Development of Silica Based Microgels and Evaluation of Their Performance in Microparticle Retention System

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ABSTRACT

The effectiveness of silica-based microgels prepared through the reaction of sulfuric acid and sodium silicate solutions as a component of Compozil system has been evaluated. Silica-based microgels with better performance in retention and drainage than a commercial colloidal silica sol have been successfully prepared.

Silica gels with the highest charge density were obtained when product pH was controlled to 9. And highly charged silica-based microgels showed greater retention and freeness performance than a commercial product. In particular the difference in retention, turbidity, and freeness between these microgels and a commercial product was eminent at low addition rate. The effects of reaction conditions including reaction temperature, process water quality and feeding rate on product efficiency in improving retention and drainage were also investigated and discussed.

1. Introduction

Paper industry has made diverse efforts during last several decades to reduce manufacturing cost and to improve productivity and quality. Web forming is one of the most critical processes in achieving these objectives since retention, dewatering and fiber flocculation at the forming part of a paper machine are directly associated with the process economy, productivity and product quality.

Different microparticle retention systems including Compozil, Hydrocol and Compamzil systems have been used in many paper mills to obtain a wide range of advantages in retention, dewatering, formation and/or strength.[1-6] These microparticle retention systems, however, are relatively expensive to use. For instance Compozil system requires anionic colloidal silica as a component which is available only at a very low solids content, and this imposes a cost burden of freight and storage to the paper industry.

It is worthwhile, therefore, to examine the possibility of producing silica-based microgels with improved performance through the reaction of sulfuric acid and sodium silica solution. In this study, silica-based microgels were prepared and their effectiveness was evaluated and compared with that of a conventional silica sol.

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2. Materials and Methods

2.1 Materials

Softwood and hardwood bleached kraft pulps and talc were used in this experiment. Crosslinked cationic corn starch with the degree of substitution of 0.05 was used as a cationic polymer for Compozil retention system. Sulfuric acid and 37% sodium silicate solution with SiO_2/Na_2O ratio of 2.11:1 were used to prepare silica microgels.[8] A commercial product of structured colloidal silica with charge density of 1.883 meq/g was used as a reference material.

Hardness and conductivity of water were controlled by adding of calcium chloride and sodium chloride. Poly-diallyldimethylammoniumchloride and sodium polyethylenesulphate were used as standard polyelectrolytes for measuring the charge density.

2.2 Methods

2.2.1 Stock preparation

Softwood and hardwood bleached kraft pulps were beaten separately to 450±10 mL CSF and mixed to obtain blended pulp furnish containing 80% of hardwood and 20% of softwood bleached kraft pulp. Part of the mixed stock were dried in a drying oven at 105℃ for 12 hours and mixed back to the blended stock. This was carried out to simulate the addition of dry broke. Blending ratio of the dried pulp was maintained constant at 10%. After blending the dried pulp, the whole stock was beaten again to 450±10 mL CSF and diluted to 0.5%. Fines content and water retention value of this stock were 23% and 1.91 g/g, respectively. Twenty percent of talc based on the dry weight of fiber was added to this stock as filler.

To see the effects of silica microgels on retention and drainage, the amount of cationic starch was adjusted constant at 1.0%.

2.2.2 Preparation of the silica-based microgel

Silica-based microgels were prepared by reacting sulfuric acid with sodium silicate. An auto titrator and a hot plate were used to control the sulfuric acid addition rate and reaction temperature, respectively (Fig. 1).
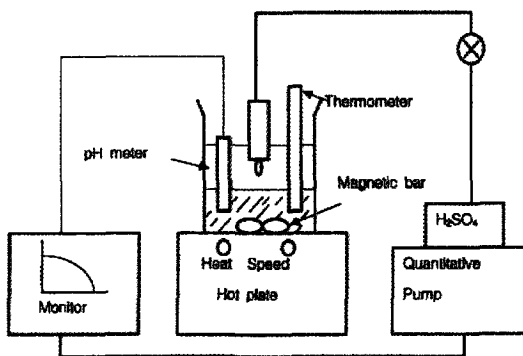

Fig. 1. Schematic drawing of the silica-based microgel preparation reactor.

The change of pH was monitored continuously, and when pH reached a set value the feeding pump of sulfuric acid was stopped. An example of the titration curve is shown in Fig. 2.

Diverse variables including the concentration of SiO_2 and H_2SO_4, product pH, aging time after complete addition of sulfuric acid, water quality, reaction temperature, and H_2SO_4 addition rate were taken into account in the preparation of silica microgels. The experimental details were shown in Fig. 3.

