



Influence of pH, Electrolytes and Polymers on Flocculation of Kaolin Particle

Nongkhran Chaiwong and Apinon Nuntiya*

Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

*Author for correspondence; e-mail: anuntiya@chiangmai.ac.th

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ABSTRACT

Flocculation is the most important procedure prior to filter press process. Floc size and floc strength were determined as a function of pH, various electrolyte and polymer flocculant concentrations. The floc size and floc strength of kaolin suspension were investigated by laser diffraction technique and Dynamic Brookfield DV III+ viscometer, respectively. From the experimental results, addition of a high concentration of electrolyte and polymer flocculant gave larger floc size and floc strength. Furthermore, the floc size and floc strength increased with increasing of cation valency in the electrolytes and increasing of molecular weight in the polymers. Sedimentation rate of 25 ppm of polyvinyl alcohol (Low molecular weight) at pH 5.6 provided slightly slower than polyacrylamide (High molecular weight) at pH 8.3 due to polymer bridging mechanism. On the other hand, polyvinyl alcohol gave higher filtration rate than polyacrylamide. From the experiments, it can be concluded that pH, the concentration of electrolyte and polymers effect on sedimentation and filter rates.

Keywords: Kaolin, flocculation, electrolyte, polyvinyl alcohol and polyacrylamide.

1. INTRODUCTION

The understanding of the particle flocculation mechanisms was induced by polymers recently. The polymers can destabilize the colloidal particles through charge neutralization, electrostatic patch, bridging, or depletion flocculation. It has been accepted that the bridging mechanism is operating in the flocculation by nonionic polymers. Flocculation is an important process in many industrial applications. In papermarking, flocculation of fine materials, i.e. filler particles and small fibre fragments, improves dewaterability. Flocculation refers to a process where a solute come out of

solution in the form of floc. The term is also used to refer to the process by which fine particulates are caused to clump together into floc. The floc may then float to the top of the liquid, settle to the bottom of the liquid. In geology, flocculation is a condition in which clays, polymer or other small charged particles become attached and form a floc. In dispersed clay suspensions, flocculation occurs after mechanical agitation ceases and the dispersed clay platelets spontaneously form flocs because of attractions between negative face and positive edge charges or used flocculants. Flocculants are chemicals that are

used to promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Many flocculants are multivalent cations such as aluminium, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals are used under appropriate pH and other conditions, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particle into the larger floc.

Kaolinite is a mineral belonging to the group of aluminosilicates. It is commonly referred to as "China Clay" because it was first discovered at Kao-Lin, in China. The term kaolin is used to describe a group of relatively common clay minerals dominated by kaolinite and derived primarily from the alteration of alkali feldspar and micas. Kaolin is an industrial mineral used primarily as an inert filler and customers combine it with other raw materials in a wide variety of applications. Kaolin is a white, soft, plastic clay mainly composed of fine-grained plate-like particles. Kaolin is formed when the anhydrous aluminium silicates which are found in feldspar-rich rocks, like granite, are altered by weathering or hydrothermal processes. The process which converted the hard granite into the soft matrix found in kaolin pits is known as "kaolinisation". The quartz and mica of the granite remain relatively unchanged whilst the feldspar is transformed to kaolinite. Smectite may also form in small quantities in some deposits. The refining and processing of the fine fraction of the kaolinised granite yields predominantly kaolinite with minor amounts of mica, feldspar, traces of quartz and, depending on the origin, organic substances and/or heavy minerals. Individual kaolins vary in many physical aspects, which in turn

influence their end use. Of particular commercial interest is the degree of crystallinity which influences the brightness, whiteness, opacity, gloss, film strength, and viscosity. The objective of this research is to study the effects of pH, type of electrolytes and polymers on clay flocculation process.

2. MATERIALS AND METHODS

2.1 Materials

Kaolin was used as the model mineral in this flocculation study. Kaolin was obtained from Lampang Kaolin, the mineral dressing in the north of Thailand. The flocculants used in study were electrolytes (0.1 M NaCl and 0.1 M CaCl₂), low molecular weight, 25 ppm of polyvinyl alcohol (PVA) and high molecular weight polyacrylamide (PAM).

2.2 Methods

Lampang kaolin was grounded in hammer mill and passed through 325 mesh sieve in the dry state. It has a volume median diameters, D [4,3] particle size of 9.47 μm, a BET surface area of 14.60 m²/g. The chemical composition and mineralogical were determined by X-ray fluorescence (XRF) and X-ray Diffraction (XRD) techniques. At 25 % (w/w) solid content in deionized water and the flocculants (electrolytes and polymers) were adjusted to pH 2-10 with 0.5 M HCl and 0.5 M NaOH, and mixed by electric mixer for 5 minutes at 500 rpm. The floc size and Bingham yield stress (floc strength) of kaolin suspension were investigated by laser diffraction technique using a Malvern Mastersizer S Particle size Analyzer and Dynamic Brookfield DV III+ viscometer, respectively. Filtration rate was determined by Filter Press model OSK9104-600-GE.

