Asian Journal of Chemistry Vol. 14, No. 1 (2002), 388–394

Investigation of the Effects of Some Operating Parameters by Using Anionic and Cationic Flocculants for Removing Solid Material in the Lignite Wastewaters

M. SARIOĞLU*, Y. CEBECI† and N. BEYAZIT
Faculty of Engg., Department of Environmental Engineering, Cumhuriyet University, 58140, Sivas, Turkey
e-mail: sarioglu@cumhuriyet.edu.tr

In this study, the effects of various operating parameters (pH, stirring rate, flocculant concentration, stirring time, flocculant feeding rate) on flocculation of lignite coal wastes were investigated. Experimental data indicated that the cationic flocculant were affected least by pH changes while anionic flocculant was affected most. Furthermore, it has been determined that there will be considerable increase in the settling rate if the other parameters are controlled well.

Key words: Flocculation, lignite coal wastes, pH, stirring rate, flocculant concentration, stirring time, flocculant feeding rate

INTRODUCTION

In mineral processing, fine particles in both enrichment and obtaining clear liquid lead to significant technical and economical problems.

Especially, in the coal industry, as a result of mechanised production methods and structural faults in the coal seams, fine particle amount increases continuously[1]. Unless fine particle amount in the coal preparation waters is not controlled, the suspended solid amount in recycling waters will increase and this may cause some problems such as change of separation density in the enrichment equipment based on density difference, also deterioration of pulp composition in the froth floatation and similar processes based on the differences of surface properties in the separation of solid particles and excessive reagent consumption due to the high surface area of fine particles. Therefore, fine particles (~ 100 μm) must always be removed from process waters. The studies performed with various coal preparation industry waters point out that total solid in these waters contained 20 to 80% coal by weight[2]. The evaluation of plant effluents is important due to allowing both the production of clean coal with low ash content as a result of increased liberation and less environmental problems in the discharge area. In order to recover fine particles in the plant wastewaters, high molecular weight

†Faculty of Engineering, Department of Mining Engineering, Cumhuriyet University, 58140, Sivas, Turkey.

flocculants are widely used. Flocculants produce aggregation by physically tying particles together. These adsorb simultaneously on different particles by what is postulated by many authors as bridging mechanism[3,4]. As a result of bridging mechanism, settling rates of particles are increased.

The choosing of a flocculant depends on a lot of factors such as the flocculation ability of determined solids, cheapness and ease of usage. Furthermore, it was mentioned that the opinion which was the main process variable of flocculant concentration was inadequate; the factors related to stirring and transport had an important effect on system performance[5].

In this study, in the light of the facts mentioned above, the effects of important operating parameters (pH, stirring rate, stirring time, flocculant concentration and flocculant feeding rates) on floc formation were investigated by using anionic and non-ionic flocculants.

EXPERIMENTAL

Preparation of sample: The coal tailing sample taken from Yozgat-Ayridam Coal Management was used in the experimental studies. According to XRD results of the sample, it was determined that the main mineral matters are kaolinite, pyrite, calcite and quartz. This sample contains 55% ash. All of the samples were ground into ~ 100 μm by using ball mill. The size distribution of the sample is given in Table-1:

TABLE 1
SIZE DISTRIBUTION OF THE SAMPLE

Particle size (μm)	Weight (%)	Cumulative under size passing (%)
–100 +63	12.07	100.00
–63 + 45	16.04	87.93
–45 + 38	17.85	71.89
–38 + 20	28.93	54.04
–20	25.61	25.61

Flocculants and their properties: In the experiments, superfloc type flocculants produced by Cyanamid Company were used. Flocculants were prepared by weight of 0.01% solution. Some properties of flocculants are shown in Table-2.

TABLE 2
SOME PROPERTIES OF FLOCCULANTS

Flocculant	Form	Type	m.w. ($\times 10^6$)
A-150	Powder	Anionic	5–15
C-521	Emulsion	Cationic	2–6

Flocculation Experimental Procedure

A number of 500 mL pyrex graduated cylinders having an inner diameter of 55 mm and a height of about 300 mm at the 500 mL mark (initial settling point) were used for the experiments.

The desired concentration of flocculant was added by means of a syringe to the cylinder containing the sample. After the mixing was completed, the time and the level of slurry-supernatant liquid interface (mud-line) were recorded and subsequently plotted. In the experiment, an adjustable speed magnetic mixer and distilled water were used.