Turbidity and absorbance of silica gels were determined using DR/2000. FTU turbidity measurement was carried out at 450 nm. On the other hand the measurement of absorbance was performed at 400 nm.

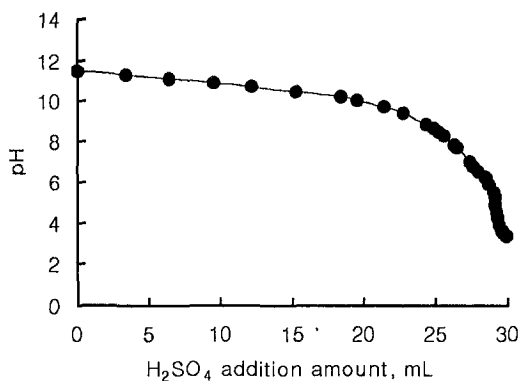## 2.2.3 The measurement of fines retention and freeness

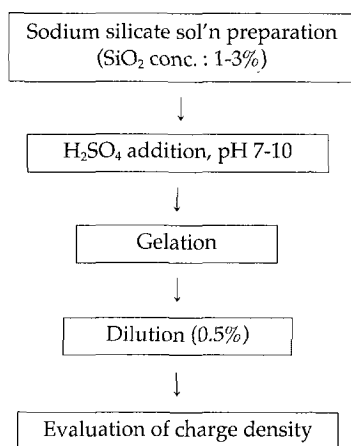**Fig. 2. Titration curve of 2% sodium silicate solution with 2 N sulfuric acid.**

Fig. 3. Flowchart for the preparation of silica-based microgels.

Same procedures described in reference (9) were followed to measure fines retention and freeness.

3. Results and Discussion

3.1 Charge density

Silica-based microgels were prepared by reacting sulfuric acid and sodium silicate solutions. Diverse microgels were prepared by reacting sulfuric acid and SiO_2 solutions at different concentrations to different product pH values. Clear or turbid silica gels were obtained depending on the reaction conditions employed. Generally as the concentration of sodium silicate or sulfuric acid increased, more turbid silica gels were obtained. In some cases coagulated silica gel particles large enough to observe with naked eyes were formed. When these coagulated silica gels were kept without stirring complete gellation occurred. These gels showed lower anionic charge density than stable gels.

When the concentrations of sulfuric acid and sodium silicate were greater than 3 N and 4%, respectively, severe gellation of silica particles occurred. Thus, in this study the concentration of sulfuric acid and sodium silicate were maintained lower than 3 N and 3%, respectively. The effect of the feeding rate of sulfuric acid was examined as well, and no significant variation of charge density arose when the feeding rate was adjusted between 0.01 mL/s - 0.03 mL/s. At higher feeding rate, however, silica gels with low
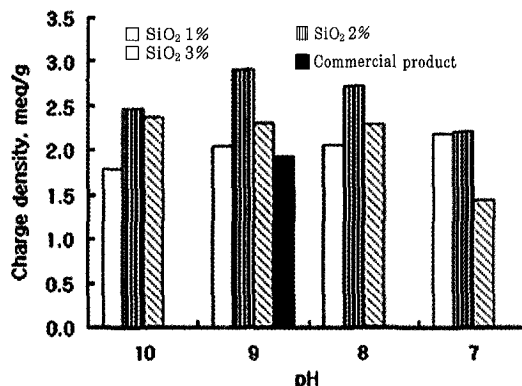

Fig. 4(a). Effects of SiO_2 and sulfuric acid concentration on the charge density of silica microgels (1 N H_2SO_4).
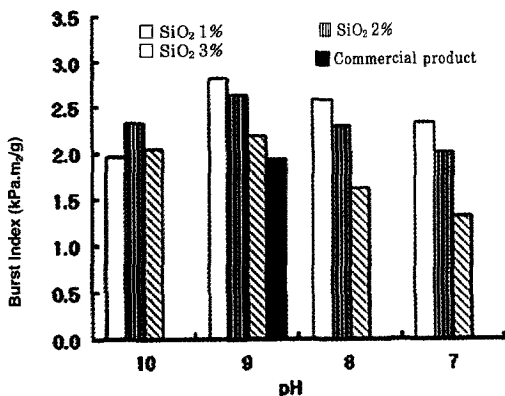
Fig. 4(b). Effects of SiO₂ and sulfuric acid concentration on the charge density of silica microgels (2 N H₂SO₄).
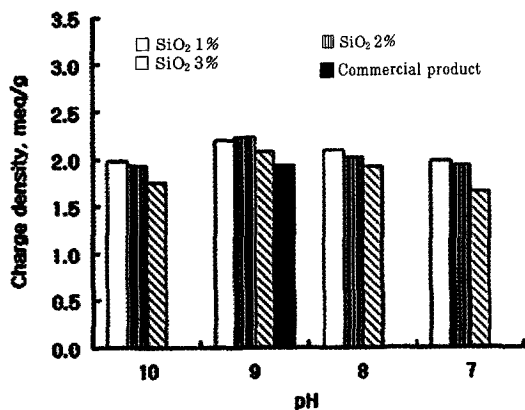

