

A study of dual polymer flocculation

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Abstract

Flocculation of alumina fines with combinations of the anionic form of a polyacrylic acid (PAA) and a high molecular weight cationic copolymer of acrylamide and quaternary acrylate salt (Percol) was investigated. Effects of PAA and Percol molecular weights as well as Percol charge density on the rate of flocculation were also investigated. In order to determine the role of the polymer conformation and changes in it due to the presence of another polymer, the fluorescence label method was employed to monitor PAA conformation at the alumina | water interface under different polymer addition modes, such as the sequential addition of the two polymers vs. co-addition. Importantly, polymer size distribution was found to have a marked effect depending on the polymer type: in the case of PAA, a broader distribution yielded better flocculation; no such effect was observed with Percol. Based on the results, an overall mechanistic picture of dual polymer flocculation is proposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polymer flocculation; Alumina fines; Polyacrylic acid

1. Introduction

Many industrial processes such as papermaking, mineral processing, water treatment, and sludge dewatering involve solid–liquid separation using polymeric flocculants. In many of these applications, use of combinations of oppositely charged polyelectrolytes under suitable conditions enhances the flocculation [1,2]. Although such combinations are increasingly used as flocculants in the industry, a limited amount of mechanistic or molecular level research has been done in the past and as a result, fundamentals of this complex

process are far from being well understood, for example, the influence of polymer molecular weight and polymer conformation on the flocculation process.

It has been known for a while that a pair of oppositely charged polymers can produce synergism in the flocculation of paper pulp [3,4]. Although most studies have been empirical, some fundamental investigations have been performed in the recent years. For example, Yu et al. [1,2] have investigated dual polymer flocculation of alumina particles by studying not only polymer adsorption, solution viscosity and particle zeta potential, but also an important parameter, polymer coiling index, as determined by the fluorescence label technique. Petzold et al. [5,6] studied the effect of charge ratios of the two oppositely

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2.2. Flocculation tests

For each experiment, a 1 g sample of alumina was put in 40 ml of 0.1 M NaCl in a 50 ml beaker and sonicated for 30 s at a power setting of 30 Watts (Lab-Line Ultratip Labsonic System, Lab-Line Instruments). The beaker was fitted with a three-bladed 2.5 cm diameter propeller, 45° pitch, rotating clockwise with pulp flow axially downwards. The desired amount of polymer solution was then added to the suspension with the propeller rotating at 300 rev min⁻¹. One minute after the first polymer was added, the second one was added and stirred for an additional two minutes at the same rpm, and then after the stirring was stopped for one minute, 16 ml of the supernatant from the top was transferred to a turbidimeter (HF Scientific) for turbidity measurements.

2.3. Fluorescence measurements

Fluorescence spectra were recorded on a Photon International PTI-LS 100 spectrophotometer. For solution and solid samples, the fluorescence experiments were conducted in a 1 cm square and 2 mm flat quartz cell respectively. The relative intensities of pyrene emission peaks at 373 nm (monomer) and 475 nm (excimer) obtained with excitation at 335 nm were recorded. The ratio of intensities of excimer to monomer peaks, I_e/I_m , was calculated and termed the coiling index, which reflects the extent of coiling of polymer chains [8,9].

3. Results and discussion

Single polymer flocculation has been well studied in the past. Polymer bridging and charge neutralization are accepted as the two major mechanisms [10]. Bridging flocculation occurs when segments of a polymer chain adsorb on different particles for inducing flocculation and link the solid particles together. In charge neutralization, oppositely charged polymer adsorbs on the particle, reduces the particle charge and destabilizes the suspension. Polymers of high molecular

weight are preferred for polymer bridging, whereas polymers of high charge density are preferred for charge neutralization. In addition to these two mechanisms, a patch model [11] was later developed for systems containing highly charged polymers where the distance between charged groups on the polymer molecule is considerably less than that between charged groups on the particle surface. A mosaic of positive patches on the surface is formed and results in initial patchwise adsorption followed by bridging. In the case of patch neutralization, both polymer molecular weight and charge density are of importance. Compared with single polymer flocculation, flocculation involving dual polymers has received very little attention.