Experimental conditions are as follows:

pH: 2–10, stirring rate: 500–1500 rpm, stirring time: 15–120 sec, feeding rate: 1.50–17.14 mg L^{-1} min^{-1}, flocculant concentration: 0.34–14.29 mg L^{-1}, solid ratio: 2.5% by weight.

RESULTS AND DISCUSSION

In the evaluation of experimental results, the effects of studied parameters on settling (sedimentation) rate were examined. The settling rate was calculated from the slope of the straight line which showed the change of interface height depending on time as pointed out in literature[7].

Effect of pH on Flocculation

As it is known, the stability of particles in suspensions mostly changes depending on pH. For a lot of solids H^+ and OH^- ions are the potential determining ions.[8, 9] The surface charge of particles changes depending on pH of solution. Generally, the surface of a particle in the acidic and alkaline medium carries the positive and negative charge, respectively. Besides ionisation, hydrolysis and the order in the pulp of the flocculants are closely related with pH. The experimental results are shown in Fig. 1.

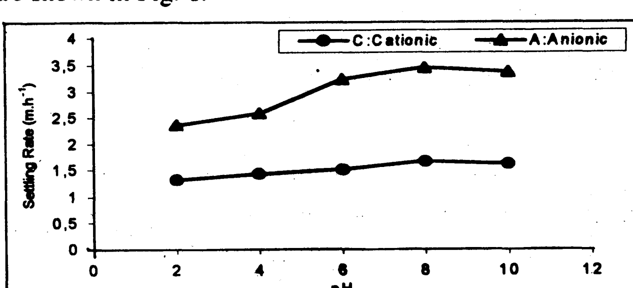

Fig. 1. The changing of settling rate depending on pH (flocculant concentration: 1.50 mg L^{-1}, stirring time: 1 min., stirring rate: 500 rpm)

As shown in Fig. 1, the tendency of the flocculate, both anionic and cationic flocculant, increases after pH 6. This increase is more outstanding with anionic flocculants.

Besides, it was determined that in very low and very high level of pH values, both flocculants did not lose their flocculation properties. The optimum *pH range* in both flocculants was found to be 6–9.

The settling rates with cationic flocculants at low pH values are lower than those at high pH values. This situation can be attributed to adsorption of less amount of particles as a result of the electrostatic repulsion between positively charged particles and flocculant molecules. In addition, high turbidity value (approximately 150 NTU) in acidic medium showed that the tendency to flocculate of cationic flocculant decreases. On the other hand, at high pH values the interaction between negatively charged sites over the particle's surface and positively charged flocculant molecules increases, due to electrostatic attraction. This phenomenon explains the mechanism of interaction "charge-patch"[2, 10]. It is shown that at low pH values, the settling rate decreases; as the pH increases, it increases with anionic flocculant.

The low settling rate with anionic flocculant in acidic medium shows that except for electrostatic attraction forces, the other forces are more effective on the interaction between negatively charged flocculant molecules and positively charged particle surfaces. In this case, it can be stated that the hydrogen bonding is effective between the polar groups of flocculant and the particle surfaces.

Moreover, at low pH values, due to decrease in ionisation of flocculants, shortening of flocculant length resulted in ringed structure in the solution. As a result of this effect, flocculant molecules adsorbed on less amount of particles. Therefore, small-sized flocs occurred and the settling rates decreased. As it is known, the particle surface charge can be changed with the adsorption of cations or hydroxy complex of cations dissolved from mineral matters in the solution. In alkaline medium (pH 8–10), the increase in settling rate can be attributed to both the hydrogen bonding between the polar parts of flocculant molecules and particle surface and the electrostatic attraction forces between negatively flocculant molecules and positively charged mineral sites.

Effect of Stirring Rate

In the pulp, the flocculation of particles and growth of flocs depend on collision of particles and/or flocs. In addition, a good flocculation depends upon the homogenous distribution and order of flocculants and the proper interaction between the flocculants and particles in the pulp. The above mentioned situations are changed depending on stirring degree of pulp. It was stated that vigorous stirring leads to high collision frequency and as a result of this effect the flocs grow very rapidly[5]. However, as known, very strong stirring causes the breaking of flocs (especially of large-sized flocs) because of shear force. Therefore, the optimum stirring rate at which floc size reaches a maximum is determined very well. Fig. 2 shows the change of settling rate depending on the stirring rate.