Fig. 4(c). Effects of SiO₂ and sulfuric acid concentration on the charge density of silica microgels (3 N H₂SO₄).

charge density were formed. Therefore, the feeding rate of 0.03 mL/s was employed for reaction in this study. The final concentration of silica gels was adjusted to 0.5%. At this concentration, the prepared silica gels could be stored for 24 hours without any turbidity change.

Charge density of the prepared silica gels was determined using particle charge detector (PCD) and depicted in Figs. 4(a)-4(c). As seen in these figures the microgels prepared by reacting sulfuric acid and sodium silicate

solutions showed greater charge density than the reference product which is commercially used. Highly charged silica gels were obtained when product pH was controlled to 9. The fact that the charge density of silica gels decreased at pH below 9 indicates silanol groups changed into non-ionized form at a pH lower than 9.

3.2 Fines retention, freeness and turbidity

Two microgels with high surface charge were selected among those shown in Figs. 4(a)-4(c) and their effectiveness on retention and drainage were tested. These two silica gels were name Gel-1 and Gel-2. Gel-1 was the silica gel prepared by reacting 2% sodium silicate solution with 1 N sulfuric acid to the final pH of 9, and Gel-2 was one obtained by reacting 2% sodium silicate solution with 2 N sulfuric acid to the final pH of 9. Charge density of Gel-1 and Gel-2 were 2.92 meq/g and 2.65 meq/g, respectively.

Effect of Gel-1 and Gel-2, when they were used as a component in Compozil system along with 1.0% of cationic corn starch, on fines retention, freeness and turbidity was examined. In testing the retention, freeness and turbidity, the conductivity and calcium hardness of the stock were adjusted to 1000 μS/cm and 100 ppm, respectively.

As shown in Figs. 5-7, Gel-1 and Gel-2 showed better retention and freeness performance than the commercial product. Difference in retention, turbidity, and freeness for those two microgels and the commercial product was eminent at a low addition rate probably because the charge density of prepared microgels were higher than that of the commercial product.

These results clearly showed that it would be possible to prepare colloidal silica gels

that are highly effective in retention and drainage. It would be needed to investigate the impact of diverse process variables on the performance of silica gels to optimize the process.
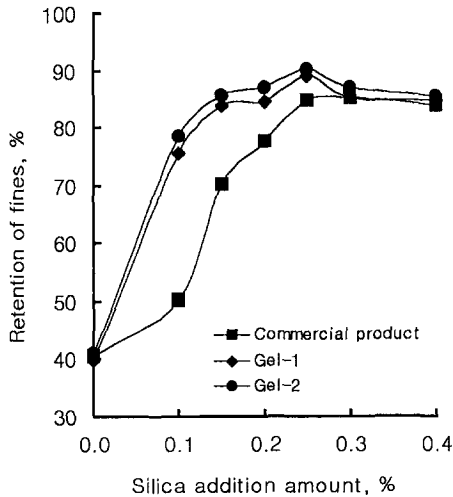

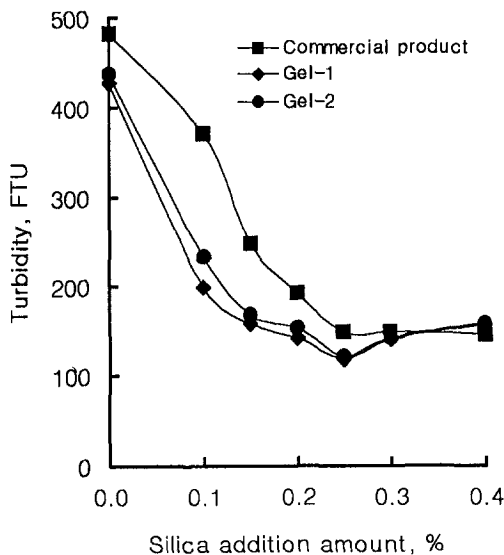**Fig. 5. Effect of the type of colloidal silica on fines retention.**

Fig. 6. Effect of the type of colloidal silica on turbidity.