3.1. Enhanced flocculation with dual polymers

The flocculation of alumina suspensions with polyacrylic acid alone is illustrated in Fig. 1 in terms of supernatant turbidity vs. time. Flocculation was enhanced when the concentration of 10k PAA was increased from 1 to 5 ppm, and then decreased upon further addition of PAA. The flocculation is not strong because neither charge neutralization nor bridging is significant with 10k PAA at pH 8. The addition of Percol 757 at 5 ppm dosage causes some flocculation but less than that by the same amount of PAA (Fig. 2), due to negligible interactions between Percol and alumina which are both positively charged. However, when both polymers were added to the suspension, flocculation was found to improve markedly. In addition, it can be seen that sequential addition of the two polymers produces better flocculation than co-addition. This phenomenon will be further discussed later in this paper. For the purpose of discussions, we term the flocs induced by PAA alone ‘primary flocs’, and those formed with two polymers ‘binary flocs’.

3.2. Effect of PAA molecular weight and size distribution

In a set of experiments, PAA was added first and was proposed to serve as the ‘anchor’ for the

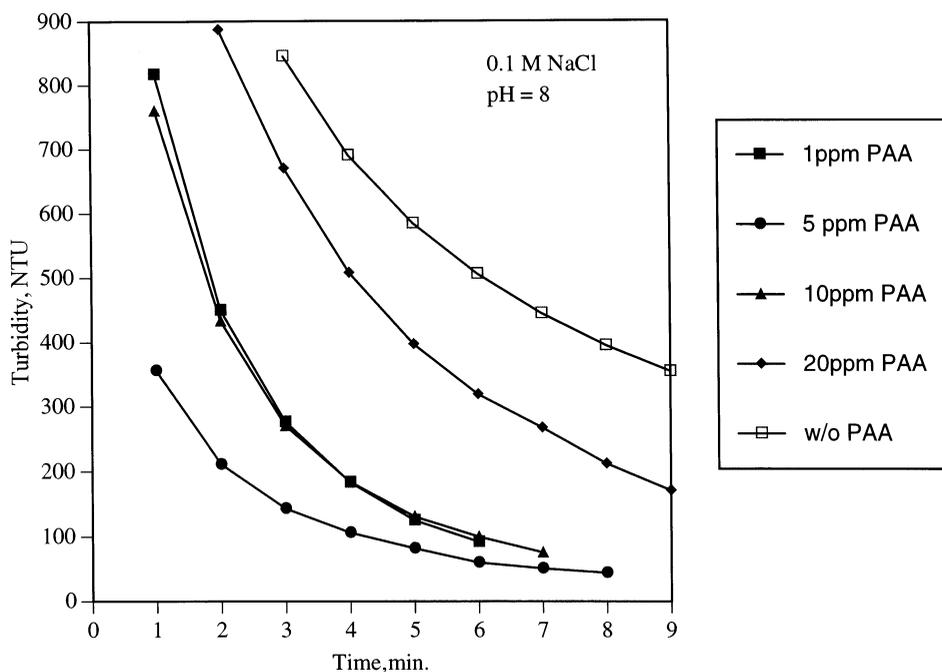


Fig. 1. Diagram illustrating flocculation of alumina fines with polyacrylic acid (PAA) (10k PAA, pH 8, 0.1 M NaCl)

adsorption of the second polymer. The addition of PAA alone produces primary flocs, which grow into binary flocs when the second polymer is added. It can be seen from Fig. 3 that there is a clear effect of the molecular weight of the PAA effect: the higher the PAA molecular weight, the less Percol 757 needed for attaining the maximum flocculation. This indicates that larger PAA molecules produce bigger primary flocs, which requires a smaller amount of the tethering second polymer to form binary flocs. It is concluded that polymer bridging exists in the formation of primary flocs for this system.