As shown in Fig. 2, for both the flocculants the high settling rates were obtained at 500 rpm. In the high stirring rates, the settling rates decreased as a result of the partial breaking of flocs.

Effect of stirring time: High settling rate is obtained with large floc size. In order to obtain large floc sizes, it is necessary to combine both the individual particles into large or small flocs and the small flocs with each other or with large flocs. The situations mentioned above are greatly related to the sufficient homogeneous distribution of flocculants in the pulp. Therefore, adequate time must be given for the homogenous distribution of flocculants and for the collision of both particle/floc and floc/floc. The effect of stirring time is shown in Fig. 3.

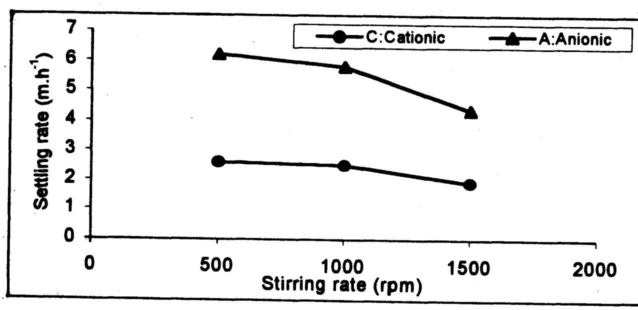

Fig. 2. The changing of settling rate depending on stirring rate (pH of pulp: 8, flocculant concentration: 1.50 mg L^{-1}, stirring time: 1 min)

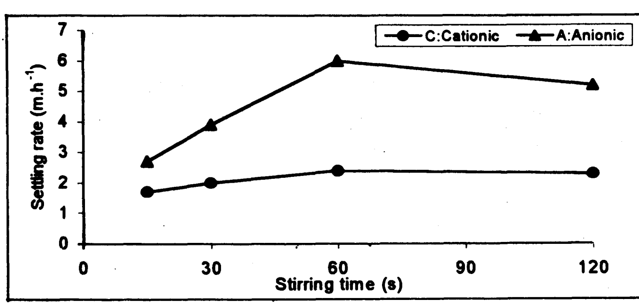

Fig. 3. The changing of settling rate depending on stirring time (pH of pulp: 8, stirring speed: 500 rpm, flocculant concentration: 1.50 mg L^{-1})

At low stirring time, since the interactions mentioned above are insufficient, settling rate is low. At high stirring time also, the settling rate is low due to the partial breakage of flocs. Therefore, for both flocculants the optimum stirring time is found to be 60 sec.

Effect of flocculation concentration: In order to determine the effect of flocculant concentration in the practice, the anionic flocculants are widely used. Therefore, the effects of flocculant concentration and flocculant feeding rate are investigated by using anionic flocculant.

As can be seen in Fig. 4, at low concentrations the settling rate is low. When the flocculant concentration is increased, the settling rate increases as parabolic up to about 6 mg L^{-1} of flocculant concentration. After about 6 mg L^{-1} the increase of settling rate becomes slower. At very low concentrations, the floc sizes are small due to insufficient flocculant bridging among the particles. As the flocculant concentration is increased, large-sized flocs occur as a resnlt of adsorption of more amount of particles. After about 6 mg L^{-1} flocculant concentration, no

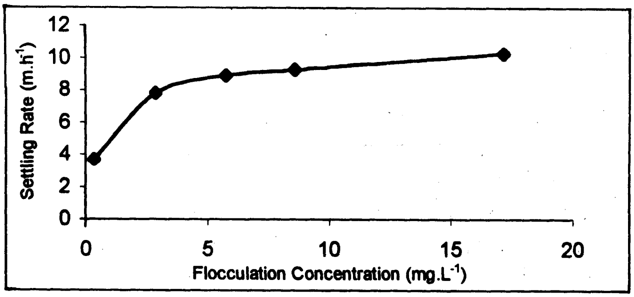

Fig. 4. Effect of flocculant concentration on the settling rate (pH of pulp: 8, stirring rate: 500 rpm, stirring time: 1 min)

considerably change of settling rate is seen. To a large extent, this situation is attributed to the adsorption of excessive amount of flocculant molecules on the flocs formed before.

Besides, at high concentration of flocculant, it is also seen that the increase of settling rate slows down as a result of insufficient distribution of flocculant and the change of order of flocculants in the pulp.

