAM-co-DMAPMA].

The obtained polymer-colloid hybrid gel was diluted to 0.5 g/L using Milli-Q water. Al-CP was purified by dialysis which retained materials with molecular weight higher than 12000 Da. The polymer solution was oven-dried at 45^oC on Teflon dish. The polymer dried was in the form of slightly milky sheet. The aluminum content in Al-CP05 was determined by atomic absorption spectrophotometer to be 0.9 wt%. The polymer hybrid is suspected to have a star-like structure like Al-PAM [3, 4].

4.4 Preparation of P[NIPAM-co-DMAPMA] in Aluminum Hydroxide Colloidal Suspension Blends

For comparison with polymer-colloid hybrid (Al-CP), CP05 was dissolved in diluted $Al(OH)_3$ colloids suspensions such that it had the same aluminum content with Al-CP05. The polymer blends {CP+Al} were prepared a day prior to their uses. The $Al(OH)_3$ colloids suspensions used had colloid sizes of 30-38 nm, zeta-potential of 30-42 mV, and in the pH range of 5.5-6.0. {CP05+Al} is a mixture of flocculant CP05 and coagulant $Al(OH)_3$ colloids.

4.5 Characterization of Temperature Sensitive Polymers

4.5.1 Molecular Weight Measurement

According to Mark-Houwink equation,

$$[\eta] = KM_v^a \tag{4-2}$$

where K and a are characteristic constants for a given polymer solution at a specific temperature [5]. M_v is the viscosity-average molecular weight, and $[\eta]$ is known as the intrinsic viscosity,

$$[\eta] = \lim_{c\to 0}(\frac{\eta_{sp}}{c}) = \lim_{c\to 0}(\frac{\eta-\eta_o}{\eta_o c}) \tag{4-3}$$

where c is the concentration of polymer solution, η_{sp} is the specific viscosity and η_o is the initial viscosity [5]. The intrinsic viscosity of polymer solution is therefore the viscosity of solution without interacting polymer coils, i.e., an infinitely diluted solution [5]. A dual Huggins-Kraemer plot was used to evaluate [η] of each polymeric flocculants [5]. At each concentration, both reduced viscosity, η_{sp}/c, and inherent viscosity, $ln(\eta/\eta_o)/c$, were determined from the measured viscosity of polymer solutions using an Ubbelohde viscometer and plotted against the concentration of polymer solution. By extrapolating both data sets, the y-intercepts of both lines should fall on the same point, and this point is known as the intrinsic viscosity of the polymer.

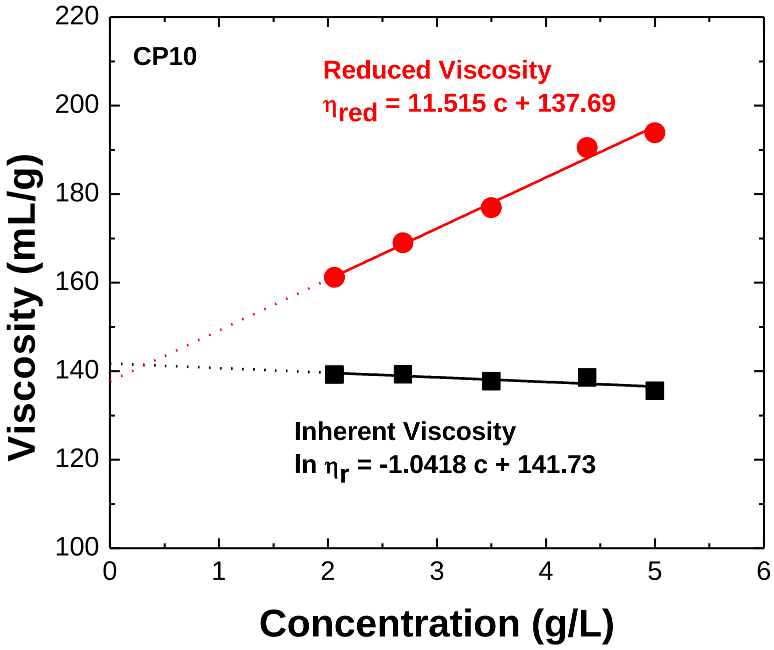

Figure 4-5-1 Dual Huggins-Kraemer Plot for CP10

The viscosity measurement was carried out using an Ubbelohde viscometer (CANNON 75-J953, Fisher Scientific). The cationic polymer (CP), p[NIPAM-co-DMAPMA], was dissolved in tetrahydrofuran (THF) at 27°C and the viscosities of CP were measured using polymer solutions of five different concentrations. A dual Huggins-Kraemer plot was produced as shown in Figure 4-5-1. Intrinsic viscosity of CP was calculated by taking the average of the y-intercepts of both lines. By assuming narrow molecular weight distribution, the viscosity-average molecular weight, M_v is approximately equal to the number-average molecular weight, M_n. Therefore, M_n of CP was estimated using the molecular weight relation of p(NIPAM), [6]

$$[\eta] = 9.59 \times 10^{-3} M_n^{0.65} \tag{4-4}$$

Since the polymer-colloid hybrid (Al-CP), $Al(OH)_3$-P[NIPAM-co-DMAPMA], had low solubility in THF, viscosity measurements of Al-CP was performed in a mixed solvent, THF/methanol at 3 to 2 volume ratio. The M_n of Al-CP was estimated. The physical properties of polymeric flocculants synthesized in this study are summarized in Table 4-5-1. Sakohara and Nishikawa synthesized p[NIPAM-co-DMAPAA] with molecular weight of 3.95MDa [1]. The synthesis of CP and Al-CP with a similar approach would achieve a higher molecular weight by adding initiator in a lower speed during the synthesis.

Table 4-5-1 Measured Viscosity and Molecular Weight of Synthesized Flocculants

Flocculants	CP05	CP10	Al-CP05	CP05+Al
Mole Ratio	95% NIPAM 5% DMAPMA	90%NIPAM 10% DMAPMA	95% NIPAM 5% DMAPMA	95% NIPAM 5% DMAPMA
Al Content (wt%)	nil	nil	0.9	0.9
[η] (ml/g)	135	140	125	135
MW (10^6 Da)	2.41	2.54	2.14	2.41

4.5.2 Measurement of Lower Critical Solution Temperature

Temperature sensitive polymers exhibit a lower critical solution temperature (LCST) above which the polymer molecules shrink into hydrophobic globules. As a result, the polymer solution appears cloudy. Based on this property of temperature sensitive polymers, LCST of temperature sensitive polymers can be estimated by measuring the turbidity of the polymer solution with increasing solution temperature. In this study, the turbidity of flocculants was measured using a tubiditimeter (HF Scientific DRT-15CE Portable Turbiditimeter, Fisher Scientific). The LCST of each flocculant at a specific pH was defined as the mid-point of the transition zone (steepest part) of the turbidity-temperature curve. Figure 4-5-2 shows the relation of turbidities of 2000 ppm polymer solutions of pH 8.5 with increasing temperature.

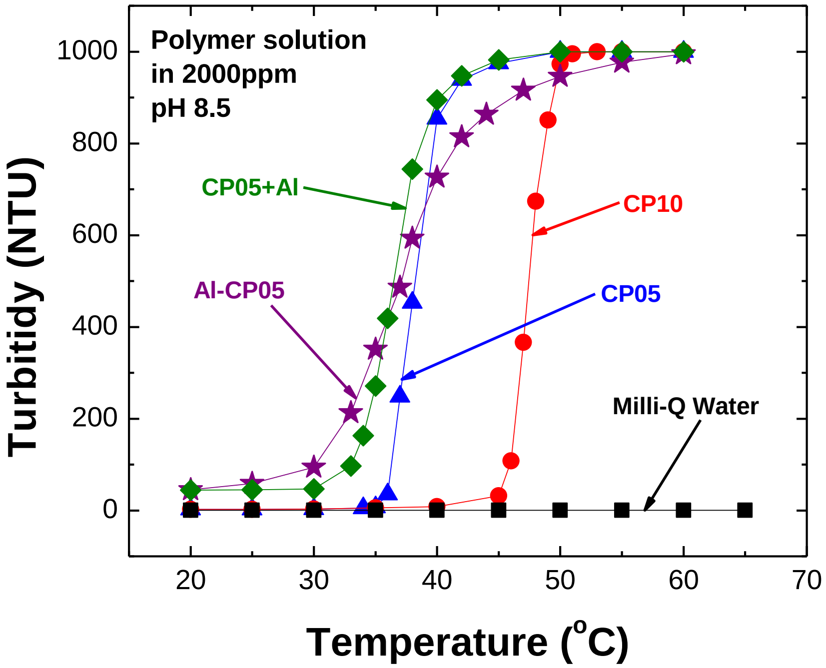

Figure 4-5-2 Lower Critical Solution Temperatures of All Flocculants at pH 8.5

Figure 4-5-2 shows, at pH 8.5, CP10 had a LCST of 48°C which is 10 degrees higher than LCST of CP05. This finding indicates that a small increase in mole ratio of DMAPMA in CP can significantly increase the LCST of the copolymer. By dissolving CP05 into $Al(OH)_3$ colloids solution {CP05+Al}, the transition of the temperature-turbidity curve became flattened and shifted slightly to lower LCST at 37°C as compared with that of CP05. The curve was flattened even more for Al-CP05, which indicates a more gradual temperature transition of Al-CP05, but the LCST remained at 37°C, controlled by CP05. The effect of pH on LCSTs of polymers was shown in Figures 4-5-3 to 4-5-6. As shown in Figure 4-5-3, the higher the pH values, the lower the LCST of copolymer CP05. At pH 8.0, CP05 started to lose its temperature sensitivity as the solubility of CP05 becomes dominated by highly hydrophilic protonated amide groups. Therefore, CP05 cannot be effectively used as temperature sensitive polymers in neutral or acidic suspensions.

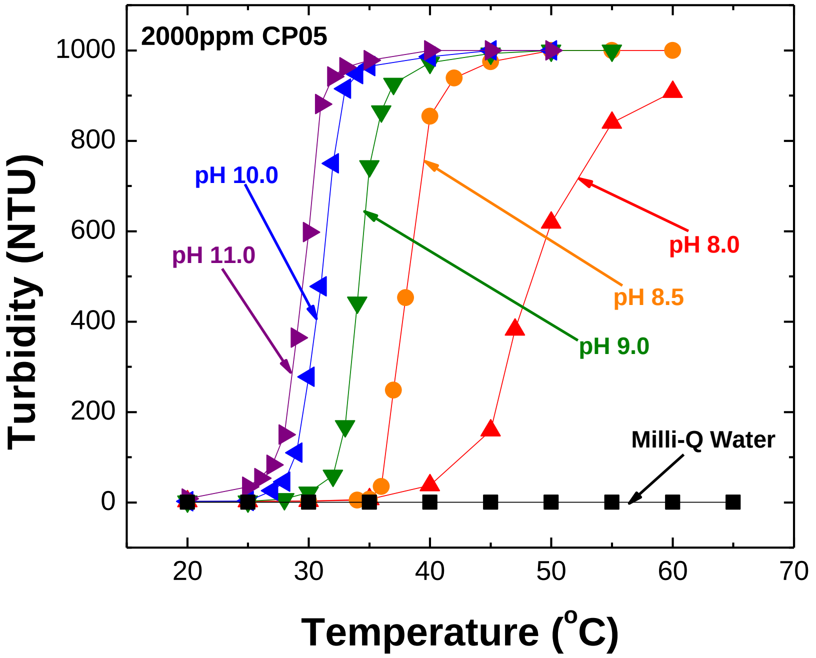

Figure 4-5-3 Lower Critical Solution Temperatures of CP05 at Different pH

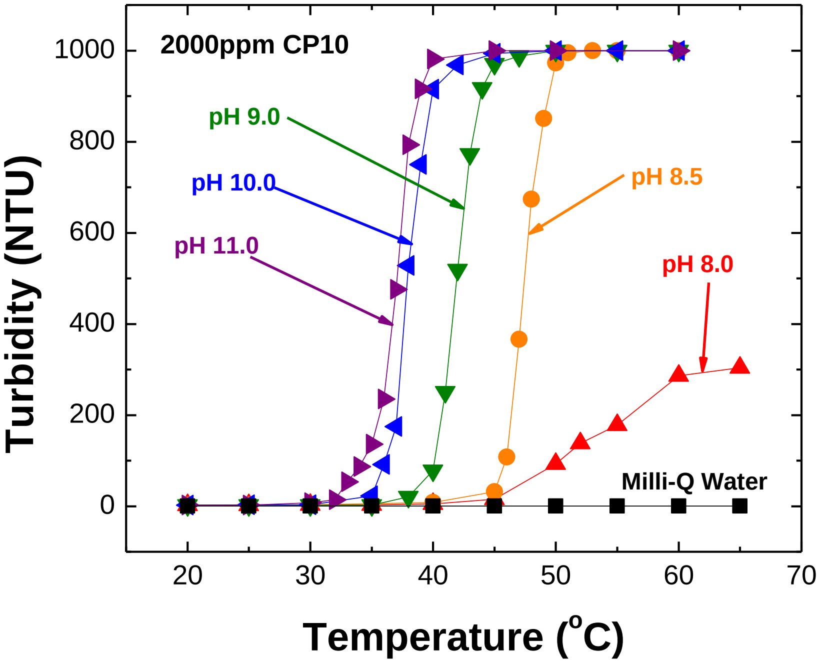

Figure 4-5-4 Lower Critical Solution Temperatures of CP10 at Different pH

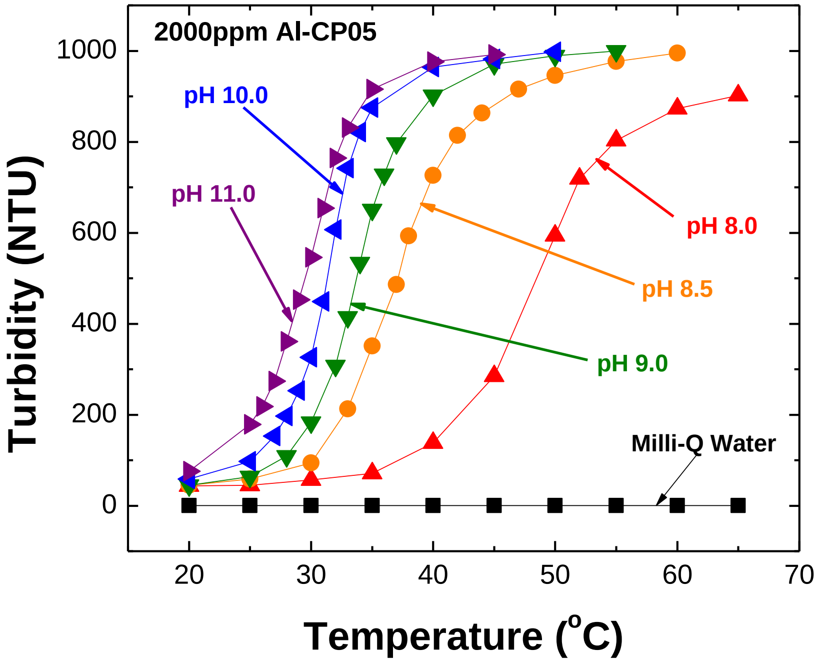

Figure 4-5-5 Lower Critical Solution Temperatures of Al-CP05 at Different pH

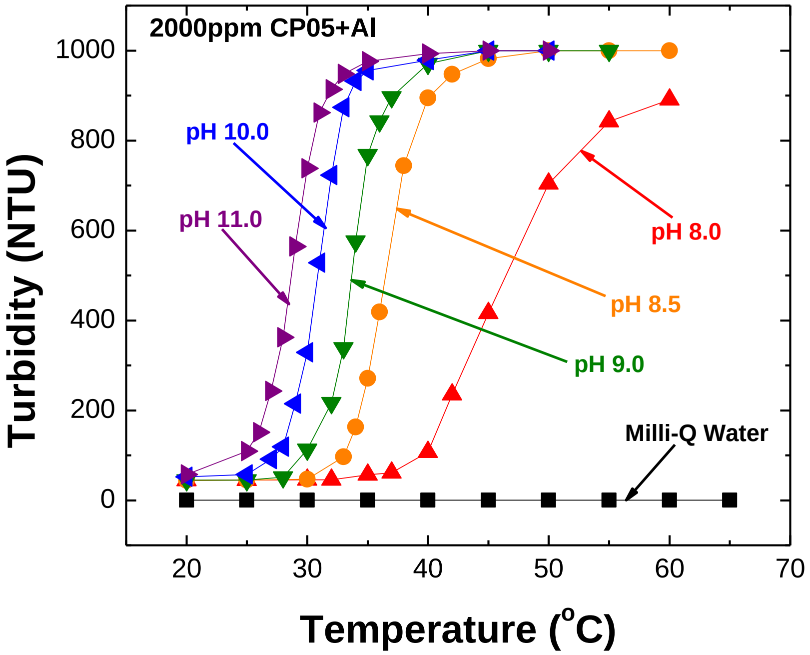

Figure 4-5-6 Lower Critical Solution Temperatures of {CP05+Al} at Different pH

The effect of pH on LCST of CP10 in Figure 4-5-4 shows a similar trend as that of CP05. The phase transition due to the change in conformation of the CP10 polymer molecule at pH 8.5 was as sharp as that of the CP05. Therefore, the increase of DMAPMA ratio in the copolymer appears to have little effect on the temperature sensitivity of CP, but shifts the LCST to a higher temperature.

In comparison with CP05, pH shows similar effect on LCSTs of both Al-CP05 and {CP05+Al}, but the transition becomes less sharp, as shown in Figures 4-5-5 and 4-5-6. Although the inclusions of $Al(OH)_3$ colloids lowered the temperature sensitivity, Al-CP05 and {CP05+Al} could still exhibit the hydrophilic/hydrophobic transition.

The results in Table 4-5-2 collectively show a strong dependence of LCST on temperature, pH and DMAPMA content in temperature sensitive polymers. The LCST increases with increasing in DMAPMA content and decreasing pH. In practice, the change in hydrophobicity of a given temperature sensitive flocculants could be achieved by changing either pH or temperature of the suspensions.

Table 4-5-2 Summary of Lower Critical Solution Temperature of All Polymeric Flocculants at Variable pH

pH	8.0	8.5	9.0	10.0	11.0
CP10	nil	48°C	42°C	38°C	37°C
CP05	~49°C (not sharp)	38°C	35°C	31°C	30°C
Al-CP05	~48°C (not sharp)	~37°C (not sharp)	~34°C (not sharp)	~32°C (not sharp)	~30°C (not sharp)
{CP05+Al}	~46°C (not sharp)	37°C	33°C	31°C	28°C

4.5.3 Interaction of Flocculants with Kaolinite Clay Particles

In order to determine the effectiveness of the synthesized polymers on flocculating kaolinite clay suspensions, zeta potentials of the clay suspension were measured using ZetaPALS as a function of flocculant dosage. The measurement was performed with 0.01 wt% kaolinite clay suspension at pH 8.5 using 0.01M KCl as supporting electrolyte. The kaolinite suspension was placed in a shaker for overnight before pH was adjusted by NaOH. KCl was added before zeta potential measurement. Flocculants were added in the form of diluted solution with micropipette at a rate of 0.1 mL/s while suspension was under continuous mixing at specific mixing speed as mentioned in Chapter 3. As shown in Figure 4-5-7, all the flocculants were able to alter the surface charge of the clay particles from negative to positive. Hence, flocculation of kaolinite clay suspension would be expected with each polymeric flocculants. Settling and filtration performances of CP05 and CP10 will be discussed in Chapter 5, while the flocculation performances of Al-CP05 and {CP05+Al} will be discussed and compared with CP05 in Chapter 6.

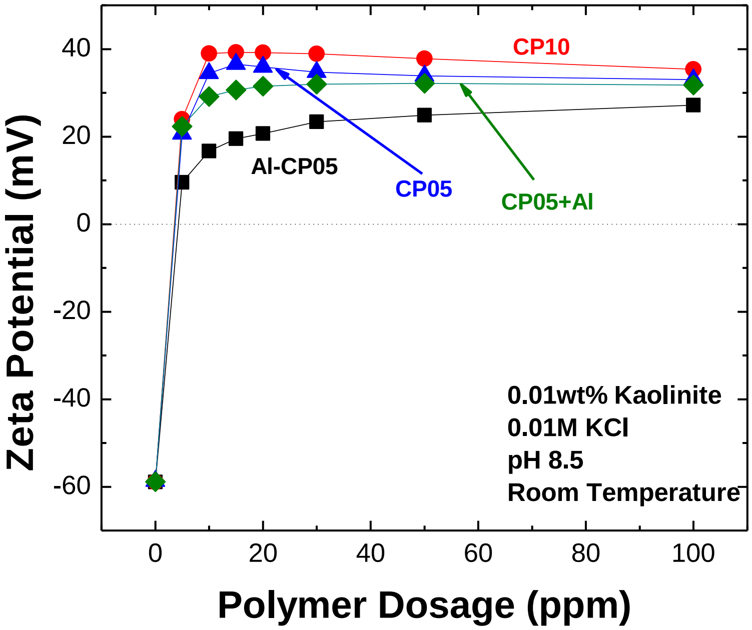

Figure 4-5-7 Effect of Flocculants on the Surface Charge of Kaolinite Particles

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Chapter 5 Effect of P[NIPAM-co-DMAPMA] on Settling and Filtration Processes on Kaolinite Suspensions

The temperature sensitive cationic poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide], p[NIPAM-co-DMAPMA] (CP), was synthesized at two different molar ratios of the monomers. Flocculants CP05 and CP10 have 5 mole% and 10 mole% DMAPMA, respectively. CP05 has a molecular weight of 2.4 MDa and LCST of 38^oC. While having similar molecular weight of 2.5 MDa, CP10 has a higher LCST of 48^oC. The flocculation behaviours of these two flocculants were studied by performing settling and filtration tests. Settling rate, clarity of supernatant, and floc strength were used to characterize the flocculation performance on sedimentation. Filtration rate and moisture content of filter cake were used to measure the efficiency of polymer aids in dewatering by filtration. Settling and filtration tests were carried out using 5 wt% kaolinite suspension in deionized water at pH 8.5. The suspension contained ultra-fine and fine particles of sizes 0.16 µm and 4.4 µm, respectively. The flocculation behaviours of the two flocculants are compared in Section 5.3.

5.1 Settling Tests

5.1.1 Effect of CP05 on Settling

CP05 was synthesized which has LCST of 38^oC and molecular weight of 2.4 MDa. CP05 was added to kaolinite suspensions at room temperature to study the effect of settling temperature on settling rate. An improvement on settling of kaolinite suspensions at all the five settling temperatures tested (20^oC, 30^oC, 40^oC, 50^oC, 60^oC) is shown in Figure 5-1-1. The higher the settling temperature, the faster the settling is. A significant jump was observed in the initial settling rate between settling at 30^oC and 40^oC. The increase of initial settling rate at 40^oC and higher temperatures was attributed to the change in conformation of temperature sensitive polymer with temperature above LCST. When settling temperature was above LCST of CP05, 38^oC, the polymer shrank into hydrophobic globules, leading to formation of denser flocs, which causes an increase in the settling rate.

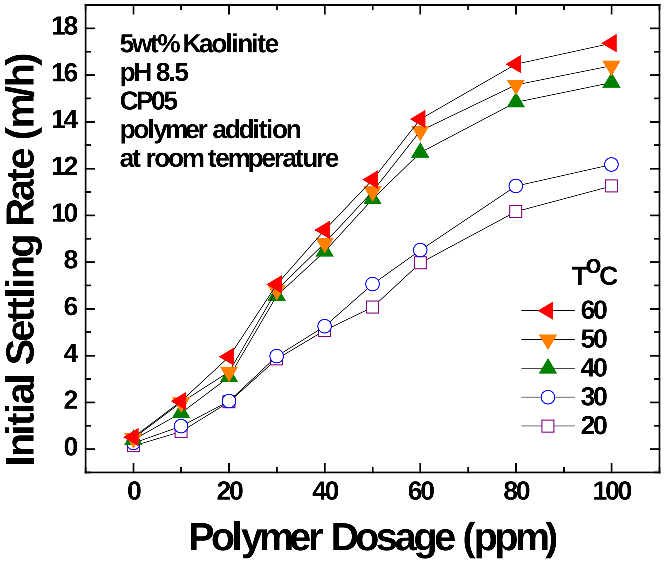

Figure 5-1-1 Initial Settling Rate of Kaolinite Suspensions with CP05 Added at Room Temperature

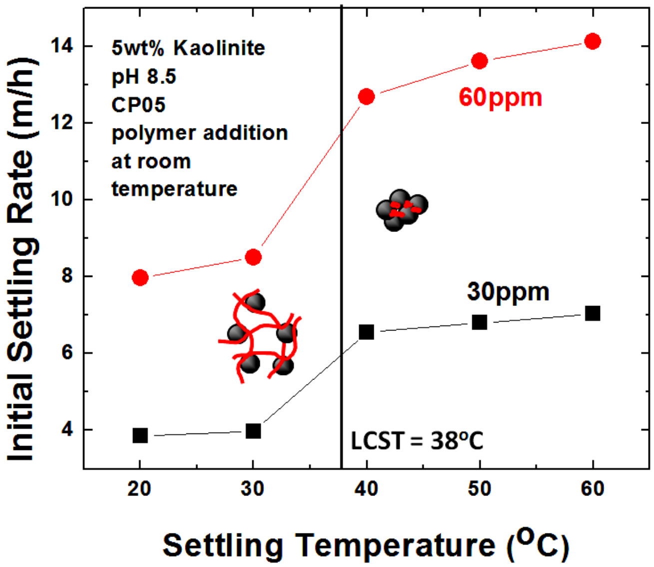

Figure 5-1-2 Effect of Settling Temperature on Settling of Kaolinite Suspensions with CP05 Added at Room Temperature

In Figure 5-1-2, polymer dosages of 30 ppm and 60 ppm were tested as a function of settling temperature to study the effect of temperature on initial settling rate. For both dosages, a jump in initial settling rate was observed with increasing settling temperature from 30°C to 40°C. This jump confirms that the settling rate is enhanced at temperatures higher than LCST.