3.3 The effects of reaction conditions

The influence of diverse process variables

including aging time, sulfuric acid addition rate, reaction temperature, etc. on the performance of the on-site prepared silica gels was examined.
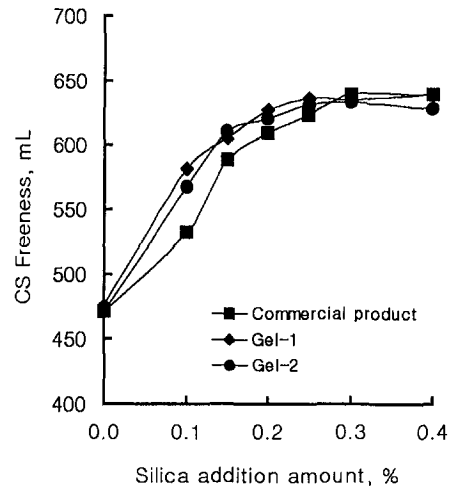

Fig. 7. Effect of the type of colloidal silica on freeness.

3.3.1 Aging time

To examine the effect of aging time on the performance of silica based microgels, retention and drainage characteristics were tested using a microgel sample aged for 0-100 minutes. Table 1 illustrated the turbidity and absorbance of the prepared microgel. It could be seen that turbidity and absorbance increased with aging time. When the microgel was aged more than 26 minutes, gel particles adhered on the reactor wall could be observed and the charge density of the gels decreased substantially.

The effect of aging times of silica microgels on fines retention and freeness when microgel was applied as a component of Compozil system is depicted in Fig. 8. As seen here, freeness and retention decreased continuously with the increase of the aging time. When it was aged for 100 minutes, retention and drainage approached the values obtained when only cationic starch

without silica micro particles was used as a retention aid.

Moffett[8] reported that 5% of maximum performance and maximum efficiency were obtained after five minutes and one hour of aging, respectively, then the efficiency of silica gel decreased afterward. This is quite different from the result obtained in this study. This difference is understandable when considering the microgel was prepared by a batch type reaction in this study. Since sulfuric acid was added at constant rate into sodium silicate solution, the reaction has already proceeded substantially when the addition of sulfuric acid was completed. In this study, this moment was considered as a starting point of aging. In other words, in the case of batch type reaction the time elapsed for adding sulfuric acid into sodium silicate solution should be considered in comparing the effect of the aging time.

3.3.2 Sulfuric acid addition rate

The effect of sulfuric acid addition rate on fines retention and freeness was shown in Fig. 9. As shown here, retention and freeness decreased with increasing the addition rate of sulfuric acid. Moreover, gel particles were formed on the reactor wall during aging when 0.5 mL/2s of addition rate was employed. Table 2 showed the turbidity and

Table 1. Turbidity and absorbance changes of the silica microgels as a function of aging time

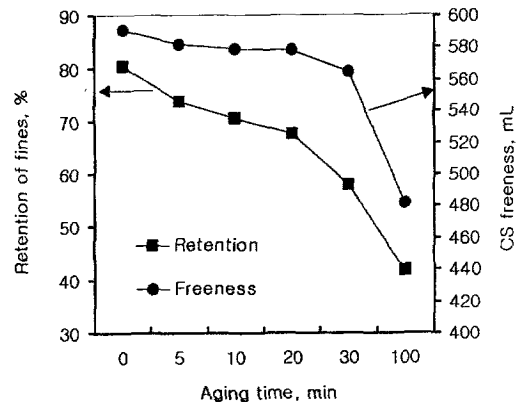| Aging time, min	Turbidity	Absorbance
0	0	0.004
5	2	0.012
10	4	0.028
20	9	0.050
30	10	0.052
100	33	0.156

Fig. 8. Effects of aging time on fines retention and freeness

absorbance of the prepared microgel as a function of the sulfuric acid addition rate. These results indicated that slow rate addition of sulfuric acid gave better mixing and promoted more homogeneous formation of silica particles.