3. RESULTS AND DISCUSSION

The main chemical compositions of Lampang kaolin sample were SiO₂, Al₂O₃,

K₂O and Fe₂O₃; small amounts of TiO₂, Na₂O, MgO, CaO and MnO were present. From the XRD profile, Lampang kaolin composed of kaolinite, illite and quartz as shown in Figure 1.

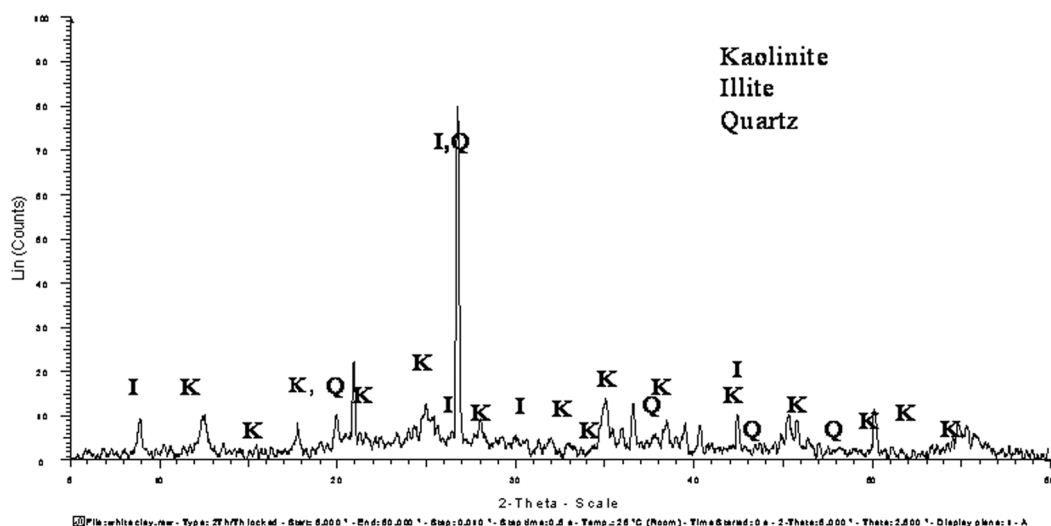


Figure 1. XRD diffractogram of Lampang kaolin [1].

3.1 Effect of pH

Table.1 showed the floc size of kaolin particles in the flocculated suspension as a function of pH. In an aqueous suspensions of platelike kaolin particles were formed in three different modes of particle interaction which were believed to occur, namely edge to face (E-F), edge to edge (E-E) and face to

face (F-F). At 25 % (w/w) solid content, the largest floc size of aqueous suspensions of Lampang kaolin showed at pH 2.0. At lower pH values (pH 2.0 and pH 4.0), there were larger floc than at pH 8.0 and pH 10.0. Because of flocculation is expected to begin at lower pH values, namely edge to face that

Table. 1. Floc size of kaolin flocculation as function of pH, electrolytes and polymers.

pH	Floc size of flocculation Volume Mean Diameters: D [4,3] (µm)				
	H ₂ O	NaCl	CaCl ₂	PVA	PAM
pH normal	17.06	13.44	14.79	16.72	32.76
pH 2.0	17.57	17.39	15.05	17.47	20.38
pH 4.0	16.69	15.59	21.24	17.01	28.49
pH 6.0	16.94	20.26	19.25	17.98	28.26
pH 8.0	16.38	19.68	20.90	27.23	35.24
pH 10.0	15.94	18.37	18.71	24.63	29.70

kaolin is positively charged and deflocculation at higher pH values it carries a net negative charge on the surface.

3.2 Effect of electrolytes and pH

Kaolin particle was dispersed in 0.1 M NaCl and 0.1 M CaCl₂ and adjusted pH at 2, 4, 6, 8 and 10, respectively. It was found that at higher pH (pH 8.0 and pH 10.0) showed larger floc than at lower pH (pH 2.0 and pH 4.0). However, the highest viscosity indicated at pH 8.0 as shown in Figure 2. Flocculation was expected to begin at higher pH values, NaCl and CaCl₂ promoted E-E and F-F structures and yield stress increased because the electrical double layers (all negatives) were compressed and energy barriers to van der Waals coagulation were reduced. At lower values, the addition of electrolyte to an E-F coagulated structure compressed the electrical double layers (reduces the thickness of diffuse ionic layer) at edges and faces, reduces the electrostatic attraction and thus lowers the yield

stress. The effect of pH changed the stability of card-house type networks is as follows. In strongly acidic medium the network composed of edge/ face contacts broke down as shown in Figure 3a. At alkaline pH produced only a modest increased of viscosity, Face/ face flocculation only occur in presence of salts when the interactions become attractive as shown in Figure 3b.