The effect of flocculant feeding amount: As shown in Fig. 5, the settling rate increases up to 8 mg L^{-1} min^{-1} of flocculant feeding rate. In the experiments, the total amount of flocculant in the pulp is constant, only the flocculant feeding

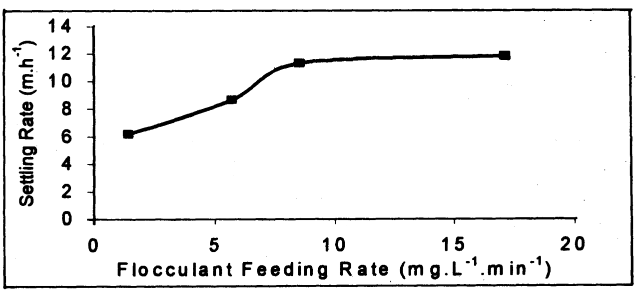

Fig. 5. Effect of feeding rate on the settling rate (pH of pulp: 8, stirring rate: 500 rpm, stirring time: 1 min.)

rate is changed. At low flocculant feeding rate, the addition time of the same amount of flocculant into the pulp is increased. Therefore, the stirring time of pulp also increases. At low feeding rate, the decreasing of the settling rate is due to the breaking of flocs in the longer stirring time. As the flocculant feeding rate is increased, the settling rate also increases. This is due to both the decreasing of total stirring time and the increasing of flocculant concentration. In this case, larger sized flocs are formed because of adsorption of flocculant molecules on a greater amount of particles.

After about 8 mg L^{-1} min^{-1} of feeding rate, there is no considerable change of settling rate. This situation can be attributed to the adsorption of added flocculants on the flocs formed before. Therefore, the optimum flocculant feeding rate is found to be 8 mg L^{-1} min^{-1}.

Conclusions

In this study, the following conclusions were found:

- The optimum pH value was found to be 8 in order to recover the fine particles in the wastewaters. In general, the settling rate determined is higher in the basic environment than in an acidic one.
- Optimum stirring rate and stirring time were determined at 500 rpm and 1 min respectively. Since the higher stirring rate and the longer time than those of optimum values resulted in floc breaking, the settling rate was partly decreased.
- However, it was observed that no remarkable change in the settling rate was obtained depending on both the flocculant concentration and flocculant feeding rate after flocculant concentration of 5.71 mg L^{-1} and flocculant feeding rate of 8 mg L^{-1} min^{-1}. No doubt, these determined optimum values may considerably change depending on solid concentration in the pulp.
- Moreover, optimising other operation parameters such as solid ratio, flocculant feeding place, the concentration of flocculant solution, studies related to recovery of fine particles in the effluent of plants must be done in all coal preparation industries currently.

REFERENCES

1. S. Kim and G. Morsi, Effect of Grinding Conditions on the Performance of a Selective Agglomeration Process for Physical Coal Cleaning, Coal Preparation (1991).
2. R. Hogg, Flocculation Problems in the Coal Industry, Fine Particle Processing, Vol. 2, p. 990 (1980).
3. P. Somasundaran, Principles of Flocculation, Dispersion and Selective Flocculation, in Fine Particles Processing, AIME, Vol. 2, Chapter 48, p. 947 (1980).
4. H.A. Hamza, A.W. Mo and R. Frenette, Chemical Reagents for Mechanical Dewatering, Industrial Practice of Fine Coal Processing, Colorado, USA, p. 231 (1988).
5. ———, Processes Design for Flocculation, Clarification and Thickening of Fine-Particle Suspensions, XVIII International Mineral Processing Congress, Sydney, 23-28 May 1993, Vol. 5, p. 1315,
6. Mining Chemicals Handbook, Mineral Dressing Notes, No. 26, American Cyanamid Company, USA (1986).
7. B.A. Wills, Mineral Processing Technology: Dewatering, 4th Edn., Pergamon Press, New York, Chapter 15, p. 645 (1988).
8. J. Leja, Surface Chemistry for Froth Floatation, Plenum Press, New York, p. 479 (1982).
9. Metcalf and Eddy, Wastewater Engineering: Treatment, Disposal and Reuse, McGraw-Hill, Chapter 6, p. 220 (1991).
10. R.R. Klimpel, Introduction to Chemicals Used in Particle Systems, ERC Particle Science and Technology, p. 5 (1997).

(*Received*: 5 September 2001; *Accepted*: 5 November 2001) AJC-2508