Table 2. Turbidity and absorbance changes of the silica microgels as a function of H_2SO_4 addition rate

Addition rate, mL/2s	Turbidity	Absorbance
0.06	2	0.006
0.1	3	0.019
0.2	6	0.035
0.5	20	0.106

3.3.3 Reaction temperature

Retention and drainage characteristics obtained when colloidal silicas prepared at different reaction temperatures were used as a component of Compzil retention system are depicted in Fig. 10. As seen in Fig. 10, no significant changes in fines retention were observed at temperatures below 50℃. Fines retention reduced greatly, however, when reaction temperature were increased to 60 ℃. In the case of freeness, maximum effect
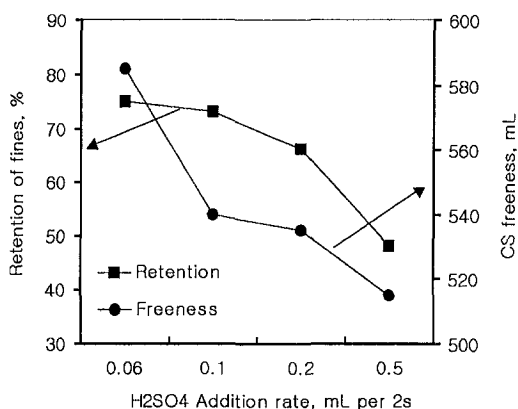
was obtained when microgel prepared at 30 ℃ was used.

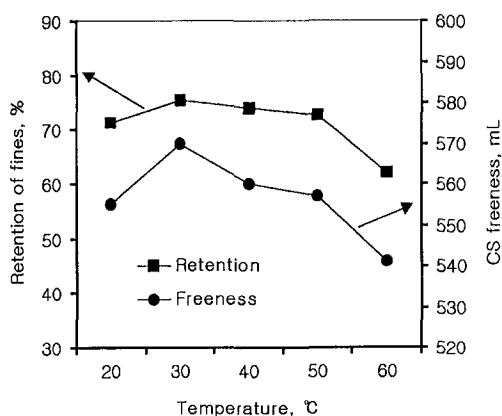**Fig. 9. Effects of sulfuric acid addition rate on fines retention and freeness.**

Fig. 10. Effects of reaction temperature on fines retention and freeness.

3.3.4 Water quality

Silica-based microgels were prepared using water containing different amounts of calcium hardness ranging from 25-100 ppm. Generally sodium silicate solution forms complex with multivalent metal ions. The turbidity of sodium silicate solution increased as calcium concentration increased. The difference of charge density of microgels prepared with different hard-

ness levels of process water was negligible. Freeness and fines retention, however, decreased with the increase of hardness as shown in Fig. 11. This showed the importance of using pure process water in preparing silica microgels.

To examine whether any difference in silica gel properties derives depending upon the types of cations present in process water, silica gels were prepared in process water containing different amounts of sodium or calcium chlorides. When sodium chloride was used to adjust the conductivity the turbidity of sodium silicate solution maintained constant at 0 or 1 FTU turbidity irrespective to the conductivity. On the other hand, the turbidity decreased substan-
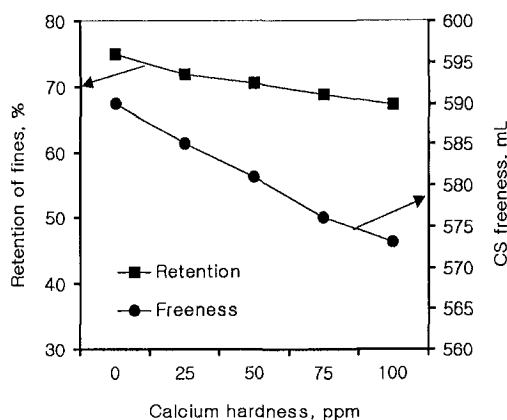

Fig. 11. Effects of calcium ions on fines retention and freeness.

Table 3. Turbidity and absorbance changes of the silica microgels as a function of water quality

Conductivity, μS/cm (Calcium hardness, ppm)	Turbidity		Absorbance	
	Ca^{2+}	Na^+	Ca^{2+}	Na^+
tap water	2	2	0.006	0.006
154(25)	2	2	0.017	0.009
316(50)	3	2	0.022	0.011
470(75)	6	2	0.034	0.012
630(100)	16	2	0.081	0.010

tially when the conductivity of sodium silicate solution was increased using calcium chloride solution.

The turbidity and absorbance of prepared microgels remained rather constant irrespective to conductivity when sodium ions were present as counter ions (Table 3). In this case the charge density of micro gels remained almost constant as well. As shown in Table 3, presence of multivalent calcium ions was harmful in preparing stable micro silica gels. This indicated the removal of multivalent metal cations is crucial for the preparation of stable silica-based microgels.

4. Conclusions

In this study silica-based microgels were prepared to examine the possibility for substituting imported colloidal silicas, and their effectiveness as a component of Compozil system was investigated. Silica-based microgels with better performance in retention and drainage than a commercial colloidal silica have been successfully prepared through a reaction of sulfuric acid and sodi-

um silicate solutions. And it was found that process water quality, solution concentration, product pH, etc should be properly controlled to get the most effective silica gels.

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