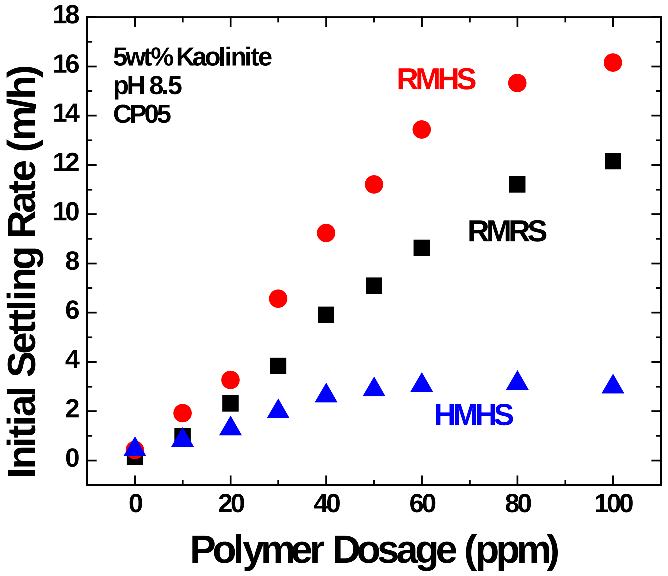

Figure 5-1-3 Settling of Kaolinite Suspensions with CP05 Addition in Different Settling Cases

To determine the effect of flocculant addition temperature and settling temperature on settling of kaolinite suspensions, settling tests were carried out in three cases, RMRS, RMHS, and HMHS, as mentioned in Chapter 3. For CP05, high temperature refers to 45°C, which is above LCST of CP05, 38°C. The results in Figure 5-1-3 show a faster initial settling rate with RMRS than with HMHS. The best settling rate is, however, yielded with RMHS. Increasing polymer dosage resulted in a much significant increase in the initial settling rate for cases RMRS and RMHS than HMHS. At 45°C which is above LCST of CP05, the polymer shrank into hydrophobic globules, losing its ability of flocculating suspended particles. RMHS led to a better settling than RMRS because the flocs formed at room temperature became more compact at settling temperature above LCST of CP05, enhancing the settling rate of flocs [1-4].

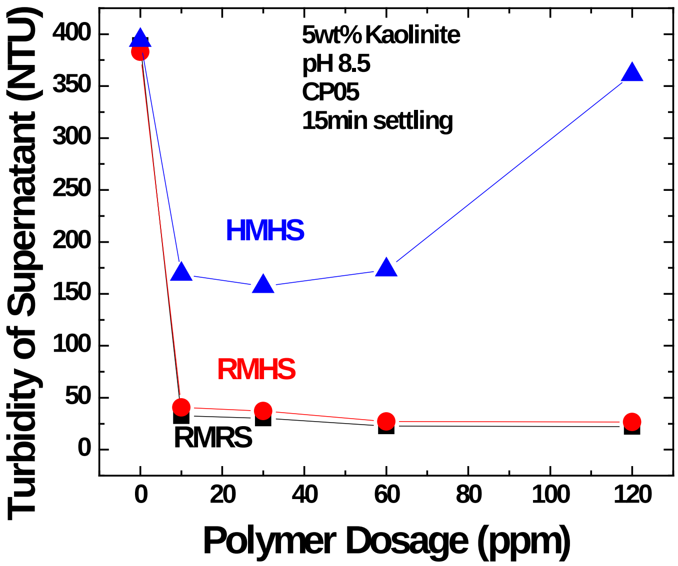

Figure 5-1-4 Supernatant Turbidity of Kaolinite Suspensions in Different Settling Cases with CP05 as Flocculant

The supernatant clarity of the settled suspension was measured after 15 min settling. Turbidities of Milli-Q water and 0.01 wt% kaolinite suspension at pH 8.5 were measured as references, and were 0.02 NTU and 132 NTU, respectively. As shown in Figure 5-1-4, HMHS produced the most turbid supernatant, corresponding to the least effective flocculation as shown in Figure 5-1-3. RMRS and RMHS produced supernatant of turbidity less than 50NTU. The difference in supernatant clarity between RMRS and RMHS cases was not significant as heating the flocculated suspension produced denser flocs and hence increased settling rate [1-4]. However, increasing settling temperature does not necessarily increase the degree of flocculation.

Some polymeric flocculants produce flocs that are easily ruptured when subjected to excessive mixing. Some of the tests in this study, therefore, were designed to prolong the agitation time to evaluate the flocculation and hence, the floc strength.

Agitation time was extended to 20 min at the same mixing speed after addition of polymer to the suspension. The results in Figure 5-1-5 show that the flocs formed by CP05 addition in all three cases are sufficiently strong to sustain the induced shear. The slight increase of settling rate with mixing time over the first 5 min for the cases of RMRS and RMHS indicates the importance of good mixing to distribute flocculant and promote collision of particles for flocculation.

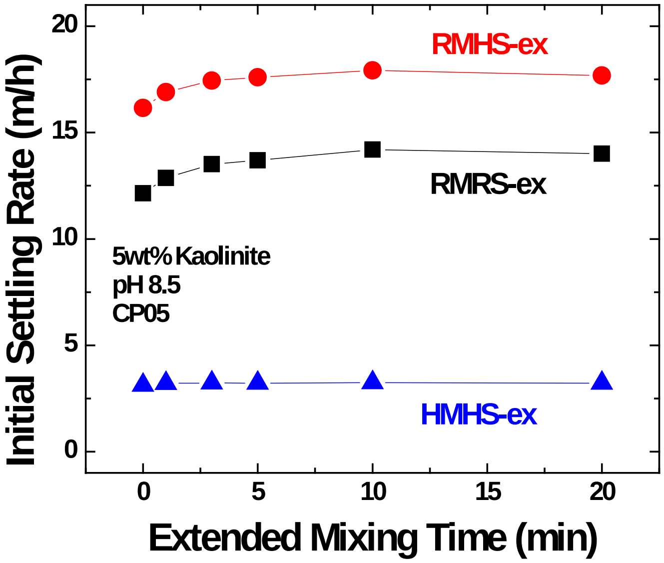

Figure 5-1-5 Effect of Mixing Time on Settling of Kaolinite Suspensions in Different Settling Cases with CP05 as Flocculant

5.1.2 Effect of CP10 on Settling

CP10 of molecular weight of 2.5 MDa and LCST 48°C was synthesized and had. Same experiments as shown in Section 5.1.1 were carried out using CP10. The synthesized CP10 was added to kaolinite suspensions at room temperature, and the suspension was then heated up to five different settling temperatures to study the effect of settling temperature on flocculation. The results in Figure 5-1-6 show an enhanced settling rate of kaolinite suspensions by CP10 addition at all five settling temperatures. Initial settling rate increases with increasing CP10 dosage.

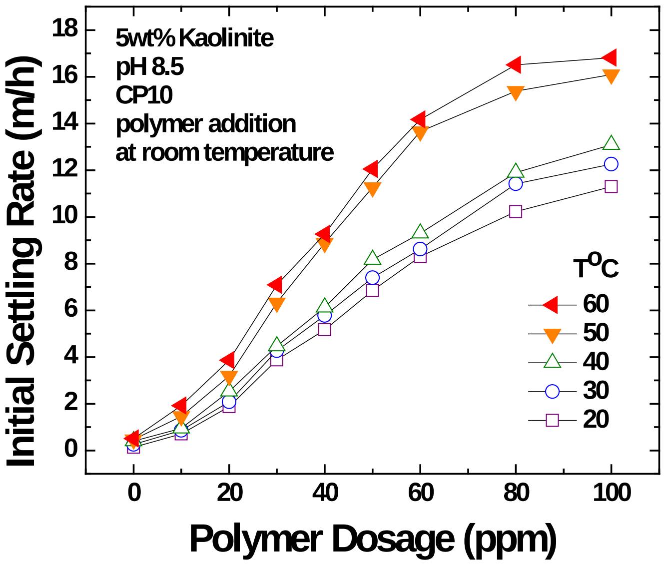

Figure 5-1-6 Initial Settling Rate of Kaolinite Suspensions with CP10 Added at Room Temperature

To investigate the effect of temperature on flocculation of kaolinite suspensions by CP10 addition, the initial settling rate at polymer dosages of 30 ppm and 60 ppm in Figure 5-1-6 is re-plotted as a function of settling temperature in Figure 5-1-7. An increase in settling rate was observed as settling temperature increased from 40^{o}C to 50^{o}C. The reason of this increase of initial settling rate at settling temperature of 50^{o}C and above was attribute to the change in conformation of CP10. At temperatures above LCST of CP10, 48^{o}C, the hydrophilic polymer chains shrank into hydrophobic globules, leading to the formation of more compact flocs, and hence an increase in the settling rate as shown schematically in the inset of Figure 5-1-7 [1-4].

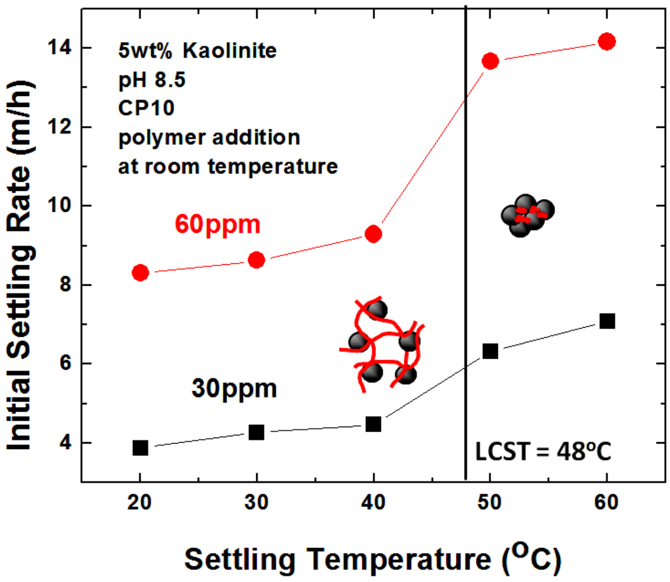

Figure 5-1-7 Effect of Settling Temperature on Settling of Kaolinite Suspensions with CP10 Added at Room Temperature

For the settling experiment with CP10, three cases, RMRS, RMHS, and HMHS as mentioned in Chapter 3, were also studied. In this Section, high temperature referred to 55°C, which is higher than the LCST of CP10, 48°C. Figure 5-1-8 illustrates the relation of initial settling rate with polymer dosage in the three cases. Lower settling rate was obtained with RMRS than with RMHS, but the lowest settling rate was with HMHS. For cases in RMRS and RMHS, increasing the polymer dosage to 100 ppm resulted in an increase in the settling rate. However, the initial settling rate with HMHS was not so sensitive to polymer. CP10 was expected to exist as hydrophobic globules when added at 55°C. As a result, it is not effective in attaching to multiple suspended kaolinite particles. Accordingly, increasing polymer dosage in this case showed little changes in settling rate. Higher initial settling rate was shown with RMHS than with RMRS because the flocs during settling were more compact when heating up the flocculated suspension, leading to better settling [1-4].

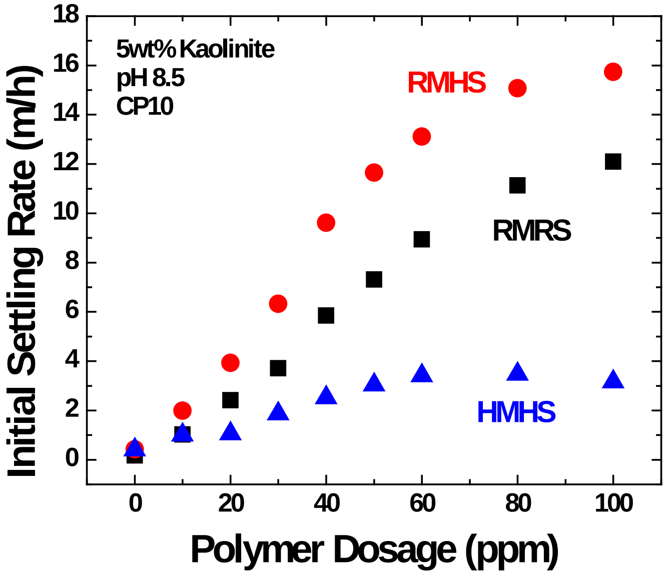

Figure 5-1-8 Settling of Kaolinite Suspensions with CP10 Addition in Different Settling Cases

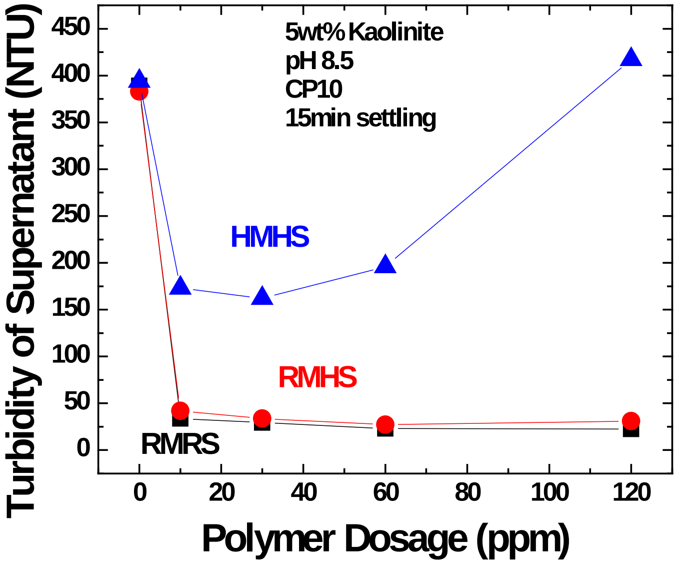

Figure 5-1-9 Supernatant Turbidity of Kaolinite Suspensions in Different Settling Cases with CP10 as Flocculant

Turbidity of supernatant of kaolinite suspensions was measured after 15 min settling. A clear supernatant of less than 50 NTU was produced at polymer dosages as low as 10 ppm with both RMRS and RMHS, as shown in Figure 5-1-9. Little difference in supernatant clarity was shown between RMRS and RMHS as heating up the suspension mainly yielded denser flocs but it did not help to increase the extent of flocculation [1-4]. Accordingly, the clarity of supernatant was not related to the extent of flocculating particles. The turbid supernatant produced by HMHS procedure shows that the shrunk polymer with HMHS could not efficiently bridging fines particles, and hence, leading to higher turbidity of supernatant.

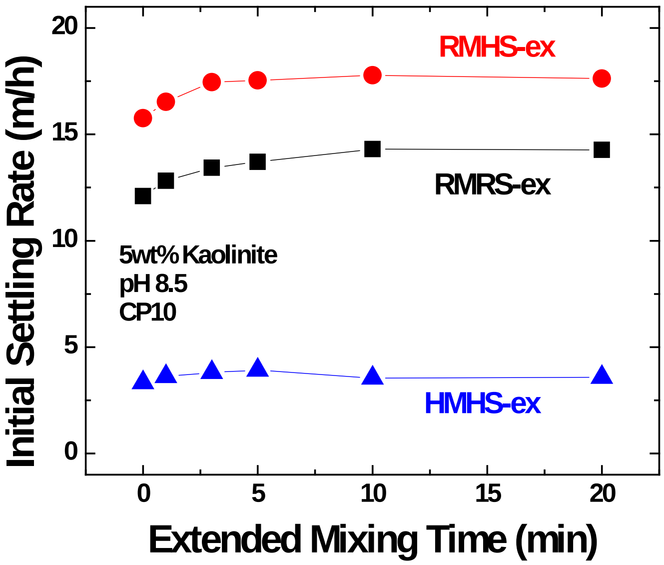

Figure 5-1-10 Effect of Mixing Time on Settling of Kaolinite Suspensions in Different Settling Cases with CP10 as Flocculant

Extended agitation was applied to the flocculated suspension to study the resistance of floc to shear. The mixing speed was kept the same as used during polymer addition. In Figure 5-1-10, the flocs in all three cases are shown to be sufficiently strong to sustain the induced shear for at least 20 min. The slight increase of settling rate with mixing time over the first 5 min for the cases of

RMRS and RMHS indicates the importance of good mixing to distribute flocculant and promote collision of suspended particles for flocculation.

5.2 Filtration Tests

5.2.1 Effect of CP05 on Filtration

In this Section, the results of using CP05 with LCST of 38°C and molecular weight of 2.4 MDa as a filtration aid on kaolinite suspensions are shown and discussed. Three kinds of procedures, RMRF, RMHF and HMHF as mentioned in Chapter 3 were used in filtration tests. The high temperature was referenced to be 45°C. The results in Figure 5-2-1 show that HMHF inhibits filtration. The higher the polymer dosage, the lower the filtration rate with HMHF. The fine particles and the shrunk polymer globules were suspected to blind the filter paper and block filter cake. RMHF gave higher filtration rate than RMRF because shrinking to denser flocs helped to build microchannel inside the cake, and hence to increase water flow passing the cake in the filter press [1-5].

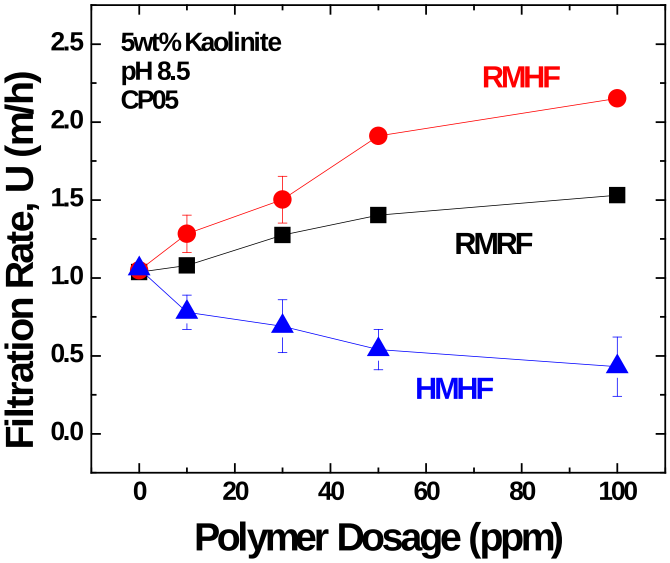

Figure 5-2-1 Filtration of Kaolinite Suspensions with CP05 Addition in Different Filtration Cases

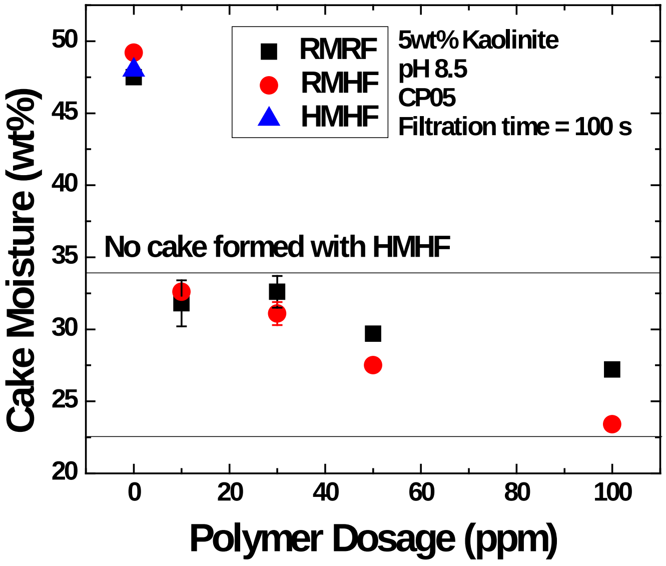

Figure 5-2-2 Moisture Content of Kaolinite Filter Cake in Different Filtration Cases with CP05 as Flocculant

The results in Figure 5-2-2 show a significant improvement in reducing cake moisture with increasing polymer dosage in particular for the cases RMRF and RMHF. Cake moisture was reduced from 48 wt% to less than 34 wt% with 10 ppm CP05 added in these two cases. It is interesting to note a lower moisture content of filter cake formed with RMHF than with RMRF. Clearly, hydrophobic nature of flocs at high temperature is beneficial for filtration. However, no filter cake was formed with HMHF because of poor flocculation of fines. The un-flocculated fines blocks filter medium, leading to poor filtration.

5.2.2 Effect of CP10 on Filtration

CP10 with LCST 48^{o}C and molecular weight of 2.5 MDa was used as a filtration aid on kaolinite suspensions. Three cases, RMRF, RMHF and HMHF were studied in terms of filtration rate and filter cake moisture content. The high temperature in this Section refers to 55°C which is higher than the LCST of CP10. Figure 5-2-3 clearly shows that CP10 reduced filtration rate with HMHF. The polymer shrank into hydrophobic globules and tended to aggregate together when mixing CP10 into hot kaolinite suspension. The polymer aggregates and the un-flocculated fines blinded the filter paper and block the filter cake, leading to a low filtration rate. Filtration rate was slower with RMRF than with RMHF. This difference may be due to the looser flocs produced with RMRF. Looser flocs retain fine pores within flocs, reducing effective size of cake pores for liquid to pass through.

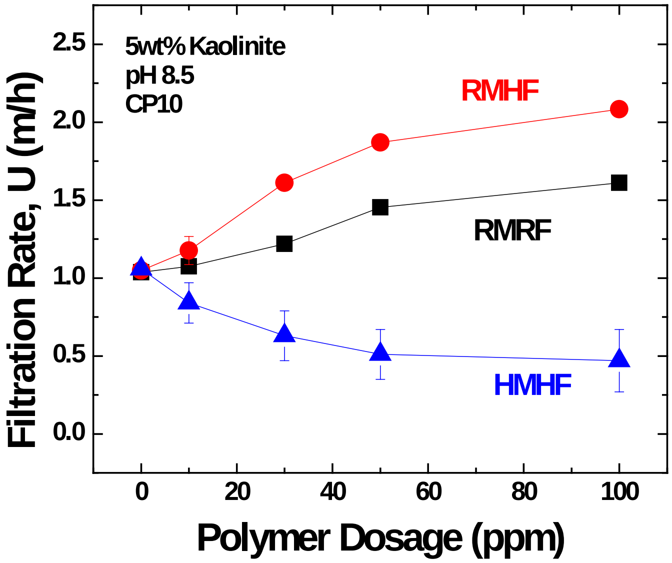

Figure 5-2-3 Filtration of Kaolinite Suspensions with CP10 Addition in Different Filtration Cases

The results in Figure 5-2-4 show that CP10 helps to produce drier cake in the cases of RMRF and RMHF. Cake moisture decreased from 48 wt% to less than 35 wt% with 10 ppm of CP10 addition. Cake moisture content with RMHF was lower than with RMRF. The hydrophobic flocs at high temperature are more compact and form more porous filter cake which liquid to pass through, leading to a lower cake moisture content [1-5]. Besides, cake moisture content decreased with increasing polymer dosage in both cases. Nevertheless, no filter cake formed due to little extent of flocculation of suspended particles with HMHF. Therefore, CP10 helped filtering kaolinite suspension when adding the polymer at temperature lower than its LCST.