Most commercial polymers have wide molecular weight distributions. In order to study the effect of polymer weight distribution, 10 and 90k M.W. PAA molecules were premixed at a 1:1 ratio to obtain a bimodal and broad molecular weight distribution. The flocculation responses obtained are shown in Fig. 4. It can be seen that with the 1:1 mixture of 10k and 90k PAA, the Percol dosage range for good flocculation is wider. Therefore, it is proposed that a wider size distribution of PAA is preferred for flocculation

in the tested molecular weight range. Possibly, a wider distribution of PAA M.W. results in a wider size distribution of primary flocs. The binary floc formation, which probably follows the patch model, i.e. patch adsorption and bridging, is possibly a non-equilibrium process. In single polymer flocculation, such non-equilibrium flocculation has been found to cause entrapment [12,13]; this could also be expected to occur in the binary floc formation.

It has to be noted that while a wider size distribution is preferred for the first polymer added, no effect on flocculation was observed when mixtures with the second polymers of different molecular weights were tested. This effect of polymer size distribution may possess some industrial significance.

3.3. Effect of Percol molecular weight and charge density

As discussed earlier, the patch model fits single polymer flocculation systems containing highly charged polymers. Similarly, the patch model can

be used to explain the formation of binary flocs where a highly charged large polymer is used [14]. For this system, both the dangling chains of PAA and the highly charged Percol ensure the patch adsorption of Percol.

The effect of Percol size and charge density on the flocculation process is shown in Fig. 5. It can be seen that a higher charge density can reduce the polymer dosage required to achieve optimum flocculation. This reduction is approximately proportional to the charge density increase, which implies charge neutralization. A larger molecule can produce bigger flocs and thus better flocculation, which suggests a bridging mechanism for flocculation. The above observations illustrate the importance of both the polymer size and the charge density in forming the secondary flocs, which are in agreement with predictions made using the patch model.

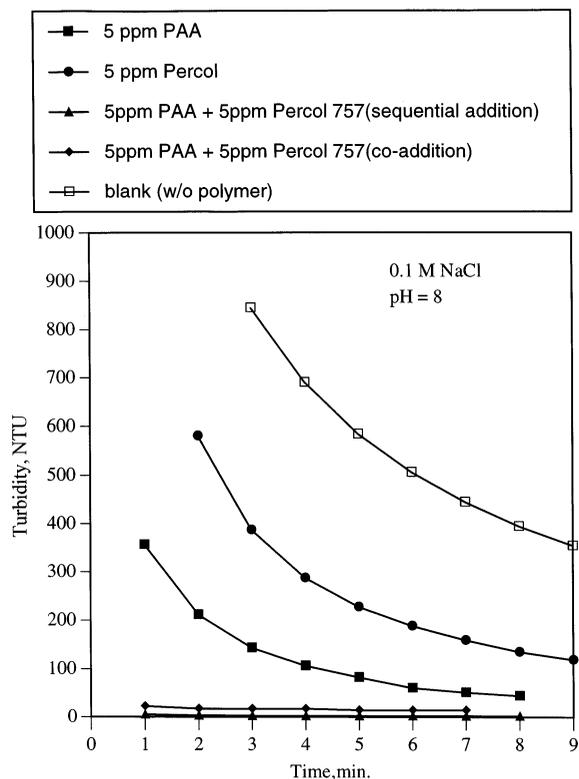


Fig. 2. Enhanced flocculation with dual polymers: flocculation of alumina particles with 10k polyacrylic acid (PAA) alone, Percol 757 alone, and combination of the two polymers under two modes of addition.