3.3 Effect of polymer flocculants

When adsorbing polymer (PVA and PAM) were mixed in the suspension of particles, a single chain might become attached to two or more particles. This was unlikely to occur simultaneously, except in concentrated suspensions, but once a chain was attached to one particle, collisions with other particles gave polymer bridging between them. PVA addition showed higher viscosity at pH 4.0 and pH 8.0. In addition of PAM could not measured viscosity because they gave the large flocs and very fast sedimentation. In the case

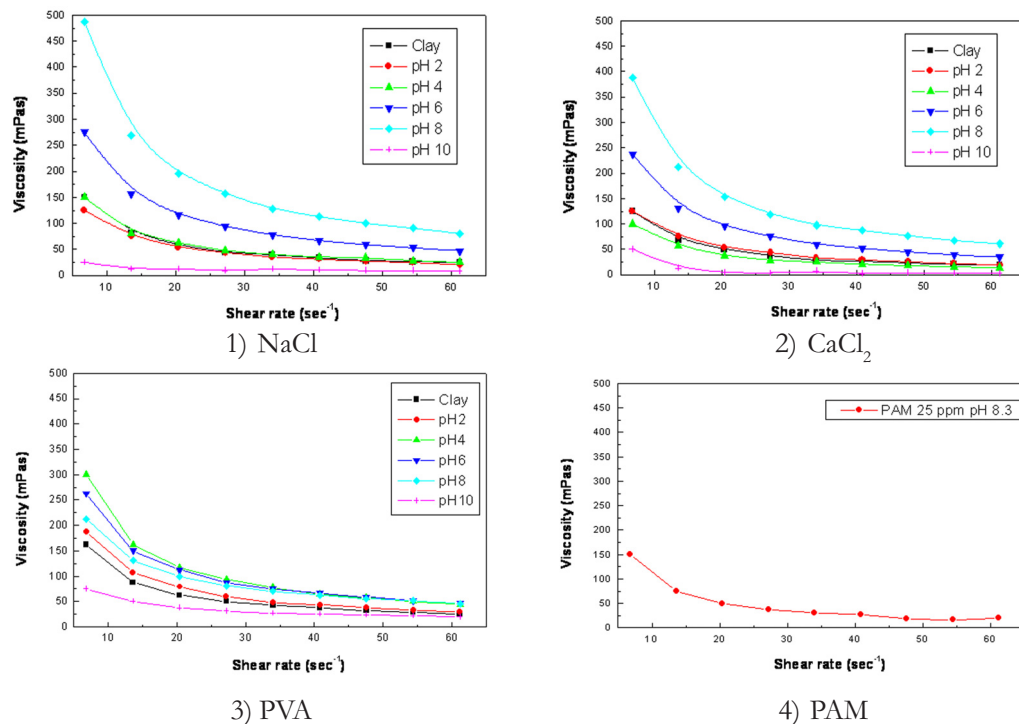


Figure 2. Viscosity of kaolin flocculation as a function of pH and electrolytes [1]

of polyacrylamide, hydrogen bonds can form between the amide groups of PAM and surface hydroxyl groups. It was well established that bridging flocculation gave aggregates (flocs) that are much stronger than those formed when salts are used to

destabilize a suspension. Linkage by polymer chains gave stronger bonds between particles than van der Waals forces. Higher-molecular-weight polymers were more effective flocculants than low-molecular-weight polymers.

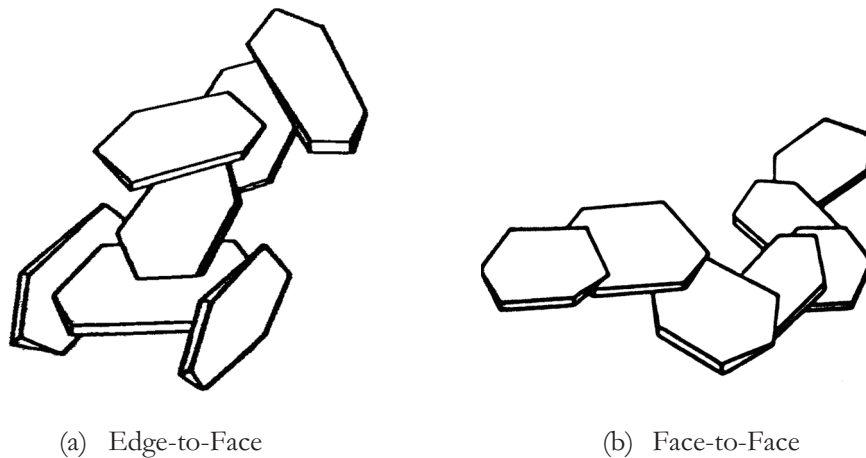


Figure 3. Flocculation of kaolin particles. [3].