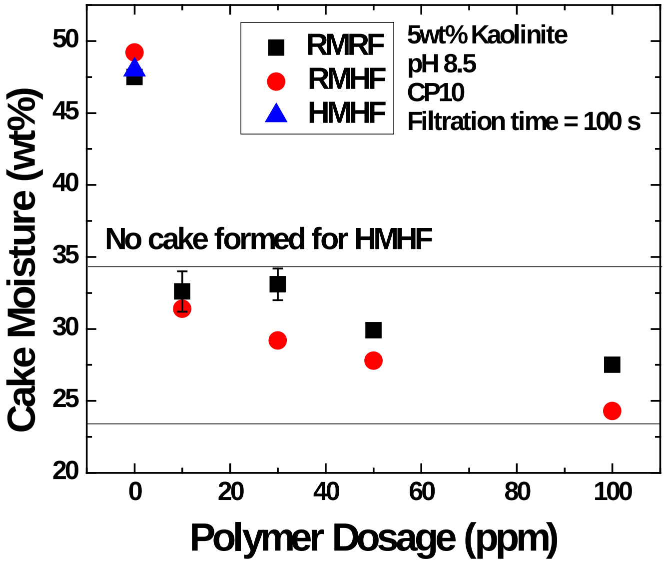

Figure 5-2-4 Moisture Content of Kaolinite Filter Cake in Different Filtration Cases with CP10 as Flocculant

5.3 Comparison between CP05 and CP10

Settling and filtration data of CP05 and CP10 were compared to determine the effect of changing molar ratio of DMAPMA of CP on flocculation process. CP05 and CP10, with similar molecular weights, were different only by their LCSTs (38^{o}C and 48^{o}C, respectively). Comparison were made in settling rate with RMRS, RMHS and HMHS cases, and filtration rate with RMRF, RMHF and HMHF cases. The high temperature in this Section referred to temperature higher than the CP's LCST, thus, 45^{o}C for CP05 and 55^{o}C for CP10.

As shown in Figure 5-3-1, the initial settling rate curves of CP05 and of CP10 are almost overlapped for each cases. Settling rate with RMRS was higher than with

HMHS; yet, the highest settling rate of kaolinite suspension was using RMHS procedure for both CPs. As a general trend, the higher the polymer dosage, the greater the initial settling rate was. Therefore, changing DMAPMA content has a negligible effect on the degree of flocculation. For all three sample treatments, the flocs produced by both CP05 and CP10 showed same good resistant to shear over the first 20 min mixing after complete addition of polymer aids.

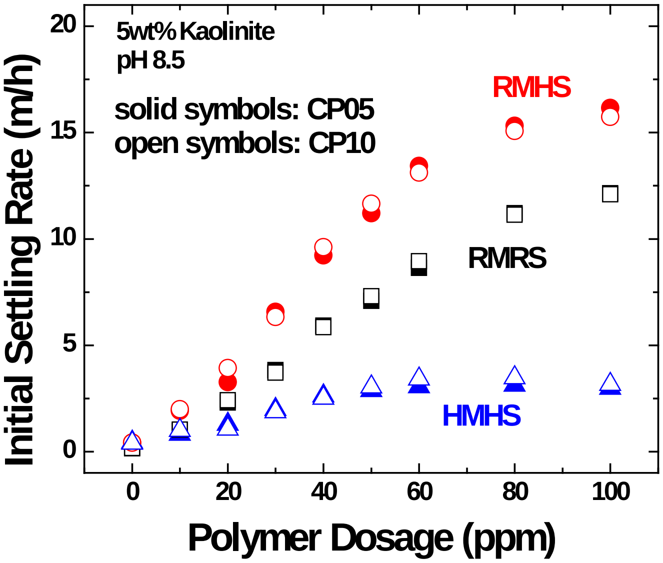

Figure 5-3-1 Comparison between CP05 and CP10 on Settling Performance in Kaolinite Suspensions

As discussed in Section 5.1, both CP05 and CP10 produced supernatant of turbidity less than 50NTU with 10ppm polymer addition after 15 min settling in the cases of RMRS and RMHS. Both CP05 and CP10 produced supernatant of 170 NTU in their optimum dosages of 30 ppm with HMHS. In this case, the turbidity of the supernatant bounced back to the level of blank sample with 100 ppm of flocculant addition for both CP05 and CP10.

The flocculation behaviour of pNIAPM and other temperature sensitive polymers in kaolinite suspensions are found in literatures. Some published data on settling of alkaline kaolinite suspensions with RMHS was discussed as follows. Li et al.

showed that addition of 500 ppm pNIPAM (3.2 MDa, LCST of 32^{o}C) gives initial settling rate of 2 m/h in 10 wt% kaolinite suspensions while settling at 40^{o}C [3]. Franks et al. claimed that pNIPAM (3.6 MDa, LCST of 32^{o}C) yields initial settling rates of 0 and 20 m/h with a dosage of 10 ppm in 5 wt% kaolinite suspensions while settling at 23^{o}C and 50^{o}C, respectively [6]. The initial settling rate of kaolinite suspensions settling at 50^{o}C drops to 2.5 m/h with addition of 10 ppm pNIPAM with a lower molecular weight of 2.0 MDa [6]. Nichifor and Zhu synthesized poly[*N*,*N*-dimethylacrylamide-co-styrene], p[PMA-co-st] (52 kDa, 5.7 mole% styrene and LCST of 41^{o}C), and poly[acrylamide-co-t-butylacrylamide], p[AA-co-TBA] (150 kDa, 30 mole% TBA and LCST of 32^{o}C) [7]. P[PMA-co-st] and p[AA-co-TBA] give initial settling rates of 0.3 and 0.6 m/h, respectively, in 5 wt% kaolinite suspensions with 1000ppm flocculant addition while settling at 65^{o}C [7]. Both CP05 and CP10 yielded initial settling rate of 16 m/h with a dosage of 100 ppm in 5 wt% kaolinite suspensions and settling at 45^{o}C and 55^{o}C, respectively. As Franks et al. showed a significant effect of molecular weight on initial settling rate, the settling behaviour of CP is expected to be improved with a higher molecular weight which can be achieved by addition of initiator at a lower speed during polymerization.

For filtration tests, CP05 and CP10 also showed similar results. As shown in Figure 5-3-2, CP05 yields similar data as CP10 did in all the cases. Both CPs enhanced filtration rate when sample treatments RMRF and RMHF were used. Among the two treatments, RMHF method resulted in a higher filtration rate because denser flocs formed led to more porous filter cake [1-5]. Filtration was suppressed with HMHF. In this case, the polymer was present as hydrophobic globules and aggregated together during flocculant addition at temperature above the LCST. Thus, most of the fines were not flocculated, and was remained dispersed, as shown by the high turbidity of the supernatant with HMHF. These suspending fines fouled the filter paper and as a result, no filter cake was formed.

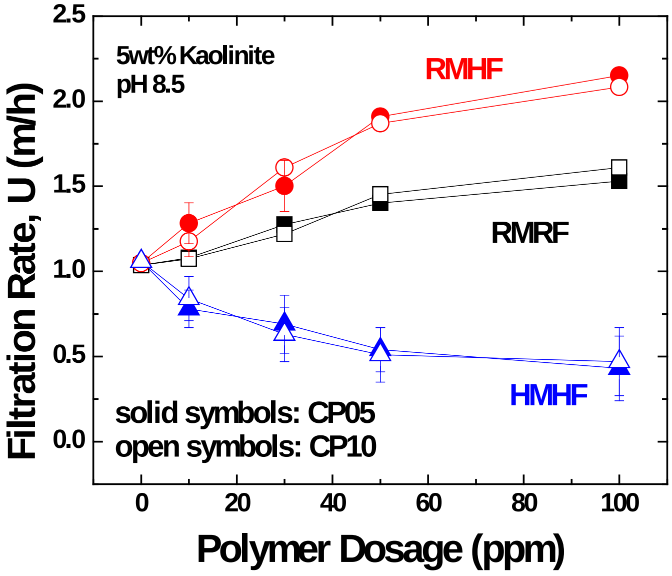

Figure 5-3-2 Comparison between CP05 and CP10 on Filtration Performance in Kaolinite Suspensions

Although no filter cake was formed for both CP05 and CP10 with treatment with HMHF, 10 ppm of polymer addition using sample treatments RMRF and RMHF helped to reduce cake moisture content considerably from 48 wt% to 34 wt%. The more flocculants added, the lower the cake moisture content could be obtained. This study clearly shows that procedures for polymer addition are of critical importance, particularly for temperature sensitive polymers.

5.4 Conclusion on P[NIPAM-co-DMAPMA]

In Chapter 4, it was shown that the higher the DMAPMA content, the higher LCST of CP could be obtained. CP was shown to adsorb on the surface of kaolinite clay particles and altered the surface charge of kaolinite from negative to positive. In this chapter, the cationic temperature sensitive polymer, poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide], p[NIPAM-co-DMAPMA] (CP), was demonstrated to be a good flocculant aid on kaolinite suspensions in terms of settling and filtration when proper sample treatment procedures are used. CP performed best with polymer addition at temperature below its LCST and settling/filtering at temperature above its LCST. Adding polymer to suspension at a temperature higher than its LCST showed a negative effect on flocculating kaolinite suspension. A 5 wt% kaolinite suspension was condensed to 65 wt% (kaolinite fines) filter cake from filtration process with 10 ppm CP addition. LCST can be adjusted by controlling the composition of DMAPMA in CP. Therefore, CP with suitable LCST could be designed to meet the operation temperature of tailings treatment without changing the flocculation power of CP as CP05 and CP10 yielded similar data on settling and filtration tests.

The structure of CP should be modified to increase the flocculation power to the level comparable wtih the commercial flocculants. Since alum has been used in purification of drinking water, and the great flocculation power of Al-PAM has been demonstrated in the studies by Yang et al. [8] and Wang et al. [9], aluminum hydroxide colloids will be added into CP as an inorganic-organic hybrid temperature sensitive polymer (Al-CP). In the following chapter, the flocculation behaviour of Al-CP in alkaline kaolinite suspension will be discussed.

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Chapter 6 Effect of $Al(OH)_3$-P[NIPAM-co-DMAPMA] and P[NIPAM-co-DMAPMA]+Al on Settling and Filtration Processes on Kaolinite Suspensions

Coagulant and flocculant are used together in water treatment as a two-stage or multistage process [1]. Common coagulants are metal ions like aluminum and ferric ions [1]. In water treatment, alum is widely used. Researches showed Al-PAM, aluminum hydroxide-polyacrylamide hybrid, exhibits a considerable increase in flocculation power than the organic PAM, polyacrylamide [2, 3]. The aluminum hydroxide colloid attached to the polymer chain gives high charge density to attract negatively charged kaolinite particles. Therefore, aluminum hydroxide colloid was dosed into poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide], p[NIPAM-co-DMAPMA] (CP), as colloids in order to increase the flocculation power of CP by the two methods as follows. First, aluminum hydroxide-poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] hybrid (Al-CP05), were synthesized from NIPAM and DMAPMA, with mole ratio 95:5, in aluminum colloid solution with procedures stated in Chapter 4. Because of the similar nature of the polymerization reaction, the polymer hybrid was suspected to have star-like structure that similar to Al-PAM as shown in Figure 2-2-1 [2, 4]. The aluminum hydroxide colloids were attached to the polymer chains. This cationic copolymer-ion hybrid had molecular weight of 2.1 MDa and LCST of roughly 37^{o}C. The flocculation results of Al-CP05 would be discussed in Section 6.1.1 (settling) and Section 6.2 (filtration). Second, a coagulant/flocculant mixture, {CP05+Al}, was prepared with CP05 and the aluminum hydroxide colloid solution such that the mixture had the same aluminum content as Al-CP05 for comparison purpose. {CP05+Al} had molecular weight of 2.4 MDa and LCST of 37^{o}C. The comparison between Al-CP05 and {CP05+Al} on their settling behaviours would be discussed in Section 6.3.

6.1 Settling Tests

6.1.1 Effect of Al-CP05 on Settling

The synthesis of Al-CP05 was described in Chapter 4, and the polymer hybrid has LCST of 37^{o}C and molecular weight of 2.1 MDa. The polymer was added into the kaolinite suspensions at room temperature, and the samples were settled at different temperatures (20^{o}C to 60^{o}C) to study the temperature sensitivity of Al-CP05 in kaolinite suspensions. A distinct improvement on settling of kaolinite suspensions with Al-CP05 addition at all settling temperatures tested is shown in Figure 6-1-1. A jump was observed in the initial setting rate between settlings at 30^{o}C and 40^{o}C. Al-CP05 shrinks from extended hydrophilic chains to hydrophobic globules when temperature passes through its LCST, leading to formation of denser flocs [5-8]. This increases the initial settling rates of kaolinite suspensions which settle at 40^{o}C and higher temperature.

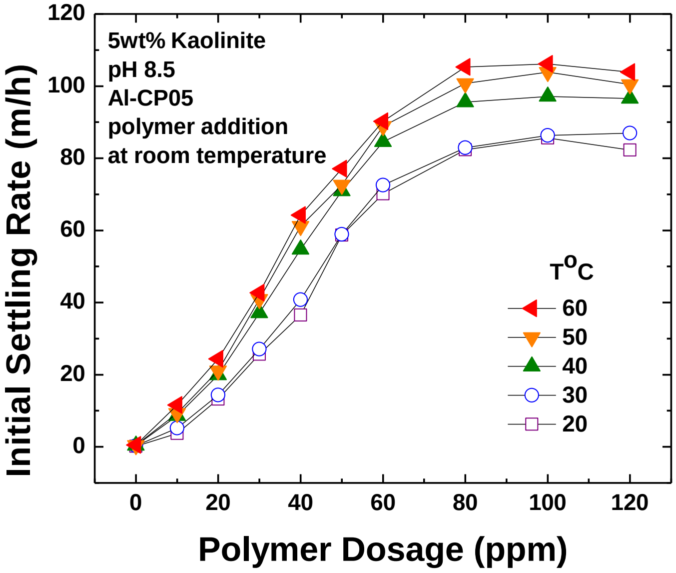

Figure 6-1-1 Initial Settling Rate of Kaolinite Suspensions with Al-CP05 Added at Room Temperature

Polymer dosages of 30 ppm and 60 ppm were tested as a function of settling temperature to study the effect of temperature on initial settling rate. A mild jump in initial settling rate was observed with increasing settling temperature from 30°C to 40°C in both dosages as shown in Figure 6-1-2. This jump confirms that the settling rate is enhanced at temperatures higher than LCST.

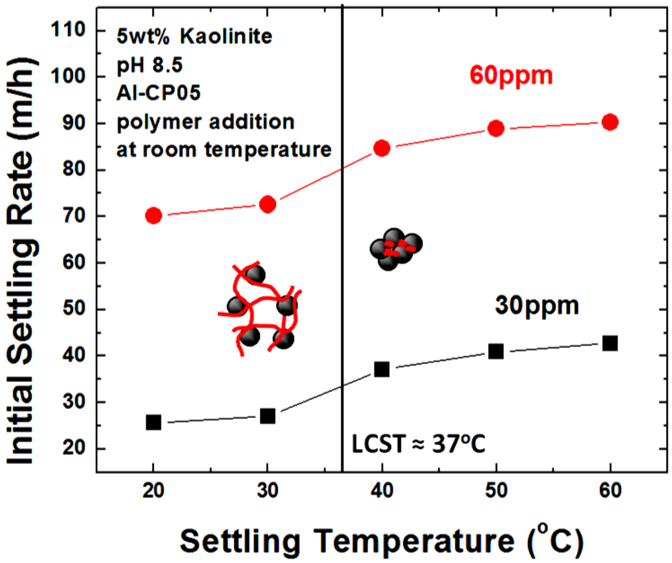

Figure 6-1-2 Effect of Settling Temperature on Settling of Kaolinite Suspensions with Al-CP05 Added at Room Temperature

The initial settling rate, the clarity of supernatant and the mixing time were studied for Al-CP05 in three cases, RMRS, RMHS and HMHS. The high temperature refers to 45°C, which is higher than the LCST of Al-CP05. The results of initial settling rate as a function of polymer dosage show a significant improvement in all cases as shown in Figure 6-1-3. Initial settling rate increased with polymer dosage and reached an optimum at about 80 ppm in all three cases. Al-CP05 gave a better settling with RMRS than with HMHS. The highest initial settling rate is, however, enhanced by treatment RMHS. Though the polymer was added as shrunk globules at temperature higher than its LCST with HMHS, the dosed aluminum hydroxide colloids made the polymer hybrid less hydrophobic and provided electrostatic force to flocculate the fine particles. Therefore, Al-CP is expected to give a significant flocculation on warm/hot tailings slurry.

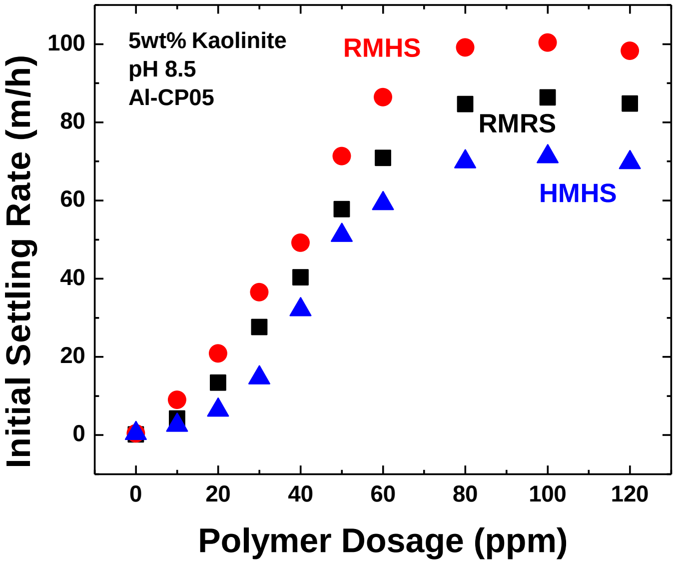

Figure 6-1-3 Settling of Kaolinite Suspensions with Al-CP05 Addition in Different Settling Cases

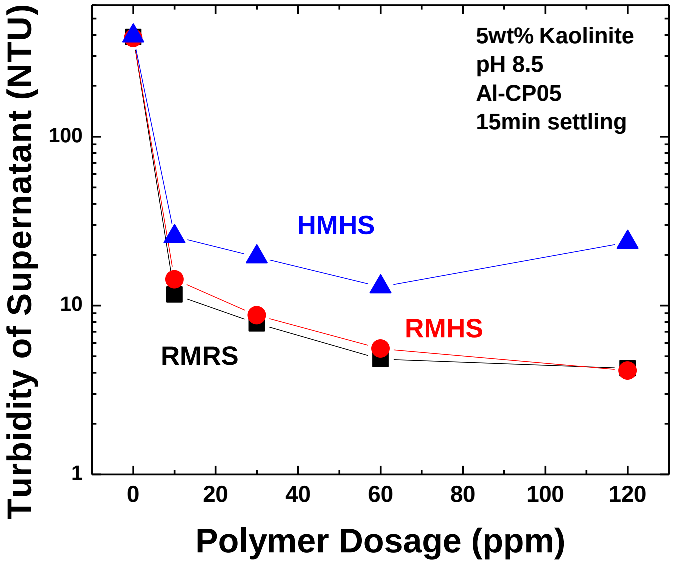

Figure 6-1-4 Turbidity of Supernatant of Kaolinite Suspensions in Different Settling Cases with Al-CP05 as Flocculant

The supernatant clarity of the flocculated suspensions was measured after 15 min of settling. The turbidities of Milli-Q water and 0.01 wt% kaolinite suspension at pH 8.5 were measured as references, and were 0.02 NTU and 132 NTU, respectively. Figure 6-1-4 shows that clear supernatant was produced by Al-CP05 addition in all cases. Addition of 10 ppm Al-CP05 produced supernatant of turbidity less than 20 NTU with both RMRS and RMHS. The more polymer solution added, a clearer supernatant was obtained. The difference in supernatant clarity between RMRS and RMHS cases was small as increasing settling temperature does not necessarily increase the degree of flocculation. An improvement on supernatant clarity with HMHS was observed and reached an optimum at 60 ppm. This agrees with the results shown in Figure 6-1-3 that addition of Al-CP05 improved flocculation of kaolinite suspensions with HMHS.

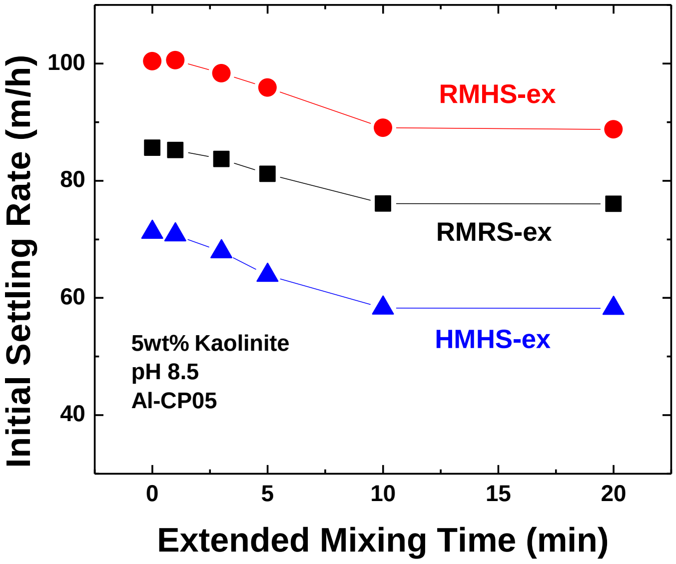

Figure 6-1-5 Effect of Mixing Time on Settling of Kaolinite Suspensions in Different Settling Cases with Al-CP05 as Flocculant

Floc strength is another characterization on flocculation behaviour because some flocs produced by polymeric flocculants are easily ruptured by shear under excessive mixing. The floc strength was evaluated by extending the mixing time to 20 min after the completion of mixing the polymer to the suspension. The results in Figure 6-1-5 show that there is a slight decrease in settling rate for 20 min extended mixing in all cases. The flocs formed by Al-CP05 addition are effective to sustain the induced shear. Extended mixing of 10min yielded to about 15% decrease in settling rate with HMHS. Agitation during Al-CP05 addition to kaolinite suspensions is sufficient to distribute flocculant and promote collision of particles for flocculation in all cases.

6.1.2 Effect of {CP05+Al} Blends on Settling

{CP05+Al} of molecular weight 2.4 MDa and LCST 37^{o}C was synthesized. Settling tests on {CP05+Al} were carried out in three different cases, RMRS, RMHS, and HMHS. High temperature in this Section referred to 45^{o}C.

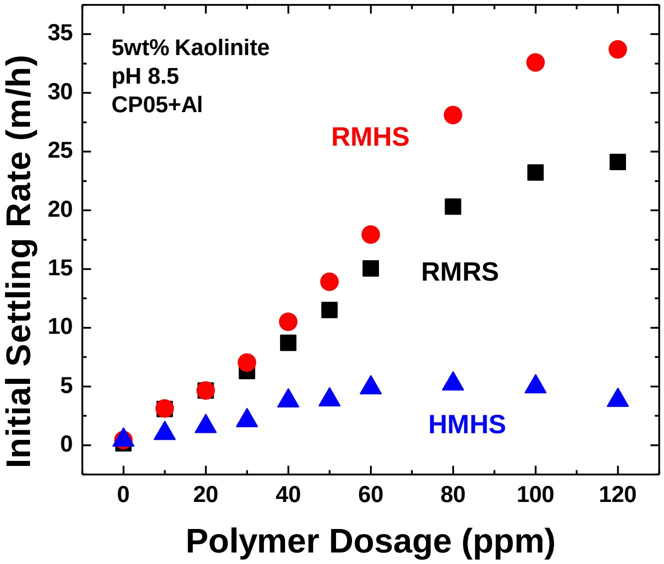

Figure 6-1-6 Settling of Kaolinite Suspensions with {CP05+Al} Addition in Different Settling Cases

The change of initial settling rate with increasing polymer dosage in the three cases is shown in Figure 6-1-6. Increasing polymer dosages increased initial settling rate with both RMRS and RMHS. Initial settling rate with RMRS was higher than that with HMHS, and yet, settling rate was the highest with RMHS. The hydrophilic polymer molecules passed through its LCST and shrank into hydrophobic globules when the flocculated suspension was heated up to 45^{o}C. This brought the floc denser together, leading to higher initial settling rate [5-8]. For case of HMHS, the polymer was hydrophobic when added to the warm suspension, and was not effective in attaching to multiple suspended kaolinite particles. In contrast to addition of polymeric flocculant only, the coagulant AL(OH)$_3$ in the blends destabilized the suspension and, therefore, the suspended particles aggregated and settled slowly with HMHS.