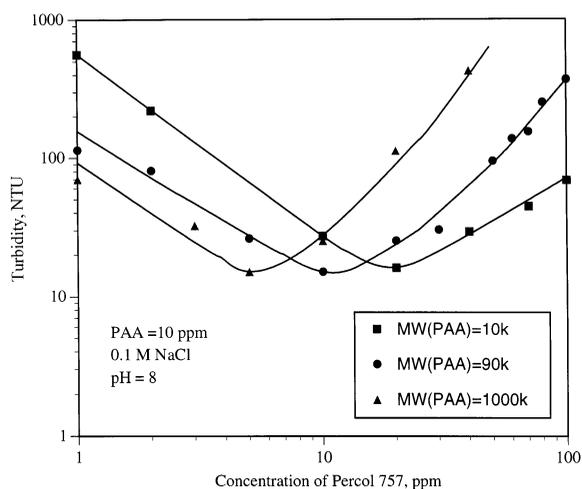


Fig. 3. Effect of molecular weight of polyacrylic acid (PAA) on the flocculation of alumina

3.4. Polymer conformation

Yu et al. [2] employed fluorescence to investigate the conformational change of anionic high molecular weight PAA as a function of the concentration of a lower molecular weight cationic polymer, polydiallyl dimethyl ammonium chloride (PDADMAC). In that case, PAA served as the bridging agent and PDADMAC as the anchoring polymer. The coiling index of the larger polymer, PAA, was found to decrease continuously with an

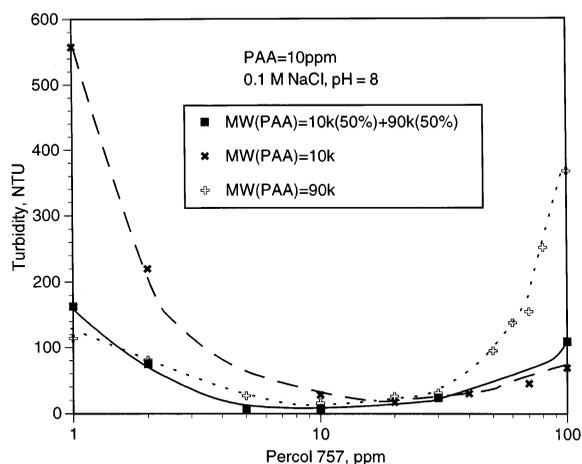


Fig. 4. Effect of polyacrylic acid (PAA) molecular weight distribution on the flocculation of alumina

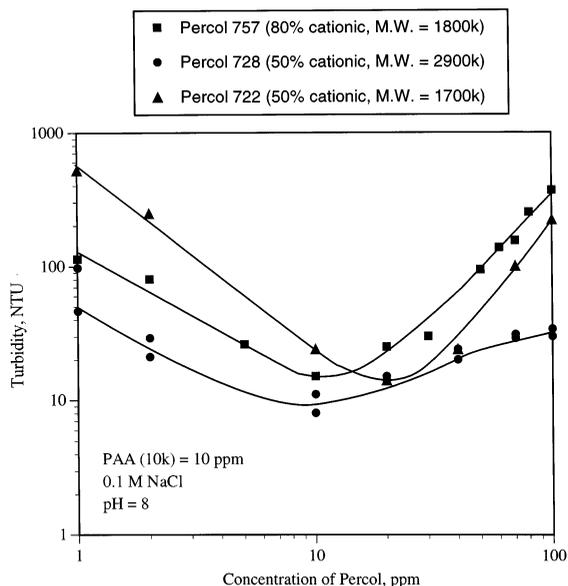


Fig. 5. Effect of Percol molecular weight and charge density on the flocculation of alumina

increase in the concentration of the smaller polymer. In other words, PAA is more stretched when there is more preadsorbed PDADMAC. In the present study, PAA serves as the anchoring polymer and Percol as the bridging polymer. Interestingly, it was found in this study that PAA gets stretched more with an increase in concentration of the second polymer (Fig. 6). In both cases, the conformation of PAA is dramatically changed. It can therefore be concluded that complexation of oppositely charged polymers does take place at the solid|water interface. As the concentration of one polymer increases, the other polymer, no matter whether it plays the role of anchoring or bridging, will become more stretched.