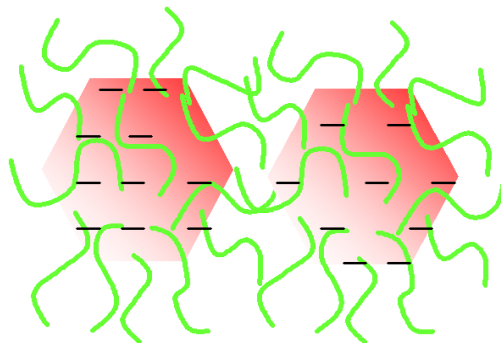


Figure 4. Model of polymer bridging flocculation of kaolin particles.

3.4 Filtration rate

Figure 5 demonstrated the relationship between filtration rate floc size and floc strength (Bingham yield stress) as function of pH at different electrolytes and polymers flocculants. CaCl_2 produced highest filtration

rate. On the other hand, PAM at pH 8.3 generated highest floc size and floc strength. It can be concluded that filtration rate is not clearly rely on floc size and floc strength but also rely on type of flocculants.

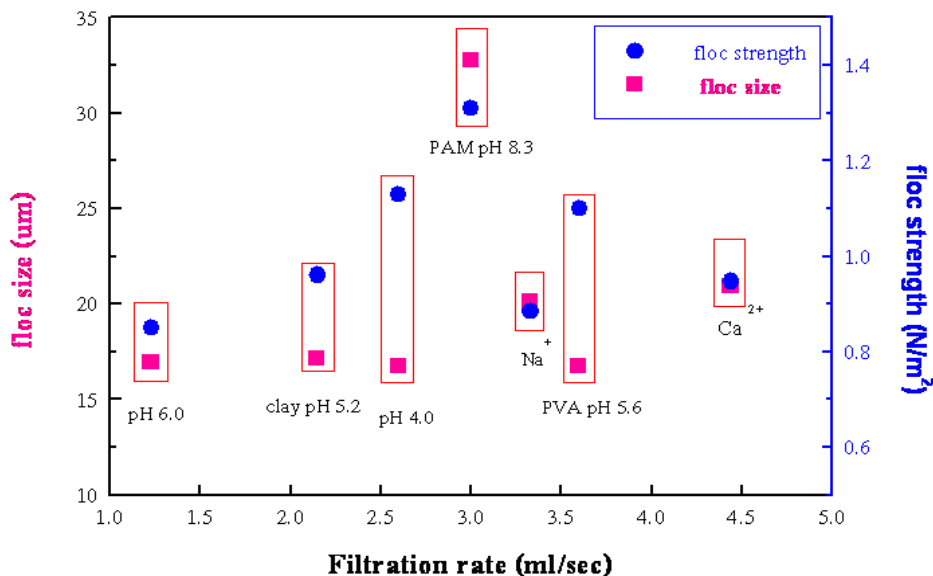


Figure 5. Filtration rate, floc size and floc strength of kaolin flocculation as function of pH at different electrolytes and polymers flocculants.

4. CONCLUSIONS

The flocculation of kaolin depended on pH, electrolytes and polymers flocculants. Floc size and floc strength increased with increasing of cation valency in the electrolytes and increasing of molecular weight in the polymers. Calcium chloride produced highest filtration rate.

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REFERENCES

- [1] Chaiwong N., Improvement of the Properties of Kaolin Slip in the Filter Press Process, M.S. Thesis (Industrial Chemistry), Chiang mai University, Thailand, 2007.
- [2] Besra, L., Sengupta, D. K., Roy, S.K. and Ay, P., Influence of polymer adsorption and conformation on flocculation and dewatering of kaolin suspensions, *Separation and Purification Technology.*, 2003; **37**: 231-246.
- [3] Bohuslav Dobias, Coagulation and Flocculation: Theory and Applications, Surfactant science series, 1993; **47**: 450.
- [4] Reed, J.S., Principle of Ceramics Processing, 2nd Edn., John Wiley & Sons, 1995; 154, 164-168.
- [5] Jianfeng Yu, Dongsheng Wang, Xiaopeng Ge, Mingquan Yan, Min Yang, Flocculation of kaolin particles by two typical polyelectrolytes: A comparative study on the kinetics and floc structures”, Chinese Academy of Sciences, China, 2006.