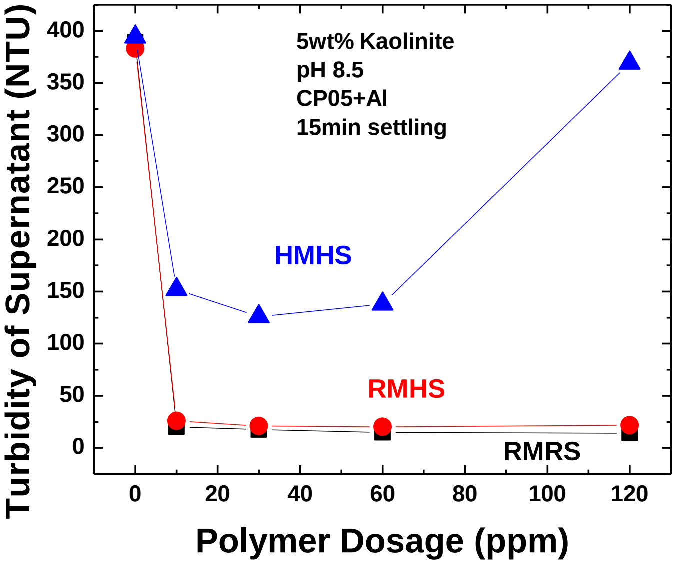

Figure 6-1-7 Turbidity of Supernatant of Kaolinite Suspensions in Different Settling Cases with {CP05+Al} as Flocculant

The supernatant clarity of the flocculated sample was measured after 15 min settling. Figure 6-1-7 shows the supernatant of about 25 NTU with 10 ppm {CP05+Al} addition with treatments RMRS and RMHS. Little difference in supernatant clarity was shown between RMRS and RMHS as heating up the suspensions mainly resulted in denser flocs but it did not help to increase the extent of flocculation [5-8]. The turbidity of supernatant with HMHS reached minimum of 130 NTU at dosage of 30 ppm, and increased to 370 NTU at dosage of 120 ppm. Little flocculation was shown in treatment HMHS because the polymer was added to the suspension as hydrophobic globules, and was not effective to bridge suspended particles. The polymer was also shown to stabilize the suspension system at higher dosages with HMHS.

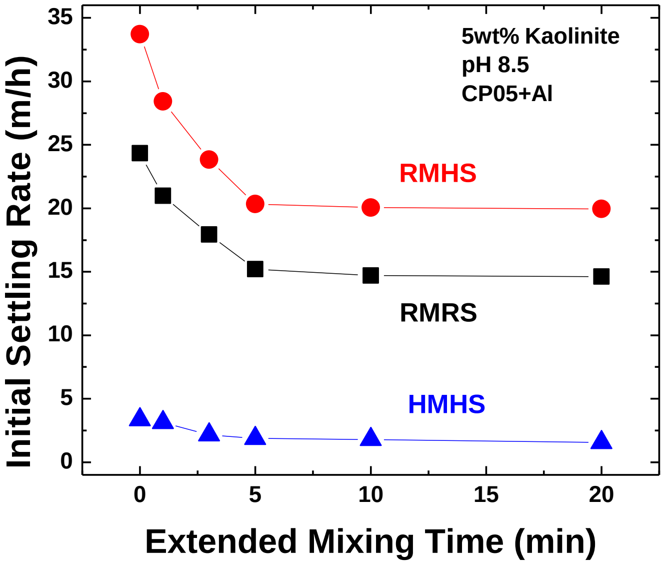

Figure 6-1-8 Effect of Mixing Time on Settling of Kaolinite Suspensions in Different Settling Cases with {CP05+Al} as Flocculant

Extended agitation was applied to the flocculated suspension to study the resistance of {CP05+Al} produced flocs to shear. There was about 40% decrease over the first 5 min extended mixing with both RMRS and RMHS as shown in Figure 6-1-8. Further agitation showed little effect on initial settling rate from the induced shear. This illustrated the flocs produced by {CP05+Al} were loose and not strong enough to sustain the induced shear. This is in contrast to the case of CP05 and CP10 as discussed previously in Chapter 5. The effect of shear on settling rate was mild as little flocs were produced with HMHS.

6.2 Filtration Tests

6.2.1 Effect of Al-CP05 on Filtration

The effect of using Al-CP05 with LCST of 37°C and molecular weight of 2.4MDa as filtration aids on kaolinite suspensions with three sample treatments, RMRF, RMHF and HMHF, are shown and discussed. High temperature referred to 45°C in this Section. Figure 6-2-1 shows significant improvement on filtration of kaolinite suspensions with Al-CP05 addition. Filtration rate was higher with RMRF than with HMHF, but it was the highest with RMHF. Al-CP05 has been showed to enhance filtration rate with HMHF due to the high flocculating power. Though Al-CP05 was added as shrunk globules at temperature higher than its LCST with HMHS, the aluminum hydroxide colloids in the polymer network made the polymer hybrid less hydrophobic and, at the same time, provided electrostatic force to flocculate the fine particles

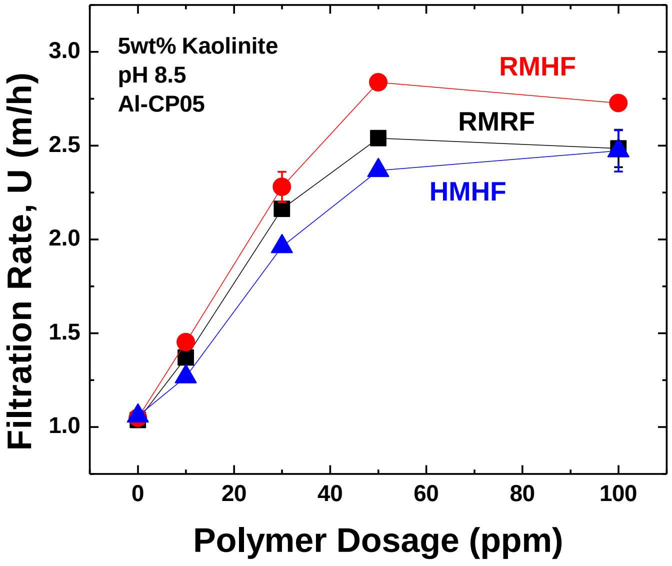

Figure 6-2-1 Filtration of Kaolinite Suspensions with Al-CP05 Addition in Different Filtration Cases

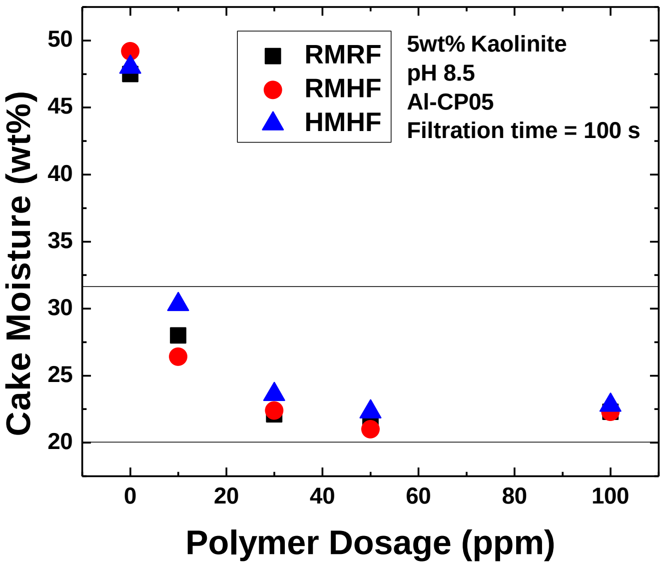

Figure 6-2-2 Moisture Content of Kaolinite Filter Cake in Different Filtration Cases with Al-CP05 as Flocculant

Figure 6-2-2 indicates a significant decrease in filter cake moisture content with addition of Al-CP05 for all three cases. No fouling occurred with treatment HMHF as the polymer hybrid could flocculate fine kaolinite particles effectively at high temperature. The cake moisture content was brought down from 48 wt% to 32 wt% with 10 ppm Al-CP05 addition even with HMHF, and 30 ppm of Al-CP05 was enough to obtain filter cake with moisture content less than 25 wt%. Higher dosages than 30 ppm had little effect on moisture content.

6.3 Comparison between CP05, Al-CP05, and {CP05+Al}

Flocculant hybrid Al-CP05 was used to compare with polymer flocculant CP05 and coagulant/flocculant mixture {CP05+Al} on the settling and/or filtration behaviour in kaolinite suspensions. All flocculants have comparable LCST, and similar molecular weight. Al-CP05 and {CP05+Al} have the same aluminum content. Three cases of sample treatments were introduced in the settling and filtration tests, and the high temperature was referred to 45^{o}C.

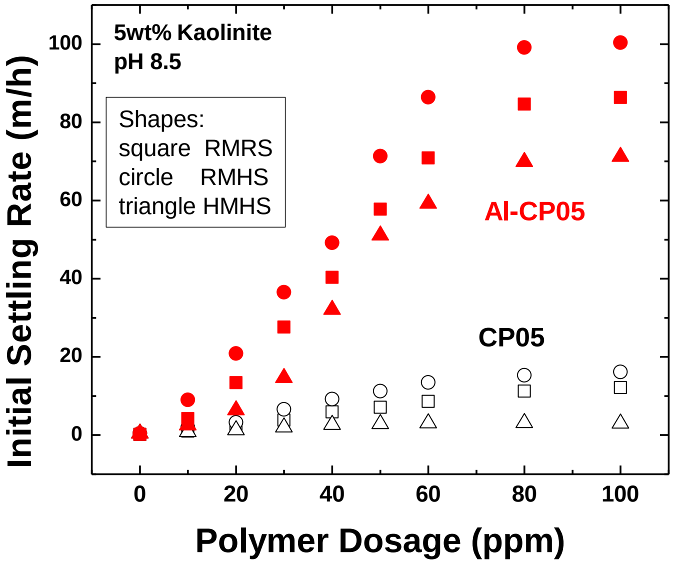

Figure 6-3-1 Comparison between Al-CP05 and CP05 on Settling of Kaolinite Suspensions

Figure 6-3-1 shows that Al-CP05 generates a significantly better performance in settling of kaolinite suspensions than CP05 does. Initial settling rate reaches 100 m/h with 100 ppm of Al-CP05 while it only reaches 18 m/h with same dosage of CP05 for case RMHS. Al-CP05, which synthesized with aluminum hydroxide colloids, yielded 5 times increase in settling rate, while keeping some extent of temperature sensitivity.

Apart from settling rate, the polymer hybrid also improved supernatant clarity as comparing with the organic flocculant. Using Al-CP05 could reduce turbidity of supernatant by almost one order of magnitude as comparing with using CP05 as shown in Figure 6-3-2. Al-CP05 was proved to help flocculating fine kaolinite particles by high degree of charge neutralization because the supernatant clarity reflects the extent of flocculation.

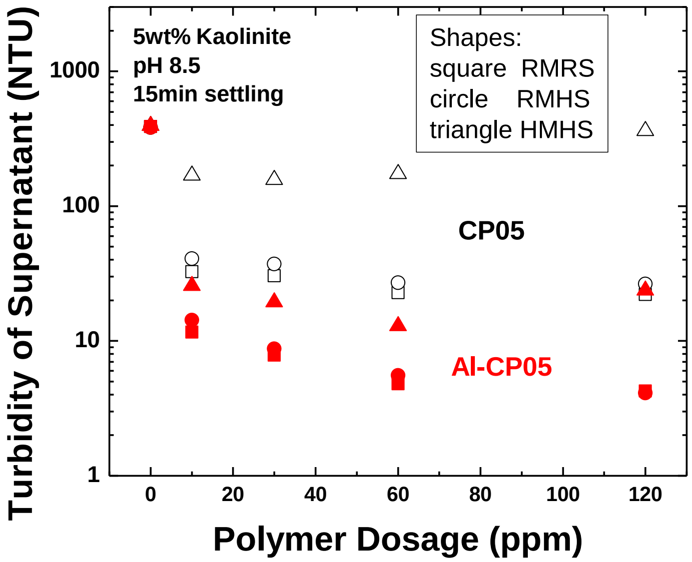

Figure 6-3-2 Comparison between Al-CP05 and CP05 on Supernatant Turbidity of Kaolinite Suspensions

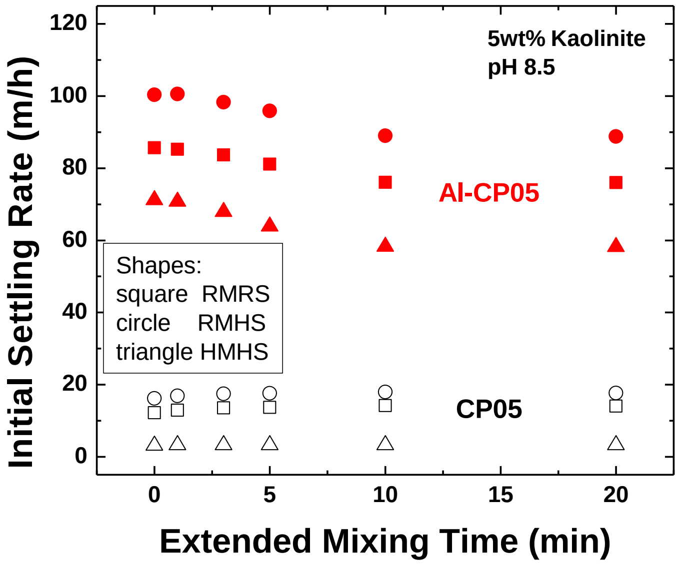

Figure 6-3-3 Comparison between Al-CP05 and CP05 on Floc Strength of Kaolinite Suspensions

Al-CP05 produced flocs were shown to be sufficiently strong to sustain the induced shear by extending the agitation time. Al-CP05, despite of a little decrease over the first 5 min, showed a 5 times higher settling power in kaolinite suspensions than CP05 did over a 20 min extended mixing after addition the flocculants. The high turbidity of the supernatant with CP05 addition for the case HMHS shows a low degree of flocculation. As little flocs were obtained with HMHS by using CP05, the effect of induced shear on initial settling rate could not be effectively measured. Filtration performance of Al-CP05 and CP05 should be more compatible as both flocculants can produce strongly shear resistant flocs.

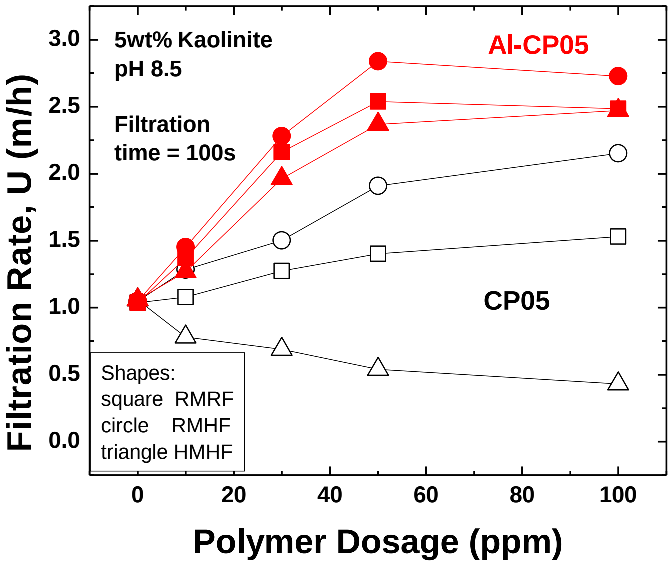

Figure 6-3-4 Comparison between Al-CP05 and CP05 on Filtration of Kaolinite Suspensions

According to the filtration tests, Al-CP05 still shows a better performance on filtration rate than CP05 does, but the difference is not as significant as in the settling tests. The results in Figure 6-3-4 show that Al-CP05 gives a higher filtration rate than CP05 does in all cases. Al-CP05 could also further reduce about 3-5wt% filter cake moisture more than CP05 with treatment RMRF and RMHF. Moreover, CP05 fouled the filter press and no cake could be formed with HMHF, while Al-CP05 gave improvement on both filtration rate and cake moisture content for filtration of kaolinite suspensions at high temperature. Al-CP05 had much lower sensitivity to preparation procedure and greater flocculation power when comparing with CP05. This means, the temperature of the suspensions during Al-CP05 addition and filtration had less effect on the flocculation behaviour. This proved that Al-CP05 could be used in hot tailings treatment process.

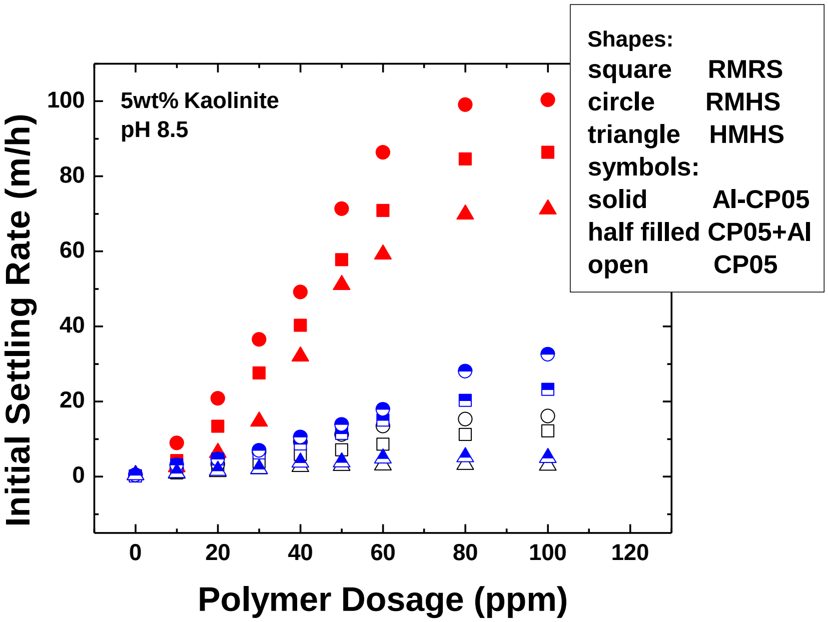

Figure 6-3-5 Comparison between Al-CP05, CP05, and {CP05+Al} on Settling of Kaolinite Suspensions

Al-CP05 is an excellent flocculant as compared with the other two flocculation aids although {CP05+Al} showed higher settling rate in each case than CP05. Adding positively charged coagulant, aluminum hydroxide colloids, was shown to help settling because the higher charge density could neutralize the negatively charged kaolinite clay particles more effectively. The polymer could consequently adsorb easier on particle surface. It also explained the higher supernatant clarity of using {CP05+Al} comparing with that of using CP05. However, the resulting flocs were not strong enough to sustain induced shear shear by mechanical mixing. Al-CP05 had an outstanding result on settling than {CP05+Al}. This emphasized the interaction between inorganic aluminum hydroxide colloid and organic polymer chain was more than just van der Waal forces in the hybrid Al-CP05.

The flocculation behaviour of hybrid flocculants in kaolinite suspensions can be found in recent research although the flocculation behaviour in more concentrated (>1 wt%) kaolinite suspensions has not been published. Yang et al. showed that Al-PAM (about 4.1 MDa and 5.67 wt% Aluminum) gives settling rates of 0.84 and 0.76 m/h with dosages of 4 and 6 ppm, respectively, in 0.25 wt% kaolinite suspensions [3]. Sun et al. also claimed to obverse flocculation with 20 ppm Al-PAM added in 0.6 wt% kaolinite suspensions [4]. Lee et al. showed flocculation of 0.03 wt% kaolinite suspensions with 2 ppm of Ca-PAM (22 wt% Calcium) at about pH 2 [9]. However, the flocculation behaviour in neutral/alkaline kaolinite suspensions was not studied [9]. Lee et al. showed flocculation of 0.03 wt% kaolinite suspensions with 4 ppm Fe-PAM (24 wt% Iron) in a wide pH range (pH 2-12) [10]. Al-CP05 yielded settling rate of 5 m/h with a dosage of 10 ppm in 5 wt% kaolinite suspensions, and is concluded to be the best hybrid flocculant of kaolinite suspensions.

6.4 Conclusion on $Al(OH)_3$-P[NIPAM-co-DMAPMA]

Aluminum hydroxide-poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino) propyl]methacrylamide] hybrid (Al-CP) is a cationic, temperature and pH sensitive salt-polymer hybrid which, comparing with poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] (CP), provides excellent flocculation power on kaolinite suspension. The charge from the aluminum hydroxide colloid destabilized the kaolinite suspension system effectively due to the presence of attached aluminum hydroxide colloids in polymer chains. At the same time, the flocculant produced denser and bigger floc molecules [4-8]. Yet, the temperature sensitivity of Al-CP was not as distinct as CP because the aluminum hydroxide colloids made the polymer hybrid more hydrophilic. Nevertheless, the attached aluminum hydroxide colloids also gave feasibility on high temperature tailings treatment process.

The settling performance of Al-CP was tested in terms of initial settling rate, clarity of supernatant, and floc strength in different experimental cases. Al-CP should be added into the kaolinite suspension at temperature lower than its LCST and settling or filtering at temperature above its LCST for the best performance. The settling rate reached 30m/h and turbidity of supernatant after 15 min settling was 25 NTU with 10 ppm Al-CP added. For filtration tests, performance of Al-CP was measured in terms of filtration rate and filter cake moisture content. The optimum temperature condition agreed with the one in settling tests. Filtration rate increased from 1.0 m/h to 1.5 m/h while cake moisture content decreased from 48 wt% to 26 wt% with 10 ppm Al-CP added.

The coagulant/flocculant mixture, poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide]+aluminum hydroxide colloids (CP+Al) also showed better flocculation power in settling compare with CP, but the improvement was limited as compare with Al-CP hybrid. The aluminum hydroxide colloid in {CP05+Al} acts as individual coagulant to neutralize or reduce the negative charge from the kaolinite particles. Using {CP05+Al}, therefore, gives more adsorption of polymer on the kaolinite particles than using only CP05. Nonetheless, the aluminum hydroxide colloid of Al-CP05 is attached in the polymer matrix, and this increases the electrostatic interaction between the kaolinite particles and the polymeric hybrid molecule. Using Al-CP05, therefore, gives even more adsorption of polymer chain on the dispersed particles than using {CP05+Al}. In Chapter 7, CP and Al-CP were tested on laboratory extraction tailings, a three-phase system with complicated water chemistry. The results of settling and filtration tests of CP and Al-CP on laboratory extraction tailings in different experimental conditions will be discussed.

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Chapter 7 Novel Flocculants for Oil Sands Fresh Tailings Treatment

Oil sands tailings slurry is a complex system containing organic matters, sands, fines clay particles, and ions. As the presence of ions affects the LCSTs of temperature sensitive polymers, the flocculation power of poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide], p[NIPAM-co-DMAPMA] (CP), and aluminum hydroxide-poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] hybrid (Al-CP) might be affected by the ion content of the tailings as well [1]. For CP, both CP05 (5 mole% DMAPMA) and CP10 (10 mole% DMAPMA) were tested. CP05 has molecular weight of 2.4 MDa and LCST of 38^{o}C, while CP10 has molecular weight of 2.5 MDa and LCST of 48^{o}C. For the colloid-polymer hybrid, Al-CP05 (5 mole% DMAPMA) with molecular weight of 2.1 MDa and LCST of 37^{o}C was tested. The composition of process water used to extract tailings was tabulated in Table 3-1-1. The lab extraction tailings contained 0.29 wt% bitumen and 11.6 wt% solids which included 47.0 wt% fines. For the settling tests, settling rate, clarity of supernatant, and floc strength were used to measure the settling efficiencies of the flocculants in lab extraction tailings. For the filtration tests, filtration rate and filter cake moisture content were used to characterize the filtration performance of the flocculants in the tailings slurry. Both settling and filtration tests were carried out with three kinds of sample treatments as discussed in Chapter 3.

7.1 Settling Tests

7.1.1 Effect of CP05 on Settling

CP05 with LCST of 38^{o}C and molecular weight of 2.4 MDa was in-house synthesized. In this Section, the higher temperature used in experiment referred to 45^{o}C. The results in Figure 7-1-1 show that CP05 improves settling rate the best with RMHS, followed by with RMRS. Heating up the flocculated tailings helped settling rate as the polymer shrinks into hydrophobic globules when the slurry temperature passes through the LCST, leading to more compact flocs [2-5]. CP05 had little effect on lab extraction tailings with HMHS. When CP05 was added at high temperature, the hydrophobic globules could not efficiently bridge suspended particles, and resulted in low initial settling rate. The complicated water system did affect the settling rate though the general trend of the settling result of CP05 in tailings slurry was similar as that in kaolinite suspensions.