It was seen from Fig. 2 that different flocculation resulted when the polymer addition mode differed. The influence of addition mode is further illustrated in Fig. 7. It can be seen that the whole curve shifted to the left with sequential addition in comparison to the co-addition mode, which means less dosage is required in the former mode. Premixing of PAA and Percol will weaken both the anchoring effect of PAA and the bridging

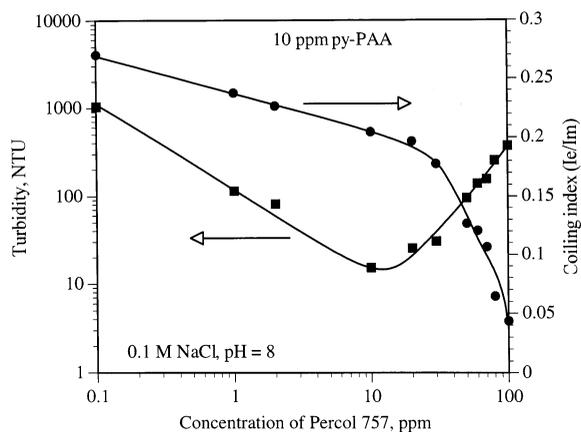


Fig. 6. Polyacrylic acid (PAA) conformational change and flocculation response as a function of Percol concentration

effect of Percol, since the number of anchors is decreased and the bridging chain is coiled before adsorption on the particles. Since polymer conformation does play a critical role in determining the flocculation response, additional polymer conformation study was conducted by comparing the coiling indexes of PAA at the alumina|water interface for two different addition modes (Fig. 8). The conformational change of PAA due to complexation with Percol 757 in the solution phase was also measured and is shown on the same figure for reference.

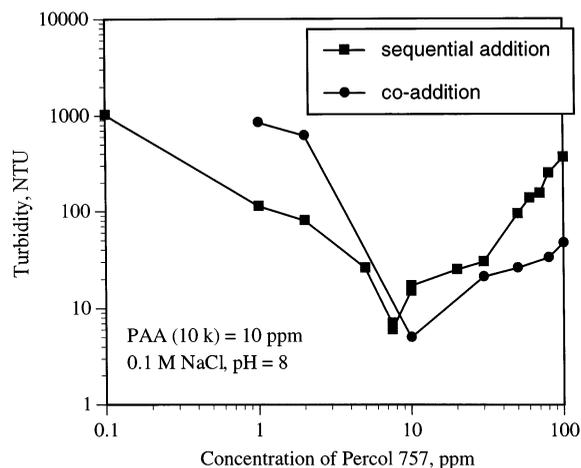


Fig. 7. Flocculation response under different polymer addition modes, sequential addition vs. co-addition.

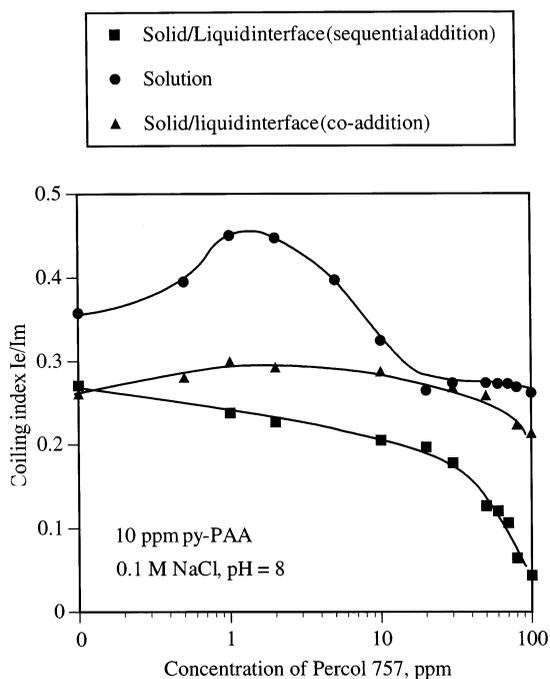


Fig. 8. Polyacrylic acid (PAA) conformational changes due to Percol addition in solution and at the alumina | water interface.