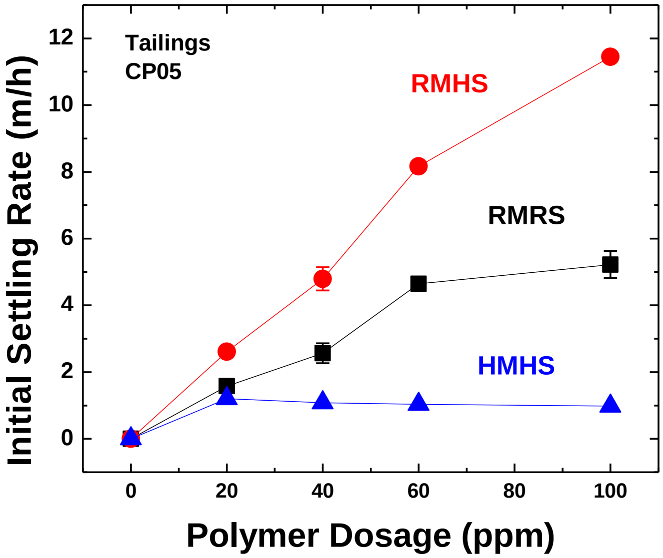

Figure 7-1-1 Settling Performance of CP05 on Tailings in Different Settling Cases

As the supernatant was highly turbid (above 300NTU) after 15 min settling, the turbidity of supernatant was measured after 1 hour settling. The results in Figure 7-1-2 show that CP05 addition with HMHS does not help supernatant clarity as the flocculation power of CP05 with HMHS was low. The supernatants with the CP05 addition with both RMRS and RMHS showed similar clarity because the turbidity of supernatant depends mainly on degree of flocculation. Heating up the flocculated tailings slurry helped settling rate but not necessarily the extent of flocculation. Hence, settling temperature had much less effect on supernatant clarity than mixing temperature during CP05 addition. CP05 shows no effect on supernatant turbidity on tailings slurry with addition with HMHS, while CP05 shows improvement on supernatant clarity on kaolinite suspension with low flocculant dosage with HMHS. This shows that the presence of ions and/or bitumen had a greater effect on addition with HMHS than with RMRS and RMHS.

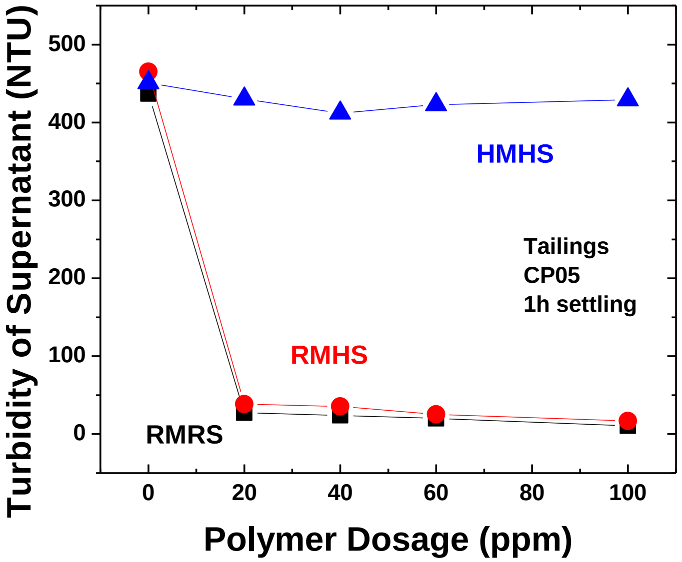

Figure 7-1-2 Supernatant Turbidity of Tailings in Different Settling Cases with CP05 as Flocculant

7.1.2 Effect of CP10 on Settling

CP10 of molecular weight 2.5 MDa was synthesized with 10 wt% DMAPMA to further increase the LCST to 48°C. The high temperature in this Section referred to 55°C. Figure 7-1-3 shows a similar trend for CP10 in settling laboratory extraction tailings and kaolinite suspensions though the settling rate was not as high as that in kaolinite suspensions. Settling in tailings slurry is affected by the presence of ions and/or bitumen. Addition of CP10 with RMHS has the highest settling, and follows by addition with RMRS, while addition with HMHS has little effect on settling rate. Heating the polymer above its LCST makes denser flocs, when the polymer chains shrank to hydrophobic globutes [2-5]. Adding

CP10 at temperature above its LCST, therefore, largely reduced its flocculation power, and led to the lowest initial settling rate with HMHS among all cases.

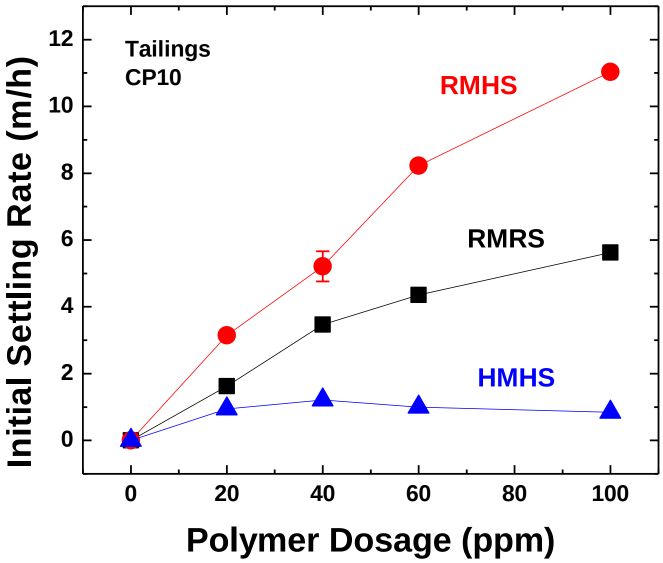

Figure 7-1-3 Settling Performance of CP10 on Tailings in Different Settling Cases

The supernatant remains turbid as little flocculation occurred with the addition of CP10 with HMHS as shown in Figure 7-1-4. Addition of CP10 with RMRS has similar supernatant clarity with addition with RMHS as heating the flocculated tailings only produced more compact flocs but did not increase the degree of flocculation [2-5]. The presence of ions and organic matters in tailings slurry had greater effect with HMHS than in the other two cases when compared with the supernatant clarity of kaolinite suspension especially with low dosage of CP10.

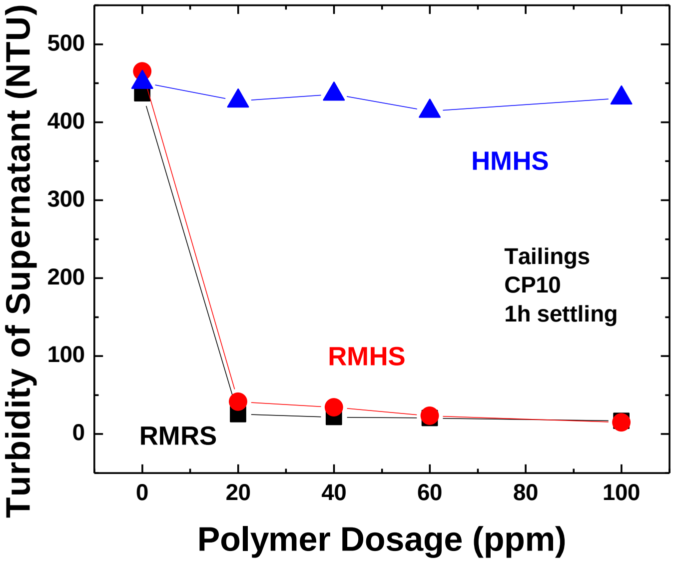

Figure 7-1-4 Supernatant Turbidity of Tailings in Different Settling Cases with CP10 as Flocculant

7.1.3 Effect of Al-CP05 on Settling

Al-CP05 was synthesized in-house with LCST of 37^{o}C and molecular weight of 2.1 MDa. In this Section, high temperature referred to 45^{o}C. Figure 7-1-5 shows little differences on settling rates obtained in cases especially at high dosage. The sensitivity of Al-CP05 to the sample treatments in tailings slurry is little. The differences on settling rate among all cases were less noticeable as compared with the results on kaolinite suspension. It means that bitumen and/or ion contents affect temperature sensitivity of aluminum hydroxide-polymer hybrid, yet the flocculation power of the hybrid polymer in tailings was comparable with that in kaolinite suspensions.

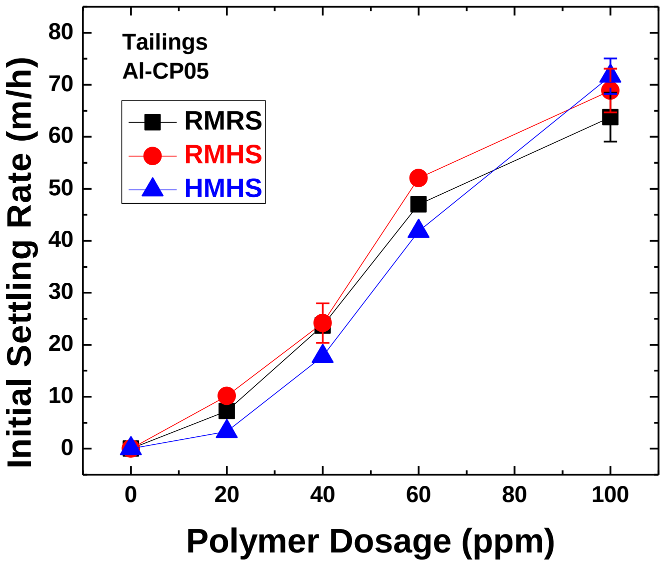

Figure 7-1-5 Settling Performance of Al-CP05 on Tailings in Different Settling Cases

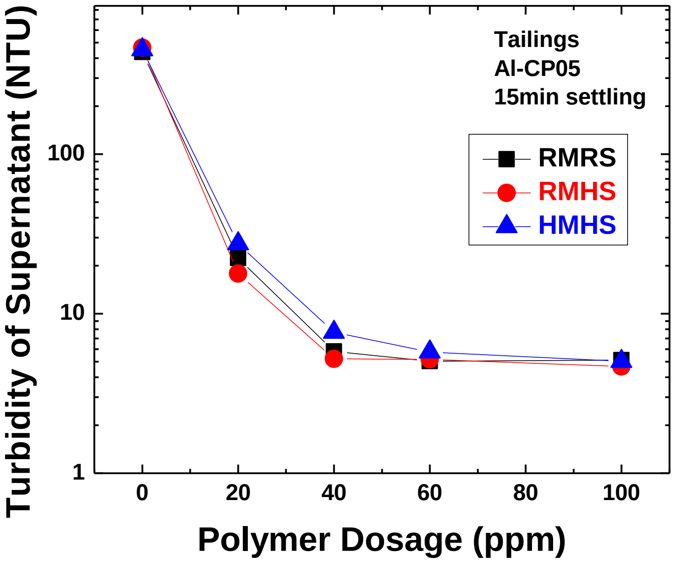

Figure 7-1-6 Supernatant Turbidity of Tailings in Different Settling Cases with Al-CP05 as Flocculant

Turbidity of supernatant was measured after 15 min settling. Figure 7-1-6 shows the similarity of the data sets of all cases on turbidity of supernatant. Differences in clarity of supernatant showed only in low polymer dosage. At polymer dosage of 100 ppm, the effect of sample treatment on initial settling rate is negligible. The flocculation power of Al-CP05 was concluded to be independent of the temperatures of settling as the turbidity of supernatant depended only on the degree of flocculation. Supernatant had turbidity of 30 NTU at dosage of 20 ppm Al-CP05 with HMHS. Higher dosages yielded supernatant of turbidity less than 10 NTU in all cases. Moreover, Al-CP05 could produce clearer supernatants with both RMRS and RMHS on kaolinite suspension than on laboratory extraction tailings. Figure 7-1-6, interestingly, shows a significant improvement on supernatant clarity with Al-CP05 addition of dosage higher that 40 ppm in case of HMHS as compared with that in kaolinite suspensions. The effect of bitumen and/or ions in tailings slurry reduced flocculation with RMRS and RMHS but promoted flocculation with HMHS especially at higher dosages.

7.2 Filtration Tests

7.2.1 Effect of CP05 on Filtration

CP05 was an in-house synthetic cationic copolymer which had molecular weight of 2.4 MDa, and LCST of 38°C. In this Section, the high temperature used in the filtration tests was 45°C. Figure 7-2-1 shows that CP05 improves filtration rate with RMRF and RMHF, but not with HMHF. CP05 increased filtration rate with RMRF, while the flocculant further enhanced filtration rate with RMHF. The polymer chains shrank into hydrophobic globules when the flocculant was added in high temperature leading to insufficient bridging to suspended particles, and hence, reduced its flocculation power with HMHF. Raw data of Figure 7-2-1 are present as filtration curves as shown in Figures B-1 to B-3 in Appendix B.

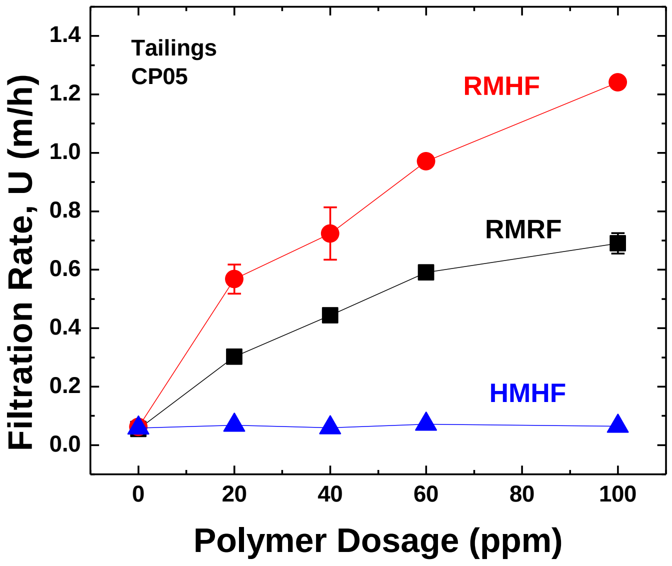

Figure 7-2-1 Filtration Performance of CP05 on Tailings in Different Filtration Cases

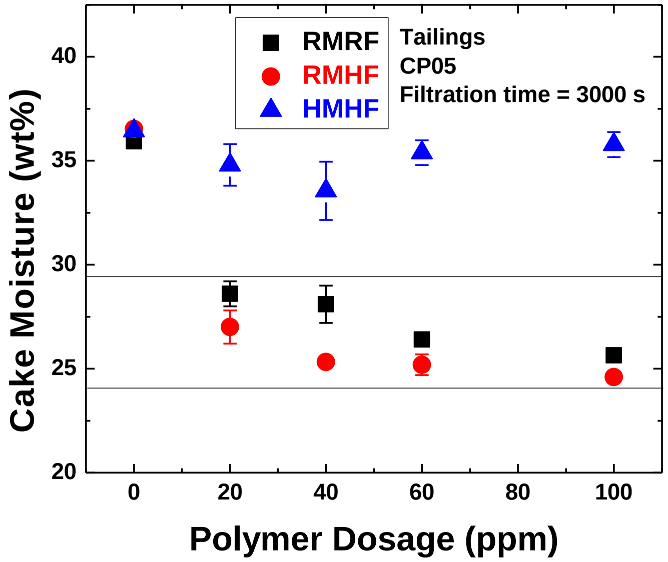

Figure 7-2-2 Moisture Content of Tailings Filter Cake in Different Filtration Cases with CP05 as Flocculant

The trends of cases RMRF and RMHF of tailings slurry were similar to the trends of kaolinite suspension. However, CP05 had little effect on filtration with HMHF on tailings slurry, while it lowered filtration rate of kaolinite suspension. The difference was contributed to the presence of coarse sands in the lab extraction tailings slurry. Fouling occurred when adding CP05 to kaolinite suspension with HMHF as most of the fines were not flocculated and blocked the pores of the filter paper, and no filter cake was produced. By contrast, the effect of coarse sands in lab extraction tailings outweighed the little flocculation power from CP05 with HMHF. The coarse sands built a strong and porous filter bed to prevent fouling by non-flocculated fines particles [6, 7]. The results in Figure 7-2-2 show that CP05 helps to produce the driest cake with RMHF and follows by RMRF. The cake moisture reduced from 36 wt% to 27 wt% with 20 ppm of CP05 addition with RMHF. Higher dosages yielded filter cake with moisture content about 25 wt%. The cake moisture content also showed a slight improvement with low dosage of CP05 with HMHF.

7.2.2 Effect of CP10 on Filtration

CP10 was synthesized in-house containing 10 mole% DMAPMA and had LCST of 48^{o}C and molecular weight of 2.5 MDa. The high temperature used in filtration tests in this Section referred to 55^{o}C. The results in Figure 7-2-3 show that CP10 improves filtration rate the most with RMHF which followed by with RMRF. CP10 had little effect on filtration with HMHF. Heating up the flocculated tailings yielded denser and stronger flocs, and hence, the filter cake was more porous and rigid, leading to an increase in filtration rate [2-6]. The polymer chains shrank into hydrophobic globules when CP10 was added to warm tailings and the flocculation power of CP10 was greatly reduced as the globules could not efficiently bridge suspended particles. Therefore, CP10 could not produce a porous filter cake with HMHF. Raw data of Figure 7-2-3 are present as filtration curves as shown in Figures B-4 to B-6 in Appendix B.

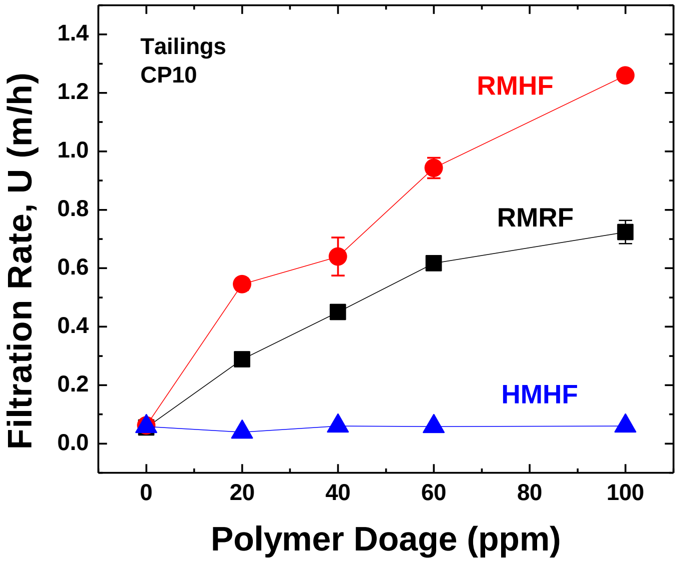

Figure 7-2-3 Filtration Performance of CP10 on Tailings in Different Filtration Cases

The trends with HMHF were different for the kaolinite suspension and the lab extraction tailings. By contrast, the trends with both RMRF and RMHF on tailings slurry were similar to the results from kaolinite suspension. CP10 gave negative effect on filtration rate in kaolinite suspension, while it had little effect on filtration rate in tailings slurry. The difference was contributed by the sands grains in tailings slurry. The sands helped to build a porous filter cake so that the non-flocculated fines did not foul the filter paper [6, 7].

The moisture content of filter cake was evaluated as shown in Figure 7-2-4. CP10 was shown to help reducing filter cake moisture content with both RMRF and RMHF. CP10 reduced little moisture of filter cake with HMHF. Although CP10 addition on settling of tailings with HMHS showed little flocculation, the coarse sands in tailings built a porous filter bed that provided more micro-channels for the water to be filtered out [6, 7]. The effect from coarse sands compensated the low flocculation power of CP10 addition with HMHF. Therefore, unlike fouling the filtration of kaolintie suspensions, CP10 addition showed little effect on filtration of lab extraction tailings.

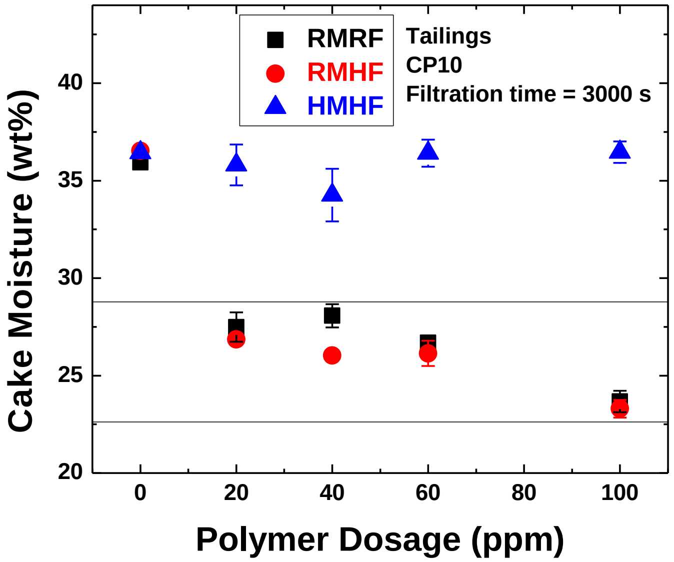

Figure 7-2-4 Moisture Content of Tailings Filter Cakes in Different Filtration Cases with CP10 as Flocculant

7.2.3 Effect of Al-CP05 on Filtration

Al-CP05 was an in-house synthesized and had molecular weight of 2.1 MDa and LCST of 37°C. In this Section, the high temperature used in the tests was 45°C. The results in Figure 7-2-5 show that Al-CP05 enhances filtration rate to similar extent in all cases. This shows that the flocculant lost the sensitivity to sample treatments on filtering tailings slurry as there is no noticeable difference among the data in all the cases. On the other hand, it shows the feasibility of high temperature tailings treatment. Raw data of Figure 7-2-5 are present as filtration curves as shown in Figures B-7 to B-9 in Appendix B.

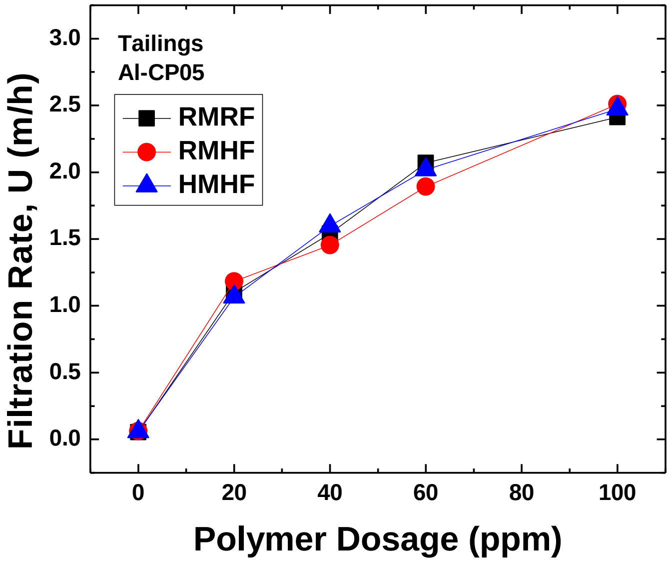

Figure 7-2-5 Filtration Performance of Al-CP05 on Tailings in Different Filtration Cases

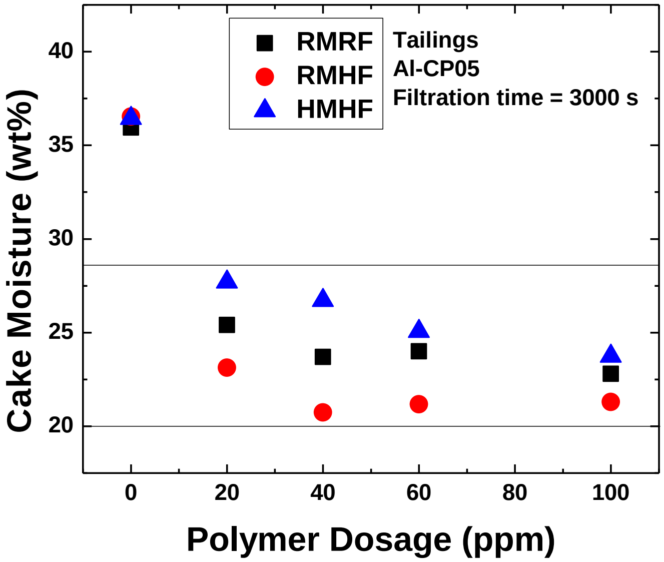

Figure 7-2-6 Moisture Content of Tailings Filter Cake in Different Filtration Cases with Al-CP05 as Flocculant

Nonetheless, the temperature treatments in filtration tests did make a difference on cake moisture content as shown in Figure 7-2-6. Al-CP05 squeezed out water in the flocs when the tailings slurry was heated to the filtering temperature with RMHF, leading to more compact flocs [2-5]. The denser flocs produced more rigid and porous filter cake and resulted in lower cake moisture content [6]. The moisture content of the filter cake with RMHF was, hence, less than with RMRF. The improvement was the least among all three cases though Al-CP05 was showed to reduce filter cake moisture content with HMHF. Al-CP05 shows slightly differences on the turbidity of supernatant in each case. The amount of non-flocculated fines in each case indicates that different degrees of flocculation were provides in different temperature treatments to the samples. The non-flocculated fine clay particles might block some of the micro-channels in the cake. Therefore, a low permeable cake was formed or the filter paper was fouled, and the liquid was not as easy to be strained out.

7.3 Comparison between CP05, CP10, and Al-CP05

The in-house synthesized CP05 and CP10 were cationic temperature sensitive polymers, CP, with LCSTs of 38^{o}C and 48^{o}C, respectively. Al-CP05 were in-house synthesized aluminum hydroxide-p[NIPAM-co-DMAPMA] hybrid with LCST of about 37^{o}C. The molecular weights of the flocculants are compatible and range from 2.1 to 2.5 MDa. The flocculants were compared on their flocculation behaviour on settling and filtration in three different cases. In this Section, high temperature used for CP05, CP10, and Al-CP05 were 45^{o}C, 55^{o}C, and 45^{o}C, respectively.

CP05 and CP10 showed similar flocculation behaviour on kaolinite suspensions such that the increase of DMAPMA in the polymer structure did not affect the flocculation power. Figure 7-3-1 compares the settling processes of CP05 and CP10 on lab extraction tailings, and both flocculants are shown to have the same effect on settling of tailings slurry in all cases. Hence, increasing the concentration of DMAPMA in the temperature sensitive polymer only increased its LCST but had no effect on flocculation power.

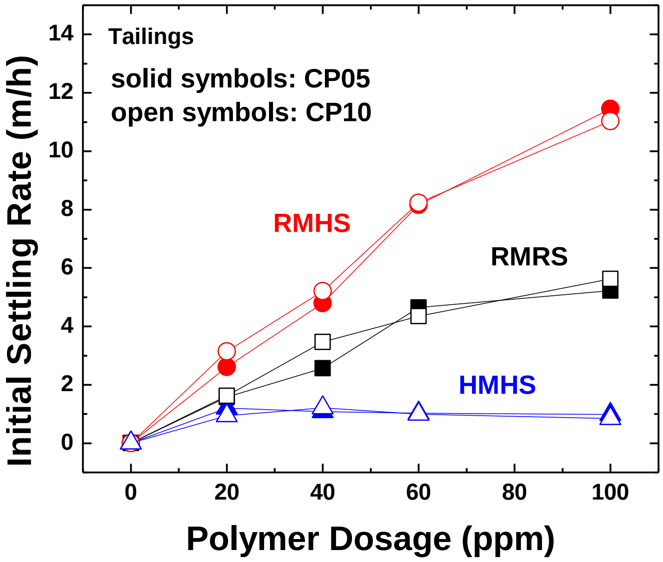

Figure 7-3-1 Comparison between CP05 and CP10 on Settling Performance of Tailings

CP05 and CP10 are shown to be able to produce similar supernatant clarity on tailings at all temperature treatments as discussed previously. Both floccultants, hence, provide the same extent of flocculation in tailings slurry. Both flocculants are shown to produce clear supernatant with RMRS and RMHS, while both flocculants has little effect on supernatant clarity with HMHS.

Figure 7-3-2 illustrates that CP05 and CP10 improve filtration of tailings slurry in the same extent for all cases. Both CPs improved filtration with RMHF more than with RMRF. Adding polymer in room temperature favoured in fines adsorption on stretched polymer chains and promoted flocculation, and hence increased filtration rate. Both CPs showed little effect on filtering tailings with HMHF. The presence of coarse sand in tailings helped to build a porous filter cake to ensure filtration which was, although, compensated by the low flocculation power of CP with HMHF [6, 7]. The filtration rate with CP addition is therefore similar to that without CP addition in case HMHF.

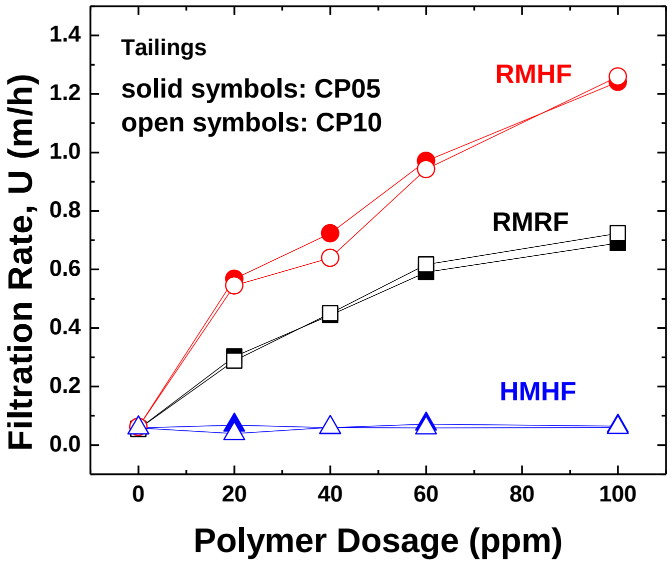

Figure 7-3-2 Comparison between CP05 and CP10 on Filtration Performance of Tailings

CP05 and CP10 also produced similar filter cake qualities. CPs had little effect on cake moisture content with HMHF. CPs reduced cake moisture content with both RMRF and RMHF. The moisture content was reduced from 36 wt% to 29 wt% with 20 ppm CP05 or CP10 addition with RMRF. The cake was slightly drier with RMHF than with RMRF. As the conformation of polymer changed at temperature higher than its LCST, the polymer changed from hydrophilic long chains to hydrophobic globules, and the flocs became denser [2-5]. The denser flocs helped to produce more porous cake, and therefore, more water was filtered out from the more permeable filter medium [6].

CP05 and CP10 were only different from their LCSTs based on the data from both the settling tests and the filtration tests. The change in polymer composition gives little effect on flocculation in both settling and filtration of laboratory extraction tailings regarding the similar molecular weight of CP05 and CP10.

Hence, CP is flexible to adjust its LCST according to the target water treatment temperature while maintaining its flocculation power.

Al-CP05 gave splendid flocculation of lab extraction tailings comparing with CP05 did as shown in Figure 7-3-3. The hybrid flocculant had a significant improvement on settling of tailings but the temperature sensitivity of Al-CP05 was reduced as compared with CP05. CP05 yielded a settling rate of 12m/h at 100 ppm flocculant addition with RMHS, while Al-CP05 had a settling rate of 70 m/h on tailings for the same flocculant dosage. Therefore, the presence of aluminum hydroxide colloids in the polymer hybrid had a 6 times increase in settling rate on tailings as compared with using CP05. However, Al-CP05 has a low sensitivity to sample treatments in tailings slurry.

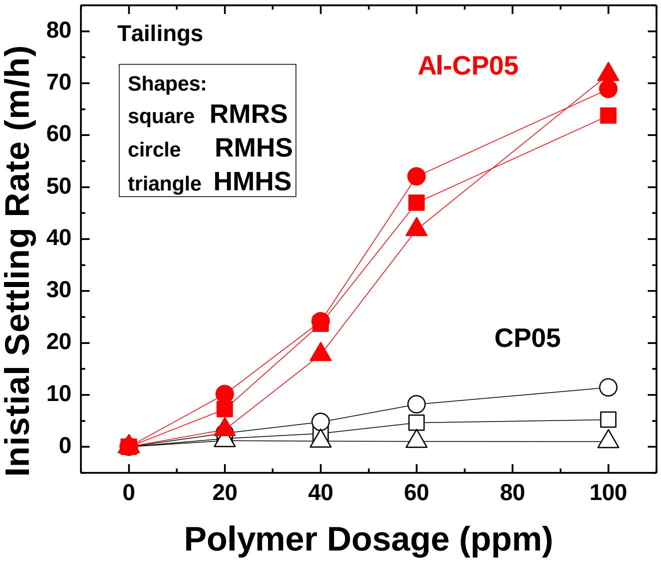

Figure 7-3-3 Comparison between Al-CP05 and CP05 on Settling Performance of Tailings

The hybrid flocculant improves the settling rate and also gives clearer supernatant than the organic flocculant did. CP05 gives supernatant of 45 NTU after 1 hour settling with 20 ppm flocculant addition with RMHS, while Al-CP05 produced supernatant of 20 NTU after 15 min settling with the same flocculants addition. Hence, Al-CP05 was shown to have a larger extent of flocculation than CP05 had as the aluminum hydroxide colloids existed in the polymer network helped to bridge fine clay particles with electrostatic force and increased the chance of adsorption of fines on polymer chains.

Al-CP05 has a comparable flocculation power as Al-PAM. Wang et al. showed that Al-PAM gives initial settling rates of 17 and 40 m/h for dosages at 30 and 50 ppm, respectively, on tailings samples consisted of 0.8 wt% bitumen and 13.5 wt% solids (40.1 wt% fines in solids) [8]. With similar tailings composition as shown in Chapter 3, Al-CP05 yielded similar values of initial settling rate for the same dosages. Moreover, Al-PAM was shown to produce supernatant of 68 NTU with 50 ppm flocculant addition after 10 min settling, while the blank sample had supernatant of 140 NTU [8]. Al-CP05 reduced supernatant turbidity from 400 NTU to less than 10 NTU with a dosage of 40 ppm after 15 min settling. Therefore, Al-CP05 gives comparable flocculation power as Al-PAM does, and at the same time, produces supernatant of same or better clarity.

Al-CP05 also showed improvement on filtration as compared with CP05. The results in Figure 7-3-4 show that Al-CP05 was twice efficient as compared to CP05 in the measure of filtration rate with RMHF though the sensitivity of Al-CP05 to the sample treatments was mostly lost in the filtration process. The filtration rates with addition of Al-CP05 in all three cases had little differences. On the contrary to Al-CP05, significant sensitivity to the sample treatments was shown in CP05. It clearly demonstrated that the organic flocculant performed better with RMHF than with RMRF, and had no effect with HMHF. Nevertheless, Al-CP05 shows the feasibility to be used in high temperature tailings treatment.

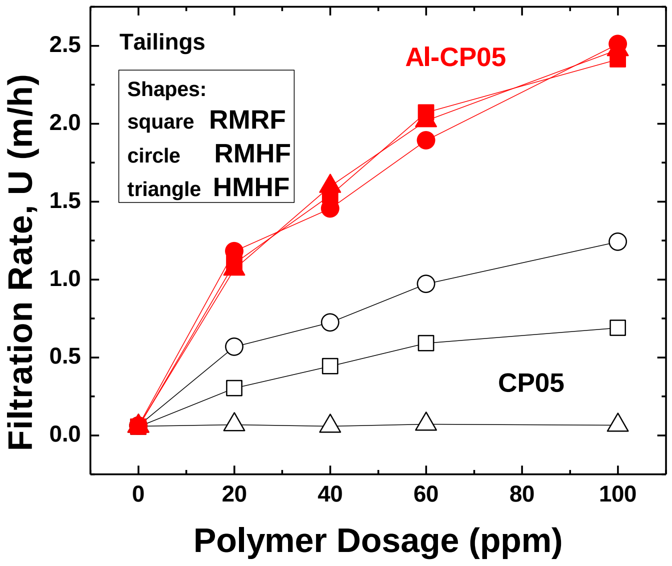

Figure 7-3-4 Comparison between Al-CP05 and CP05 on Filtration Performance of Tailings

Despite the absence of temperature sensitivity from the data of filtration rate, Al-CP05 did show some sensitivity to the sample treatments in the measure of cake moisture content as shown in previous Section. Both CP05 and Al-CP05 have distinct filter cake moisture content with each sample treatment. CP05 showed little effect on cake moisture with HMHF while Al-CP05 showed a noticeable improvement when comparing Figures 7-2-2 and 7-2-6. CP05 reduced cake moisture from 36 wt% to 27 wt% with 20 ppm flocculants addition with RMHF, while Al-CP05 reduced cake moisture to 23 wt%.

7.4 Conclusion of P[NIPAM-co-DMAPMA] and Al-P[NIPAM-co-DMAPMA]

Poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] (CP) is a cationic, temperature and pH sensitive copolymer. CPs were synthesized as CP05 and CP10 which were different by polymer composition. CP05, having 5 mole% DMAPMA, was in-house synthesized with LCST of 38^{o}C and molecular weight of 2.4 MDa. CP10, having 10 mole% DMAPMA, was in-house synthesized with LCST of 48°C and molecular weight of 2.5 MDa. Aluminum hydroxide-poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] hybrid (Al-CP) is a cationic, temperature and pH sensitive polymer hybrid. Al-CP05, having 5 mole% DMAPMA, was in-house synthesized with LCST of 37°C and molecular weight of 2.1 MDa.

CP was shown to be a good flocculant of tailings when mixing the polymer into tailings at room temperature. Adding flocculant to tailings at temperature higher than LCST had little flocculation effect. The polymer exists as hydrophilic elongated chains below the LCST that promote bridging of fines. Polymer molecules shrink to hydrophobic globules above the LCST that reduce chance of fines adsorption on polymer, and hence, provide little flocculation. Settling or filtration at temperature higher than polymer’s LCST improves settling or filtration rates as denser flocs were produced when the polymer shrinks into globules and squeezes out water from the flocs [2-5].

Al-CP was illustrated to be an excellent flocculant of tailings in all cases tested. The higher flocculation power was contributed by the aluminum hydroxide colloids present in the polymer molecules. Aluminum hydroxide colloids provide electrostatic force to attract negatively charged clay particles, and increase the chance of adsorption on polymer chains. For the settling tests, Al-CP was shown to be a better focculant than CP in terms of settling rate, supernatant clarity, and floc strength. For the filtration tests, Al-CP acted as a better filtration aid than CP in terms of filtration rate and filter cake quality. Although its sensitivity to sample treatments was highly reduced, the hybrid flocculant was effective at high temperature tailings treatment. Al-CP showed slightly weaker temperature sensitivity in kaolinite suspensions than CP did. The further increased difference on temperature sensitivity in tailings slurry system might due to the presence of bitumen and/or ions in the lab extraction tailings.

Reference

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Chapter 8 Conclusions

In this study, three kinds of polymeric flocculants were synthesized and one flocculant/coagulant mixture was prepared to compare their effects on oil sands tailings treatment. The flocculants and the flocculant/coagulant mixture were compared for their flocculation power on settling and filtration in two different systems. They were kaolinite clay suspension as model tailings and laboratory extraction tailings slurry.

Two types of poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide], p[NIPAM-co-DMAPMA] (CP) were synthesized to study the effect of LCST on flocculation power. CP05, having 5 mole% DMAPMA, LCST of 38^{o}C and molecular weight of 2.4 MDa, was in-house synthesized. CP10, having 10 mole% DMAPMA, LCST of 48^{o}C and molecular weight of 2.5 MDa was also in-house synthesized. Aluminum hydroxide colloid-poly[*N*-isopropylacrylamide-co-*N*-[3-(Dimethylamino)propyl]methacrylamide] hybrid (Al-CP) was synthesized as Al-CP05, having 5 mole% DMAPMA, LCST of 37^{o}C and molecular weight of 2.1 MDa. The effect of aluminum hydroxide colloid in the polymer structure on flocculation power was explored at different temperature conditions in the experiments. The flocculant/coagulant mixture {CP05+Al} was prepared by dissolving CP05 into the aluminum hydroxide colloidal suspension. {CP05+Al} contained same amount of aluminum hydroxide colloid in order to compare the flocculation power with Al-CP05.

All the four flocculants showed both temperature and pH sensitivities. The conformation of the temperature sensitive polymer changed from hydrophilic elongated coils to hydrophobic globules when the polymer solution was heated to above its LCST. The hydrophobic globules in water present as a colloidal solution reflected light ray and reduced light transmittance of the polymer solution. LCSTs were measured by the turbidity of the polymer solution with temperature and pH changes, respectively. The higher the DMAPMA content, the higher the LCST the polymer would have. Furthermore, the higher the pH, the lower LCST the polymer would have. Hence, the CP polymer molecules could be shrunk into hydrophobic globules by either increasing the temperature or decreasing the pH. Apart from that, all the four flocculants were proven to be able to alter surface charge of kaolinite clay particles from negative to positive at pH 8.5.

The laboratory extraction tailings slurry was extracted from a high fines ore (with 25.5 wt% fines in solids) with a pH 8.5, and comprised 0.29 wt% bitumen, 11.6 wt% solids and 47.0 wt% fines in solids. The laboratory extraction tailings slurry used in this study thus contained about 5 wt% fines. The model tailings was prepared as 5 wt% kaolinite suspension in Milli-Q water at pH 8.5 in order to minimize the effect of any ions on the LCSTs of the polymers. The experiment was divided into two major parts – the settling test and the filtration test. For the settling test, initial settling rate, clarity of supernatant, and floc strength were used as the measures of the flocculation power of the flocculants. For the filtration test, filtration rate and filter cake moisture content were used to assess the ability of the flocculants as a filtration aid. Three temperature conditions were employed in each test to illustrate how temperature would affect flocculation power of the flocculants throughout the tailings treatment processes.

- RMRS/RMRF (Room temperature Mixing and Room temperature Settling/Filtering) was referred as the addition of polymer into the tailings sample and the settling/filtration of the flocculated sample at room temperature.
- RMHS/RMHF (Room temperature Mixing and High temperature Settling/Filtering) was the addition of polymer at room temperature and the settling/filtration of the sample at temperature higher than LCST of the polymer.
- HMHS/HMHF (High temperature Mixing and High temperature Settling/Filtering) meant the addition of polymer and the settling/filtration at temperature higher than LCST.

According to the results of CP05 and CP10 experiments, the DMAPMA content changed only the LCST of the polymer but not its flocculation power. The CP series performed best with polymer addition at room temperature and settling/filtering the flocculated tailings at temperature higher than the LCST

(cases RMHS/RMHF). Polymer addition at temperature higher than LCST gave little flocculation on both kaolinite clay suspension and laboratory extraction tailings. In such a case, CP caused fouling on filtration of kaolinite suspension. CP suppressed filtration rate and no filter cake could be formed for HMHF. For tailings slurry, the presence of coarse sands helped to build up porous filter cake such that CP had little effect on filtration for HMHF. Both CP05 and CP10 polymers had very similar results in settling and filtration tests which indicated the polymers were only different by their LCSTs. Therefore, it is feasible to adjust the LCST of CP to match up the targeted operating temperature of tailings treatment processes.

Although CP showed improvement in tailings treatment, its flocculation power is expected to be improved by hybridization with ionic compounds as discussed in Chapter 1. CP was then synthesized with aluminum hydroxide colloids as Al-CP to achieve high flocculation power and reasonable temperature and pH sensitivities. The LCST of Al-CP05 was not as sharp as that of CP05. The LCST of Al-CP05 existed as a phase transition zone rather than a point, which indicated that the hybrid was less temperature sensitive. The aluminum hydroxide colloids contributed for a more hydrophilic structure of the polymer. Al-CP05 was shown to have high flocculation power and was able to enhance both settling and filtration in kaolinite clay suspension. Al-CP05 was about 4 times more effective than CP05 in settling and twice effective as CP05 in filtration. The hybrid flocculant performed the best for RMHS/RMHF and the worst for HMHS/HMHF. Yet, the flocculation power of Al-CP05 for HMHS/HMHF was relatively high as compared with CP05 because of the presence of aluminum hydroxide colloid. From data of tailings slurry experiment, Al-CP05 was less responsive to the sample treatments. The presence of bitumen and various ions from the tailings might cause the reduced temperature sensitivity of the hybrid flocculant. Al-CP05 had lower settling rate in laboratory extraction tailings than in kaolinite suspension, but it had little effect on filtration. Therefore, the presence of coarse sands had greater effect on filtration than on settling.

Comparison of {CP05+Al} was used to confirm the role of aluminum hydroxide colloid in Al-CP05. The settling tests of {CP05+Al} were thus only performed in kaolinite suspension. According to the experiment, {CP05+Al} showed better settling results than CP05, yet the flocculant/coagulant mixture was inadequate to compare with Al-CP05. The aluminum hydroxide colloid in {CP05+Al} acted as a coagulant to destabilize the suspension system, and hence it helped flocculation. On the other hand, the aluminum hydroxide colloid in Al-CP05 existed as a part of the polymer molecule to attract negatively charged kaolinite clay particles by its high positive charge density. This effectively enhanced the chance of adsorption of kaolinite particles on polymer chains.

To summarize, Al-CP05 was the best flocculant among the four flocculants in this study. It provided excellent flocculation power on both kaolinite clay suspension and laboratory extraction tailings. On top of that, this polymeric hybrid is a good alternative to Al-PAM due to its feasibility of tailings treatment at high temperature and the possibility of preventing the polymer from entering recycle stream of the process water in the extraction process. Last but not least, the sensitivities on temperature and pH and the alternation of the polymer LCST and the aluminum content are advantageous in the design of water treatment processes.

Chapter 9 Recommendations for Future Research

This study revealed the effect of temperature sensitive aluminum hydroxide-polymer hybrid as a flocculant and filtration aid on oil sands tailings treatment. Recommendations for future research on oil sands tailings treatment with ion-polymer hybrid are listed as follows:

1. The adaptability of ion-polymer hybrid to different oil sands ores, i.e good processing ore, poor processing ore and weathered ore should be studied.
2. Roles of ions, bitumen, coarse sands and fines in tailings slurry play in both LCST and the flocculation power of polymer hybrids.
3. How both molecular weight and aluminum content affect on both LCST and flocculation power of polymers.
4. The interaction forces between clay fines, fine particles and bitumen in polymer solution should be measured for further study.
5. The structure of the polymer hybrid and the mechanism of the pH effect on the LCST of the polymer hybrid should be studied.
6. Instead of temperature effect, effect of pH on oil sands tailings treatment should be studied on the grounds of the pH sensitivity of the polymer.

Although the results presented in this study showed an inorganic-organic hybrid polymer could enhance settling and filtration in tailings treatment, the exact mechanism was not explored. Further studies can hence help understand the properties and the confirmation of the polymer, and provide possibility for further modification of the polymer structure in favour of oil sands tailings treatment.

APPENDICES

Appendix A – Temperature Effect on Viscosity of Water in Settling Test

According to Stokes' Law, as most of the tests were carried out at high temperatures ($30^{o}C$ to $60^{o}C$), the change in viscosity of fluid should be taken into consideration [1]. Hence, it is important to characterize the flow regime using Reynolds number, *Re*. Reynolds number was estimated using the correlation described by Turton and Clark [2],

$$Re = Ar^{1/3}\left[\left(\frac{18}{Ar^{2/3}}\right)^{0.824} + \left(\frac{0.321}{Ar^{1/3}}\right)^{0.412}\right]^{-1.214} \tag{A-1}$$

where, *Ar* is the Archimedes number which is defined as:

$$Ar = \frac{{d_p}^3(\rho_p - \rho_f)g}{{\eta_f}^2 \rho_f} \tag{A-2}$$

where, d_p is the diameter of particle, ρ_p is the density of particle, ρ_f is the density of fluid, g is the acceleration due to gravity, and η_f is the kinematic viscosity of fluid.

Assuming that fluid has the same properties as water and floc has a density of 1500 kg/m^3. At temperature above $50^{o}C$, the polymer becomes hydrophobic and shrinks in water. The flocs are then aggregated together due to hydrophobic attraction and forms larger flocs with diameter of more than 5mm. Re of the settling is larger than 1000, and the viscosity effect on settling rate is considered sufficiently small enough to be negligible.