In solution, PAA chains become coiled and then stretched until a constant coiling extent is reached. Coiling with Percol at low dosage is attributed to charge neutralization. With further addition of the cationic polymer, the polymer complex may become positively charged with resultant restretching. It is interesting to note that the stretching reaches a constant value when the Percol concentration is above 20 ppm. This constant value is somewhat lower than that for PAA alone, and can be attributed to the higher charge density of Percol 757 relative to PAA. As expected, the polymer conformation curve for co-addition lies between those for the solution phase and the sequential addition mode at the solid | liquid interface.

With both addition modes, there should be competition between the particle and Percol for PAA due to their electrostatic attraction with PAA. In the case of sequential addition, PAA adsorption on the particle surface takes place first. Percol competes with the surface adsorption sites and becomes dominant at higher concentrations,

which results in increased stretching of PAA. In the co-addition mode, PAA is first complexed with Percol and the surface adsorption sites have only the residual sites on PAA to complex with. With greater amounts of Percol in the complex, the particle surface has less influence so that the co-addition curve is more similar to that of complexation in solution and deviates markedly from the sequential addition curve. It is clear that the conformation and hence flocculation is affected drastically by the environment (free in bulk or bound on the surface) in which the two polymers encounter each other.

4. Conclusions

The results of the investigations reported above may be summarized as follows.

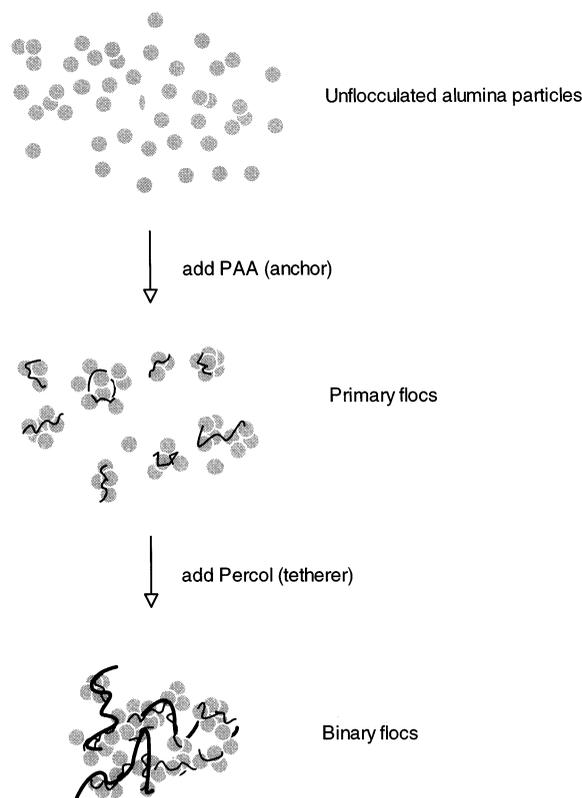


Fig. 9. Schematic representation of the dual polymer flocculation process.

(1) Flocculation can be markedly enhanced by choosing an appropriate pair of oppositely charged polymers (Fig. 9). The polymer that is added first adsorbs on the alumina particles and produces primary flocs. It also serves as anchors for the adsorption of the second polymer. In addition to charge neutralization, bridging contributes to the primary floc formation for the system under study.

(2) Larger PAA is preferred since bigger primary flocs can be formed which will decrease the optimum dosage of the second polymer required. A wider molecular distribution of PAA M.W. can also widen the optimum dosage range of the second polymer and is hence preferred.

(3) With the second polymer, bigger flocs are formed with the larger polymer, and an increase in charge density reduces the optimum polymer dosage. This is explained using a patch model.

(4) Increase in the concentration of one of the two polymers is found to make the other polymer more stretched.

(5) Sequential addition is a better mode than co-addition, i.e. polymer complexation should occur after the adsorption of the first polymer, since the polymer adsorption is essentially irreversible. In this mode, a maximum amount of the second polymer is available for complexation coupled with bridging.

Acknowledgements

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