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Appendix B – Sample Raw Data of Filtration of Laboratory Extraction Tailings

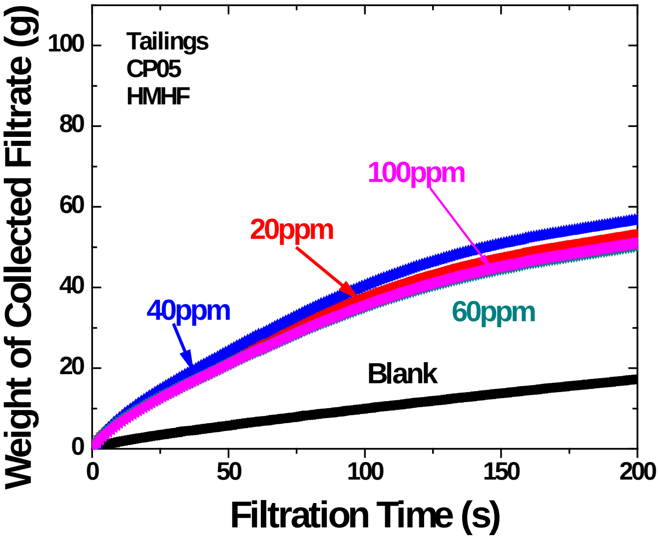


Figure B-1 Filtration Curves of Mixing CP05 with and Filtration of Laboratory Extraction Tailings both at Temperature above Corresponding LCST

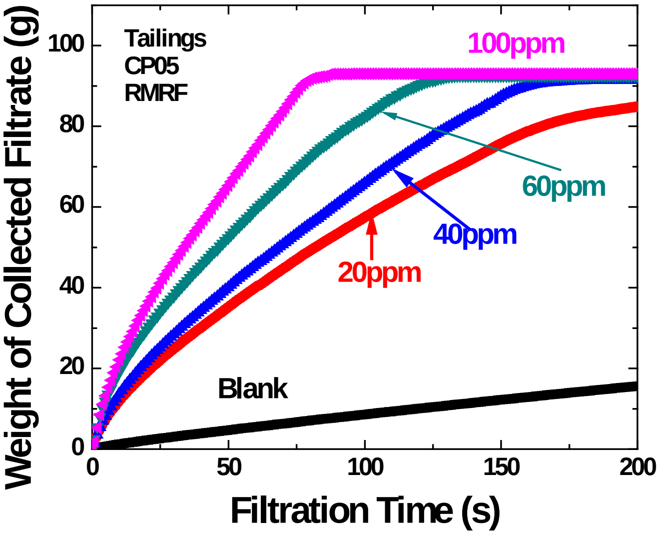


Figure B-2 Filtration Curves of Mixing CP05 with and Filtration of Laboratory Extraction Tailings both at Room Temperature

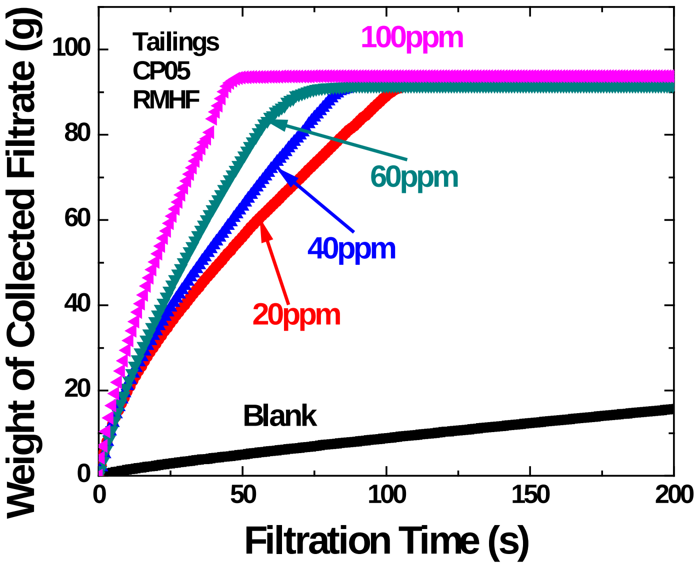


Figure B-3 Filtration Curves of Mixing CP05 with Laboratory Extraction Tailings at Room Temperature and Filtration at Temperature above Corresponding LCST

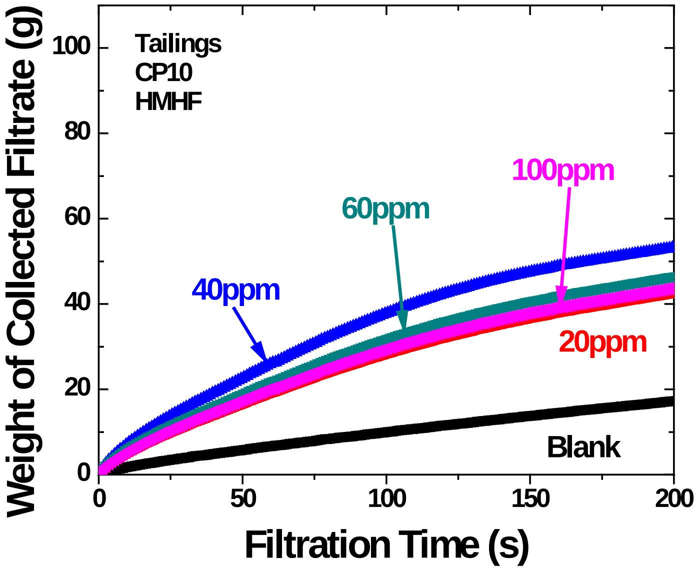


Figure B-4 Filtration Curves of Mixing CP10 with and Filtration of Laboratory Extraction Tailings both at Temperature above Corresponding LCST

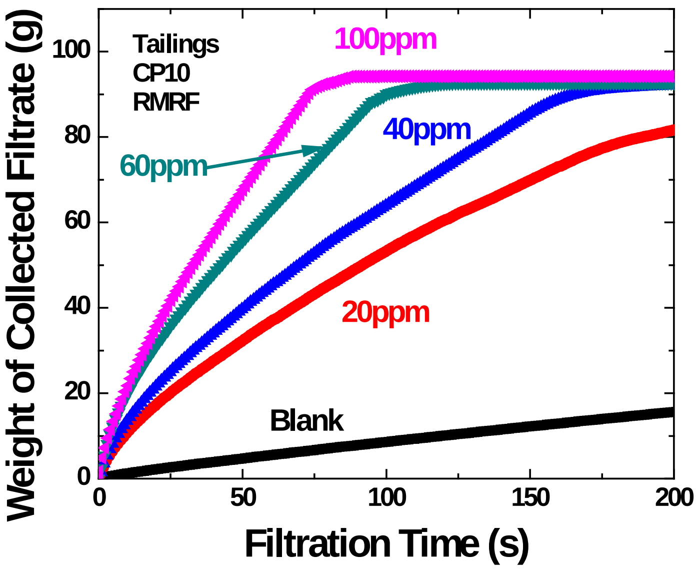


Figure B-5 Filtration Curves of Mixing CP10 with and Filtration of Laboratory Extraction Tailings both at Room Temperature

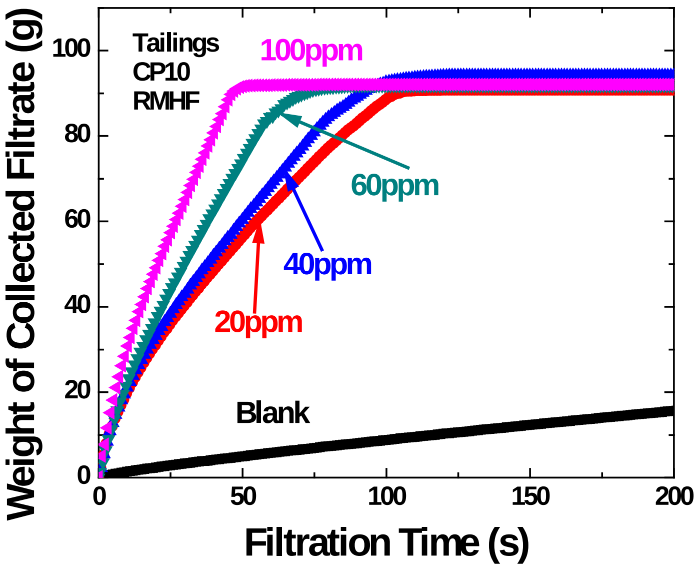


Figure B-6 Filtration Curves of Mixing CP10 with Laboratory Extraction Tailings at Room Temperature and Filtration at Temperature above Corresponding LCST

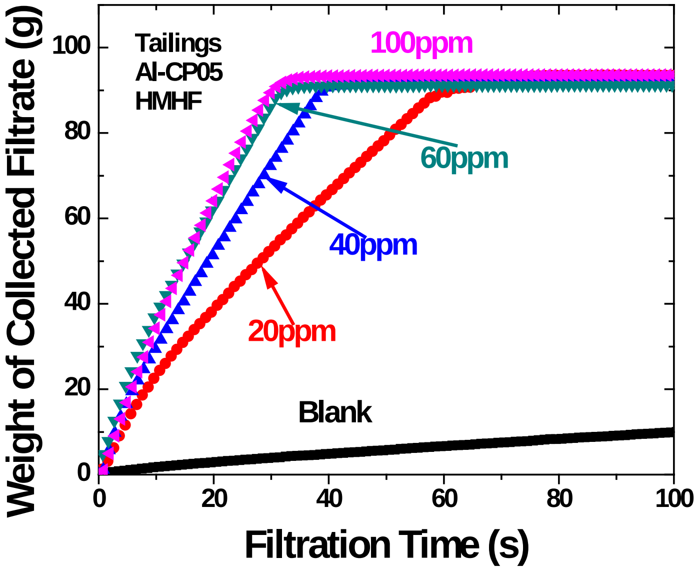


Figure B-7 Filtration Curves of Mixing Al-CP05 with and Filtration of Laboratory Extraction Tailings at Temperature above Corresponding LCST

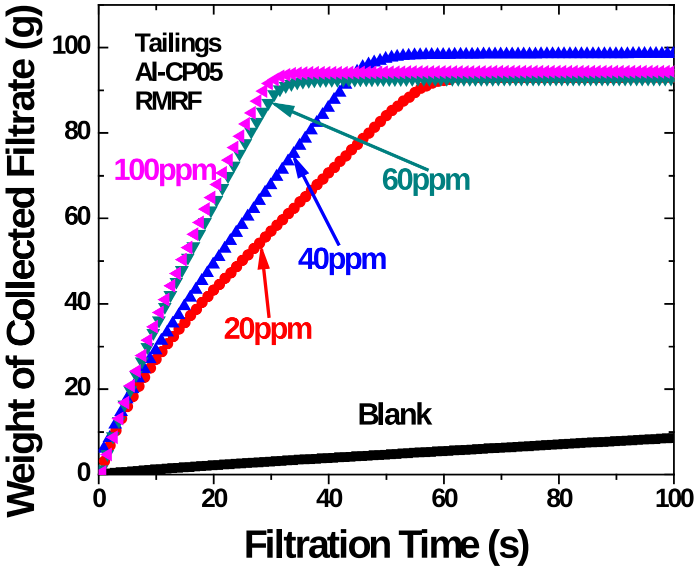


Figure B-8 Filtration Curves of Mixing Al-CP05 with and Filtration of Laboratory Extraction Tailings at Room Temperature

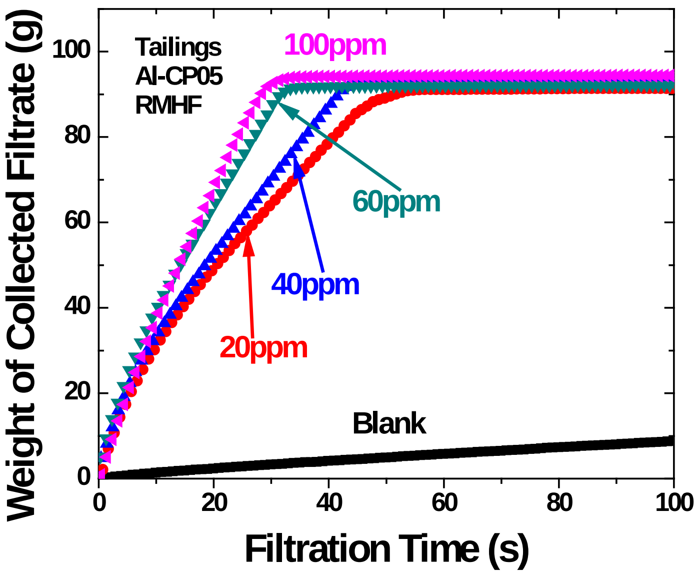


Figure B-9 Filtration Curves of Mixing Al-CP05 with Laboratory Extraction Tailings at Room Temperature and Filtration at Temperature above Corresponding LCST

Appendix C – Analysis on Filter Cake Resistance

The filterability of a suspension can be measured quantitatively as the specific resistance to filtration (SRF, m/kg) [1]. A small SRF value represents a high permeability of a filter cake. SRF is derived as follow. A modified version of Equation (3-3) can be expressed as [2-5],

$$u = \frac{1}{A}\frac{dV}{dt} = \frac{\Delta P}{\eta_f \rho_f (R_c + R)} \tag{C-1}$$

where:

u : superficial velocity of filtration (m/s)

A : area of filter (m^2)

V : volume of collected filtrate at time t (m^3)

t : filtration time (s)

ΔP : pressure drop (Pa)

η_f : viscosity of filtrate (m^2/s)

ρ_f : density of filtrate (kg/m^3)

R_c : resistance of filter cake (m^{-1})

R : resistance of filter media, e.g. filter paper (m^{-1})

The resistance of filter cake R_c would be directly proportional to the mass of cake deposited assuming the cake is incompressible.

$$R_c = SRF \cdot \omega \tag{C-2}$$

where ω is the mass of filter cake per unit area (kg/m^2) [1]. The mass of incompressible cake is defined as,

$$\omega = \frac{V}{A} c \tag{C-3}$$

where c is the solid concentration in the suspension (kg/m^3) [6]. Substituting Equations (C-2) and (C-3) into Equation (C-1) gives

$$\frac{dV}{dt} = \frac{A\,\Delta P}{\eta_f \rho_f (SRF \frac{V}{A} c + R)} \tag{C-4}$$

Integrating Equation (C-4) with initial condition of $V = 0$ at $t = 0$ leads to

$$t = \frac{\eta_f \rho_f\, SRF\, c}{2\, A^2\, \Delta P} V^2 + \frac{\eta_f \rho_f\, R}{A\, \Delta P} V \tag{C-5}$$

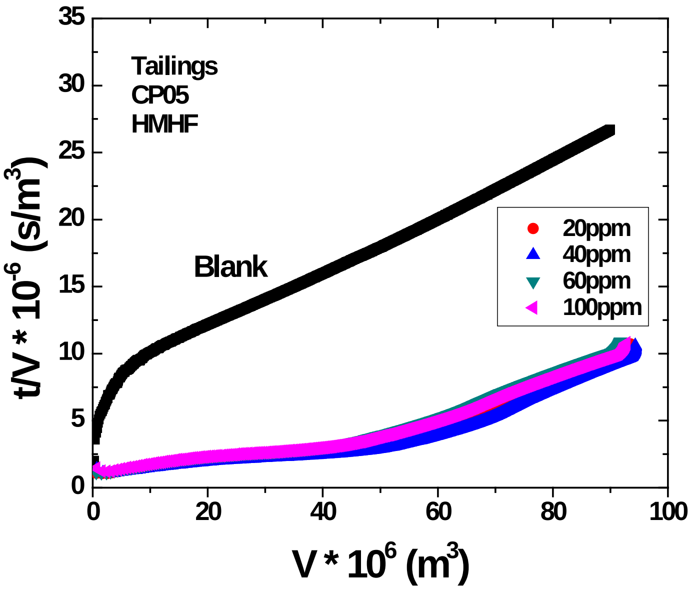
Dividing Equation (C-5) with V yields

$$\frac{t}{V} = \frac{\eta_f \rho_f\, SRF\, c}{2\, A^2\, \Delta P} V + \frac{\eta_f \rho_f\, R}{A\, \Delta P} \tag{C-6}$$

Therefore, SRF can be calculated from the slope of the plot of t/V as a function of V.

$$SRF = \frac{2\, A^2\, \Delta P}{\eta_f \rho_f c} slope \tag{C-7}$$

In this study, pressure drop was kept at 15×10^3 Pa, filter area was 45.8×10^{-4} m^2, and $\eta_f \rho_f$ was measured to be about 1×10^{-3} Pa·s.



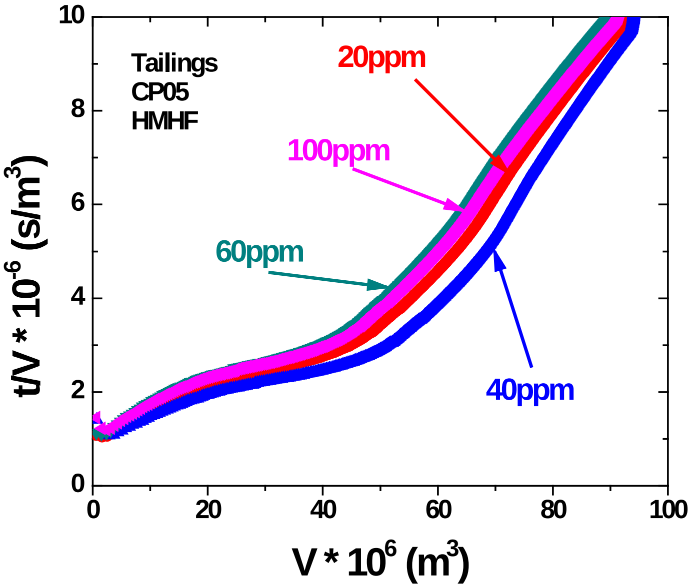


Figure C-1 Specific Resistance of Filtration of Tailings with CP05 Addition at Temperature above Corresponding LCST: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

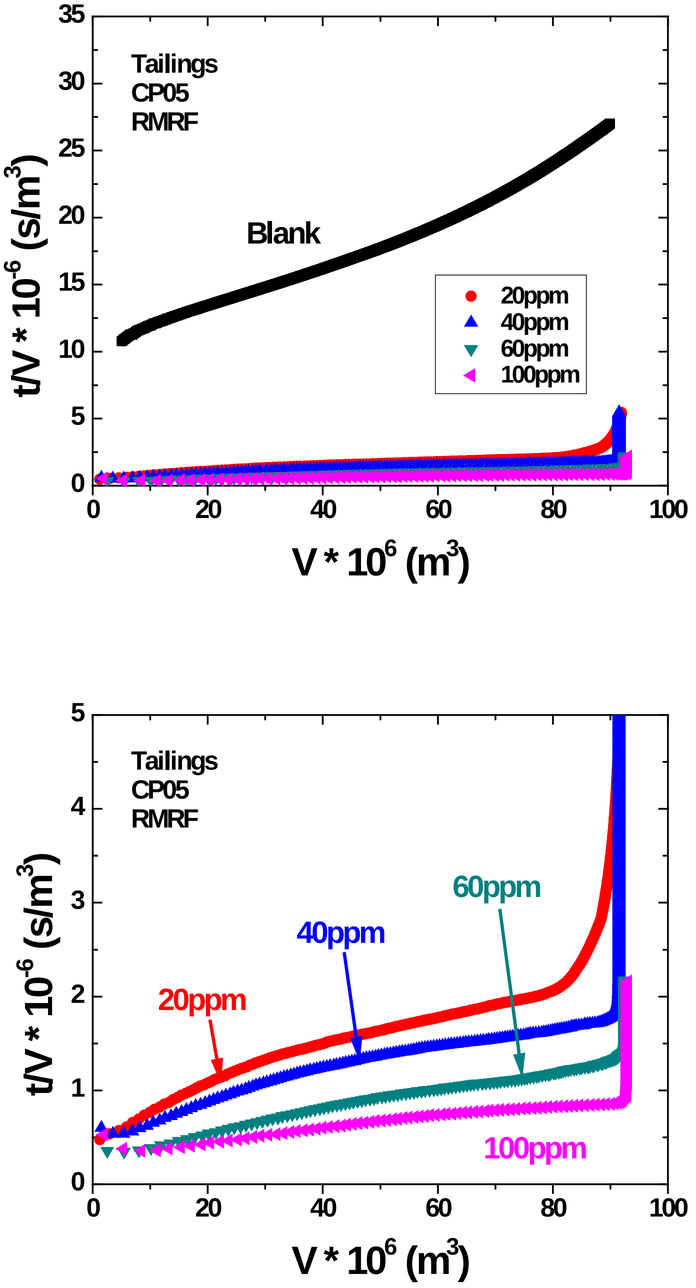


Figure C-2 Specific Resistance of Filtration of Tailings with CP05 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

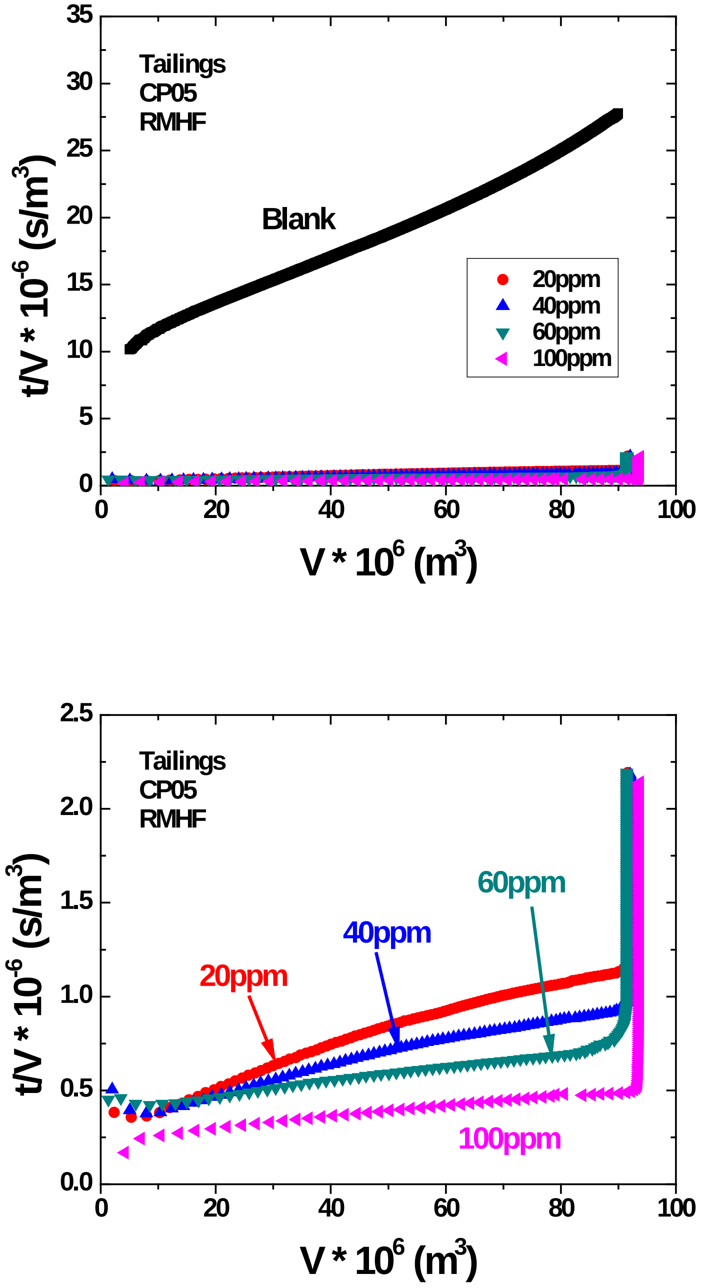


Figure C-3 Specific Resistance of Filtration of Tailings at Temperature above Corresponding LCST with CP05 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

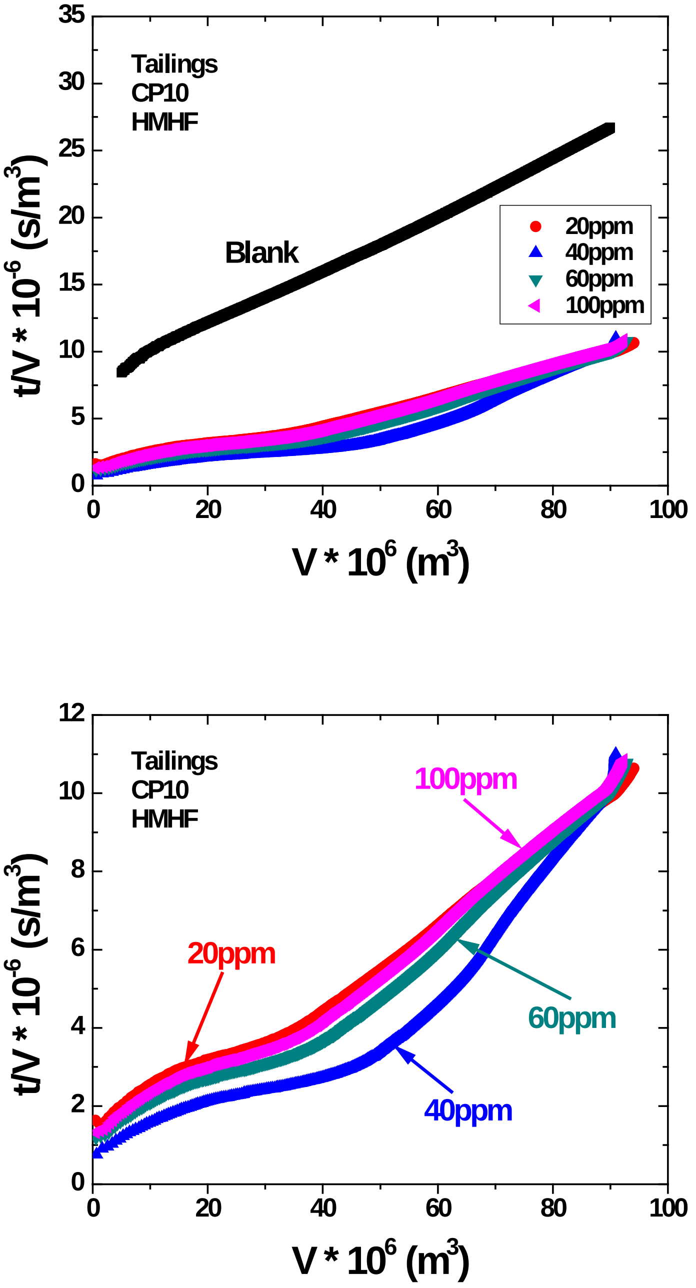


Figure C-4 Specific Resistance of Filtration of Tailings with CP10 Addition at Temperature above Corresponding LCST: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

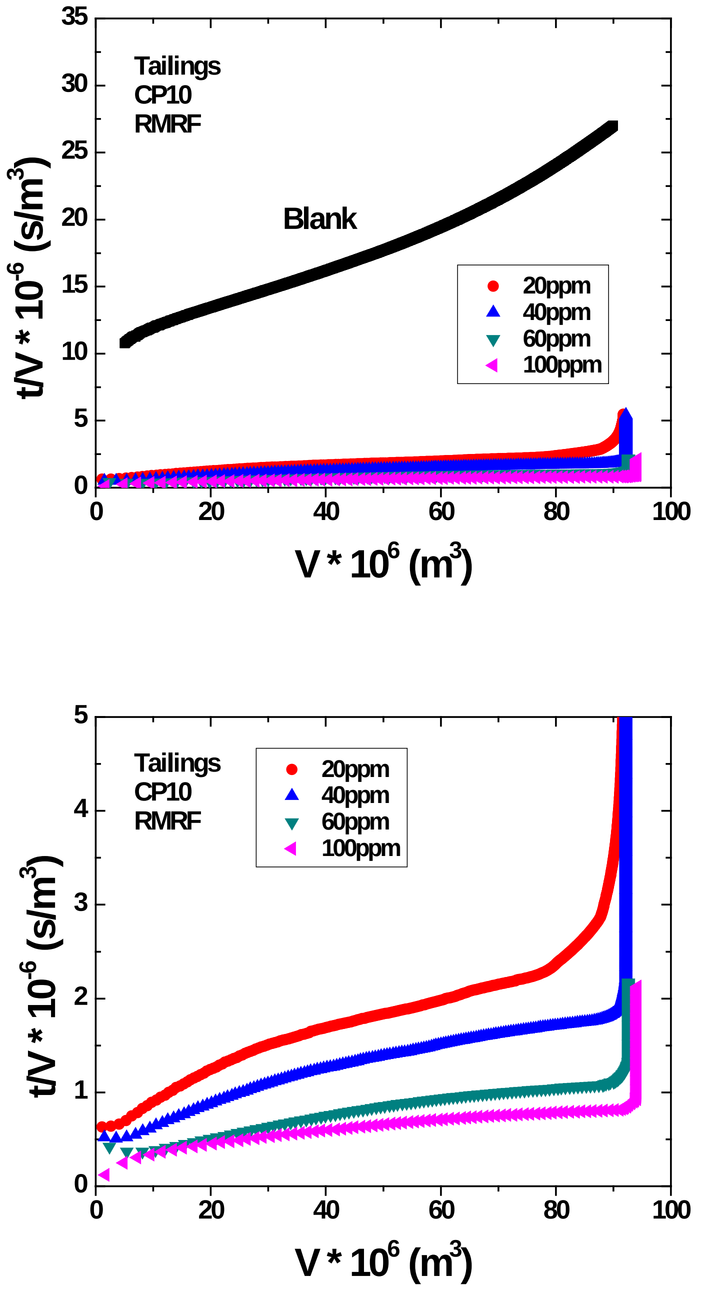


Figure C-5 Specific Resistance of Filtration of Tailings with CP10 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

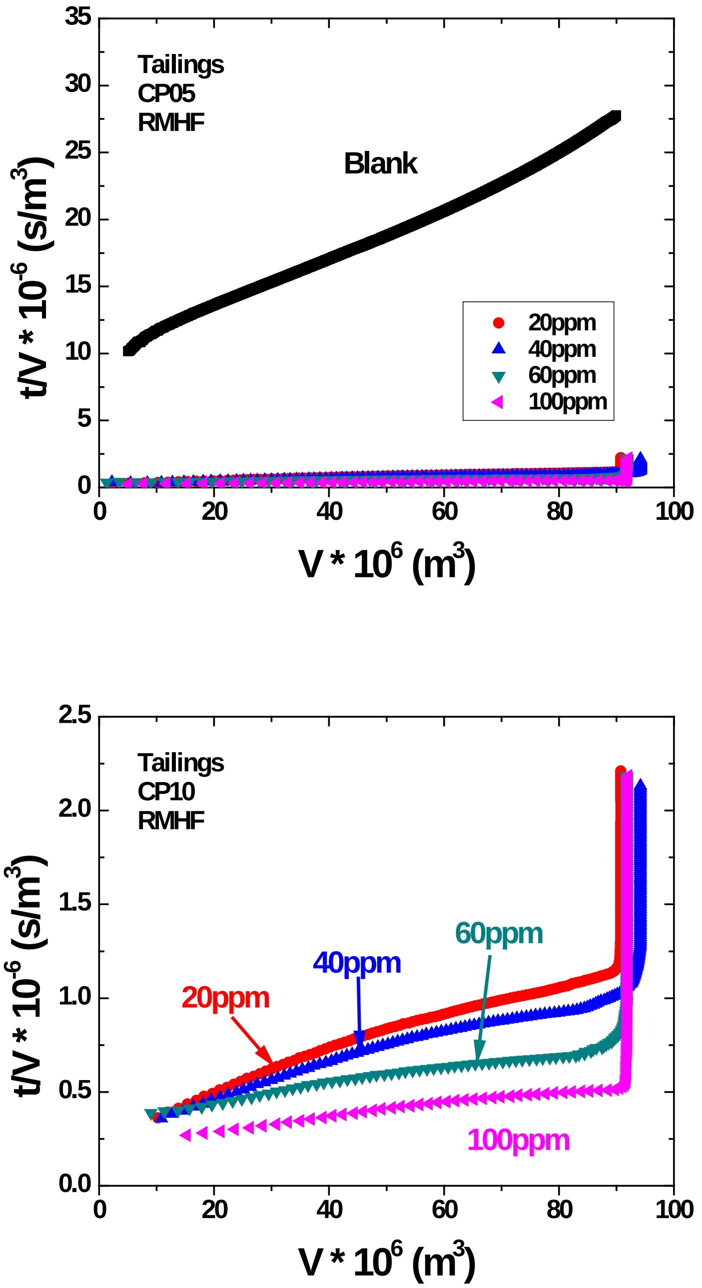
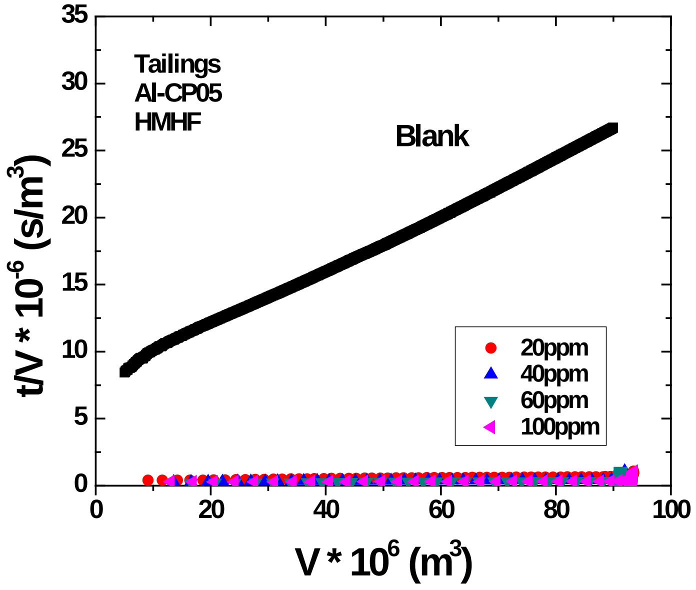


Figure C-6 Specific Resistance of Filtration of Tailings at Temperature above Corresponding LCST with CP10 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages



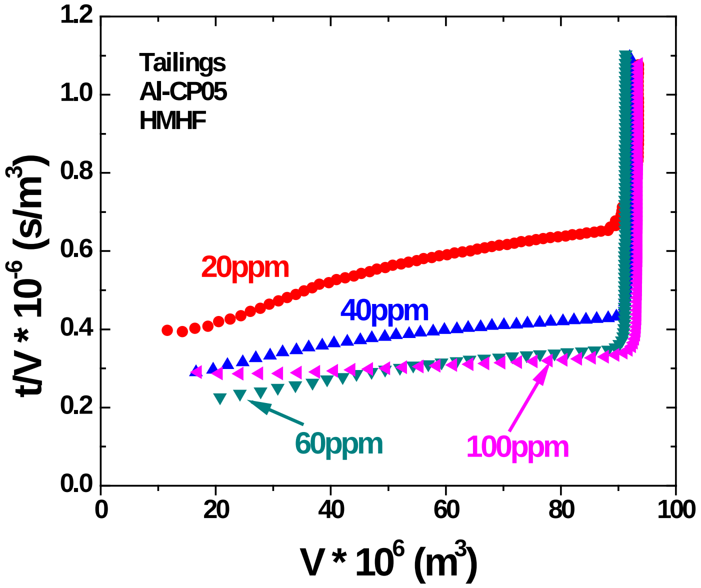


Figure C-7 Specific Resistance of Filtration of Tailings with Al-CP05 Addition both at Temperature above Corresponding LCST: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

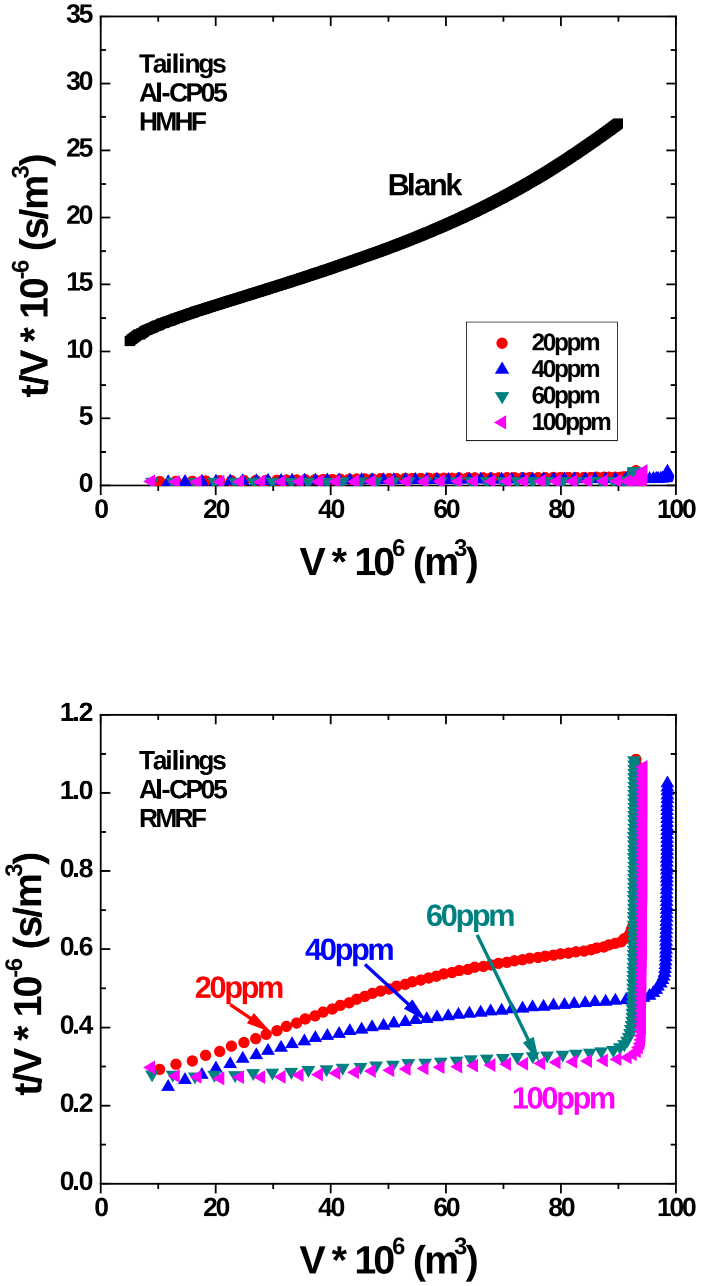


Figure C-8 Specific Resistance of Filtration of Tailings with Al-CP05 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

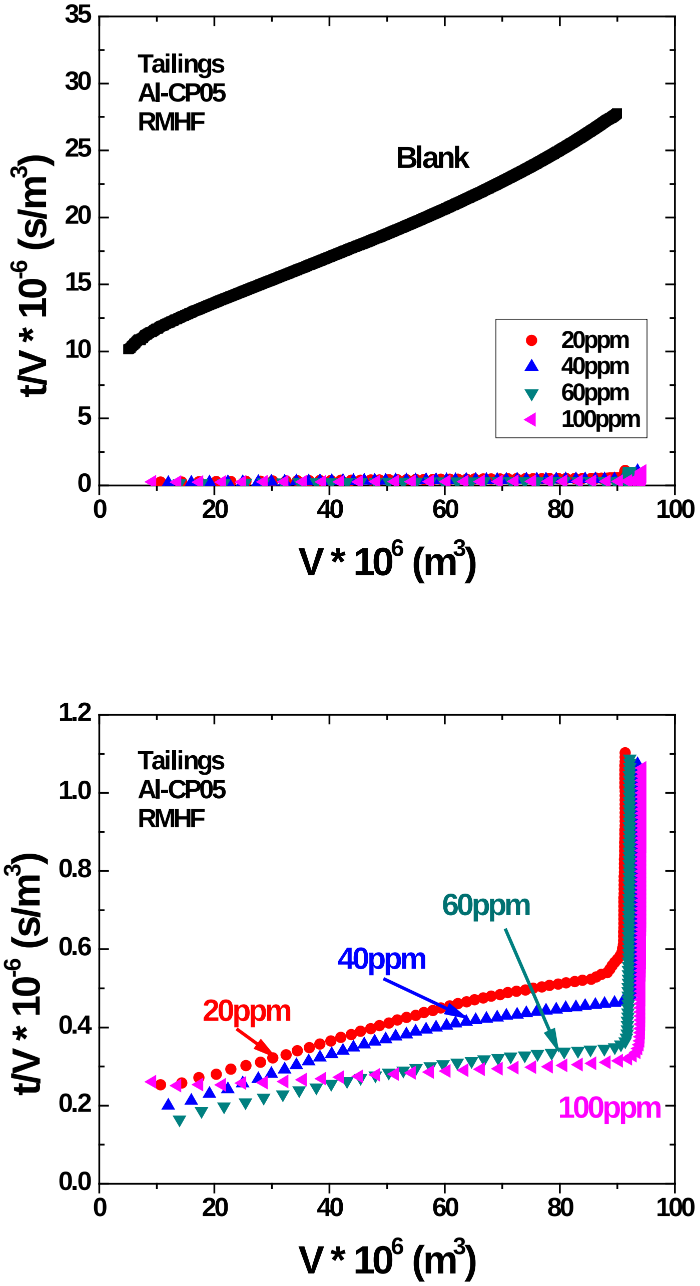


Figure C-9 Specific Resistance of Filtration of Tailings at Temperature above Corresponding LCST with Al-CP05 Addition at Room Temperature: (top) Comparison with Blank Sample (bottom) Magnification of Curves of Different Dosages

The SRF values were calculated using Equation (C-7) and the slopes obtained from Figures C-1 to C-9, and were plotted as a function of flocculant dosages as shown below in Figures C-10 to C-12. The SRF is shown to decrease with the increase flocculant dosage of all flocculants tested. The filter cake with Al-CP05 addition is the most permeable in all sample treatments. The permeability of filter cake with CP05 addition or CP10 addition is roughly the same in all sample treatments. Therefore, among the three tested flocculants, Al-CP05 produces the most permeable filter cake, and hence, is the best flocculant for filtration of tailings. 20ppm of Al-CP05 provided a SRF of 2.2×10^{10} on extraction tailings which the SRF of blank sample was 1.1×10^{12}. This is comparable to a SRF of 9.9×10^{9} on oil sands tailings with 10ppm Al-PAM addition while the SRF of the blank sample in Wang's study is 8.2×10^{10} [5].

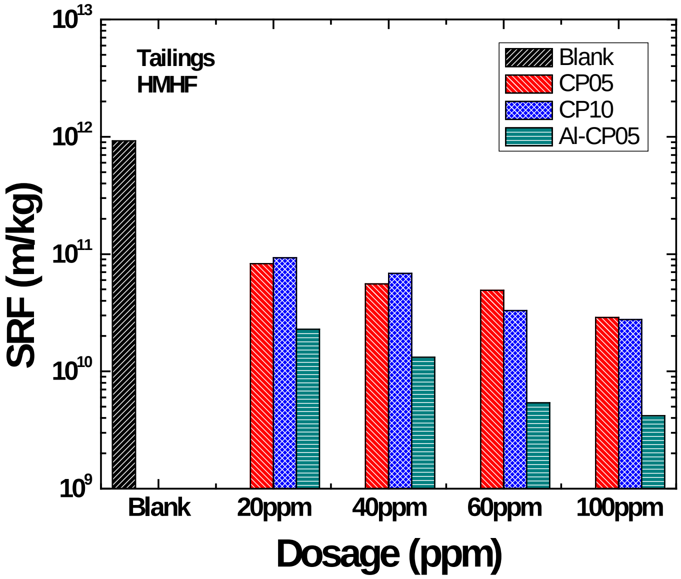


Figure C-10 Specific Resistances to Filtration of Tailings with Different Flocculants Added at Temperature above Corresponding LCST

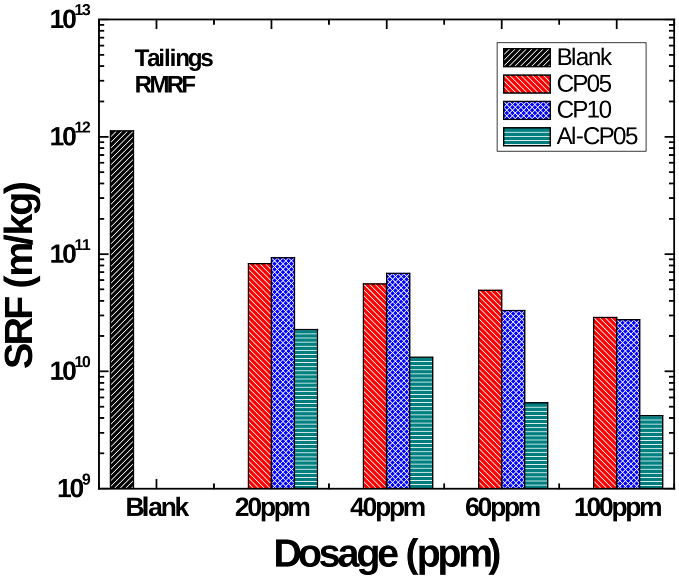


Figure C-11 Specific Resistances to Filtration of Tailings with Different Flocculants Added at Room Temperature

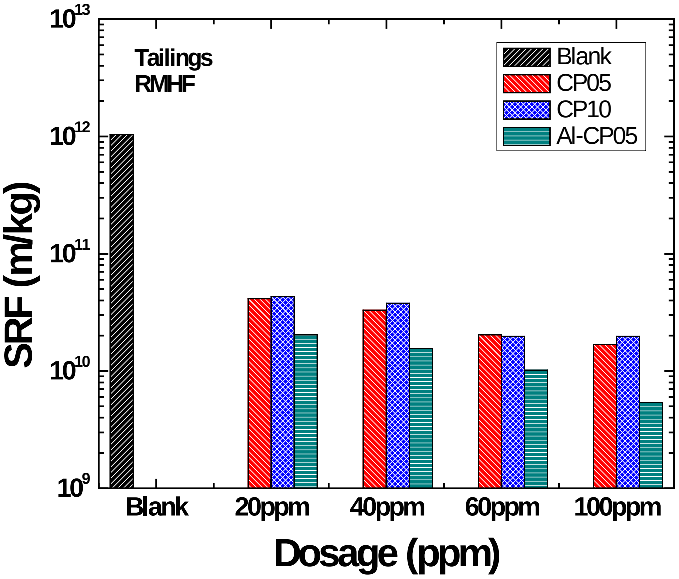


Figure C-12 Specific Resistances to Filtration of Tailings at Temperature above Corresponding LCST with Different Flocculants Added at Room Temperature

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Appendix D – Effect of pH on the Coil-Globule Transition of All Flocculants

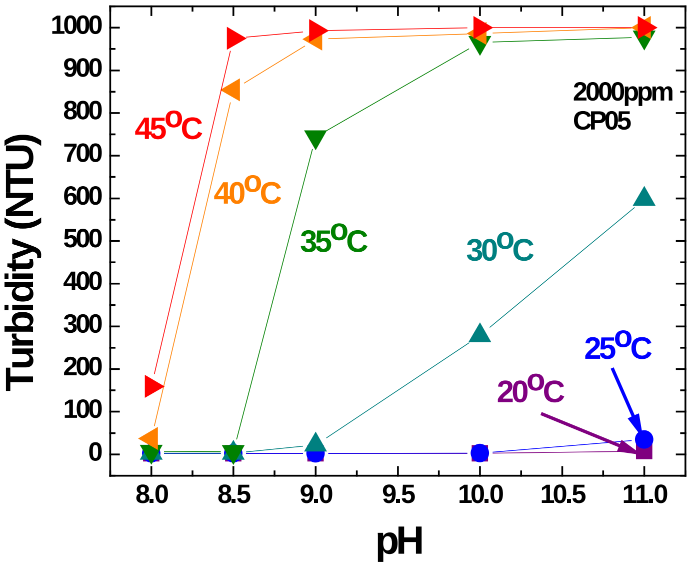

Figure D-1 The pH Induced Coil-Globule Transition of CP05

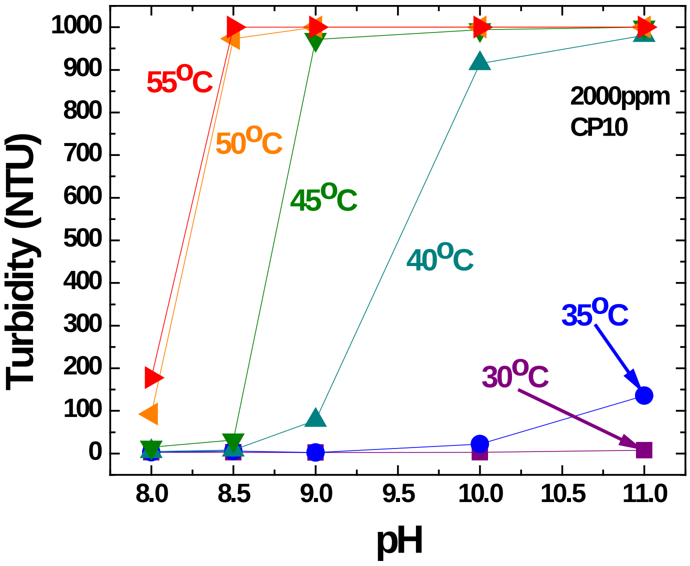

Figure D-2 The pH Induced Coil-Globule Transition of CP10

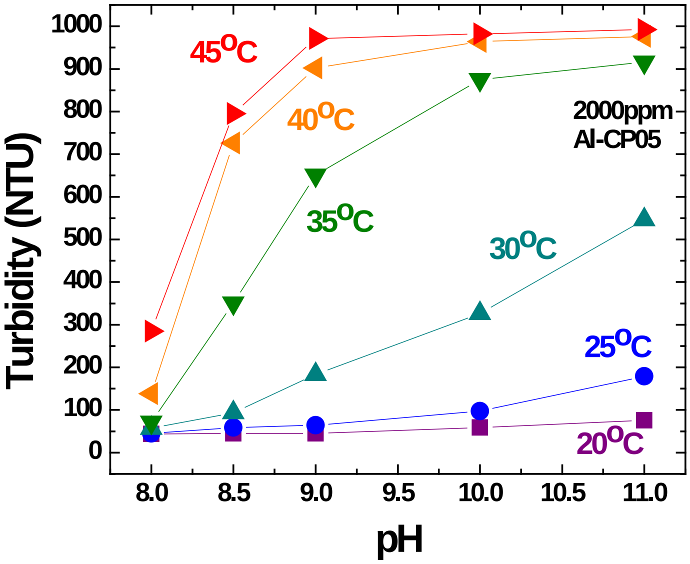

Figure D-3 The pH Induced Coil-Globule Transition of Al-CP05

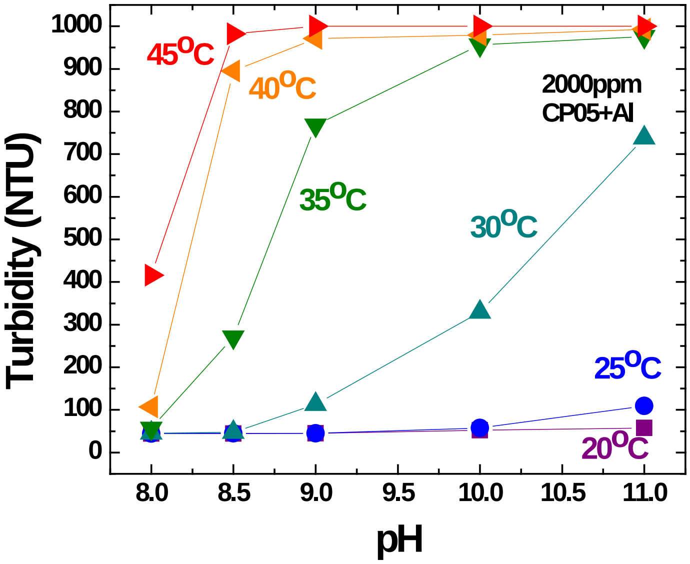

Figure D-4 The pH Induced Coil-Globule Transition of CP05+Al