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Influence of Crosslinked Cationic Starches and Silica Microgels on the Performance of Microparticle Retention System

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ABSTRACT

Effectiveness of the microparticle retention systems in improving drainage, retention, formation has been recognized for many years. In this study the effectiveness of crosslinked cationic corn starches and silica-based microgels as components of Compozil system has been evaluated. It was shown that improvements in retention and strength could be achieved by employing crosslinked cationic corn starches especially at high conductivity. Silica-based microgels with better performance in retention and drainage than a commercial colloidal silica sol have been made through a reaction of sulfuric acid and sodium silicate solutions.

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 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, which imposes a cost burden of freight and storage to paper industry. The other component required for Compozil system, i.e., a cationic starch, is also critical for its performance. Raw materials for cationic starches differ depending on the region. In Europe potato is the predominant raw material for cationic starches while in North America and Asia corn is most widely employed (7). The types of raw materials affect the quality of cationic starch. Cationic starches made from potato are superior to corn-based ones since they are high in molecular weights and amphoteric in nature (5,7). It is required, therefore, to find a modification method of corn starches that provides the level of performance of potato starches (8).

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In this study the performance of crosslinked cationic corn starches and anionic silica microgels prepared on-site as components of Compozil system were investigated.

2. Experimental

2-1 Materials

Softwood and hardwood bleached kraft pulps and talc were used in this study. Two types of potato starches with nitrogen contents of 0.45 % and 0.60 % and four different corn starches with the degrees of substitution (DS) of 0.03, 0.05, 0.08 and 0.1 were kindly supplied by Samyang Genex Co. Crosslinking treatment of the corn starches with DS of 0.05 and 0.08 was carried out to increase molecular weights. As shown in Table 1, average particle size of the potato starches was about twice larger than that of corn starches. The particle size of corn starches decreased as crosslinking proceeded indicating the swellability of corn granules was decreased by this crosslinking treatment (7). The cationic starches at a concentration of 1 % were cooked in a waterbath at a temperature of 95 ℃ for 25 minutes and diluted to 0.5 %. Fresh cooked starch solutions were prepared every day for the experiments.

Brookfield viscosity of the potato starch was greater than that of corn starch as seen in Table 1. This suggests that the molecular weights of potato starches are still higher than those of crosslinked corn starches. Brookfield viscosity of the crosslinked cationic corn starch ranged from 4.3-5.5 cPs and it increased as the level of crosslinking increased. On the other hand the charge density of cationic corn starches decreased with crosslinking indicating crosslinking imparts three dimensional network-like structure to starch molecules which prevents the charged groups inside the molecular structure from reacting with poly-DADMAC, the titrant used to measure the charge density.

Sulfuric acid and 37 % sodium silicate solution with SiO_2/Na_2O ratio of 2.11:1 were used to prepare silica microgels (4,9). A commercial product of structured colloidal silica with charge density of 1.883 meq/g was used as a reference material.

Table 1. Properties of cationic starches

			Charge density (meq/g)	Viscosity cPs, 28℃	Particle size(㎛)
Potato	N 0.45% (DS 0.055)		---	80	51.51
	N 0.60% (DS 0.074)		---	153	63.62
Corn	DS 0.03		0.370	---	---
	DS 0.05	Untreated	0.884	5.5	27.10
		Corn 490	0.834	11.5	22.19
		Corn 620	0.802	20	21.01
	DS 0.08	Untreated	0.905	5	26.42
		Corn 600	0.812	22.5	25.02
		Corn 800	0.734	17.4	20.93
		Corn 1380	0.832	41	21.31
	DS 0.1		0.998	4.3	---

2.2 Experimental Methods

2.2.1 Stock preparation

Softwood and hardwood bleached kraft pulps were beaten separately to 450°±10 mL CSF and mixed at a ratio of 8:2. Part of the mixed stock were dried in a drying oven at 105℃ for 12 hours and blended with the mixed stock. The blending ratio of the dried pulp was 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 the stock were 23 % and 1.91g/g, respectively. 20 % of talc was used as filler.

Calcium hardness and conductivity of the stock prepared with tap water were 56ppm and 460 $\mu S/cm$, respectively. When investigating the influence of stock conductivity, the hardness level was adjusted to 100ppm with calcium chloride then stock conductivity was adjusted to either 2000 or 4000 $\mu S/cm$ with sodium chloride. When evaluating the performance of the cationic starch, 0.2 % of anionic silica was added. To evaluate the effectiveness of silica microgel, the amount of cationic starch was adjusted constant to 1.0 %.

2.2.2 Silica microgel preparation

Silica 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). The change of pH was monitored continuously, and when pH reached to 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 sulfuric acid addition, water quality, reaction temperature, and H_2SO_4 addition rate were taken into account in the preparation of silica microgels.

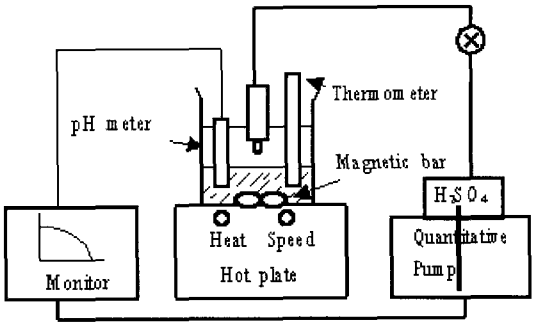


Fig. 1. Schematic drawing of the silica microgel preparation apparatus.

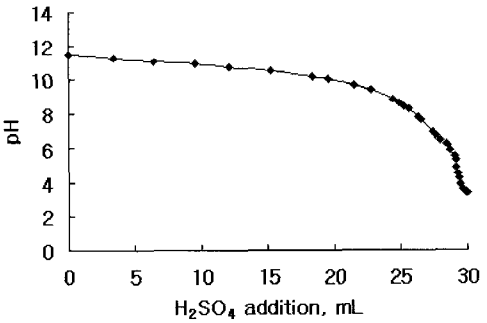


Fig. 2. Titration curve of 2 % sodium silicate solution with 2N sulfuric acid.

2.2.3 The measurement of fines retention and freeness

Fines retention and freeness were measured as depicted in Fig. 3 for three combinations of starch and anionic silica shown in Table 3. FTU turbidity of the filtrate was measured using DR/2000, and charge density was determined by PCD 03-pH and expressed as meq/g.

2.2.4 Handsheet forming and physical properties measurement

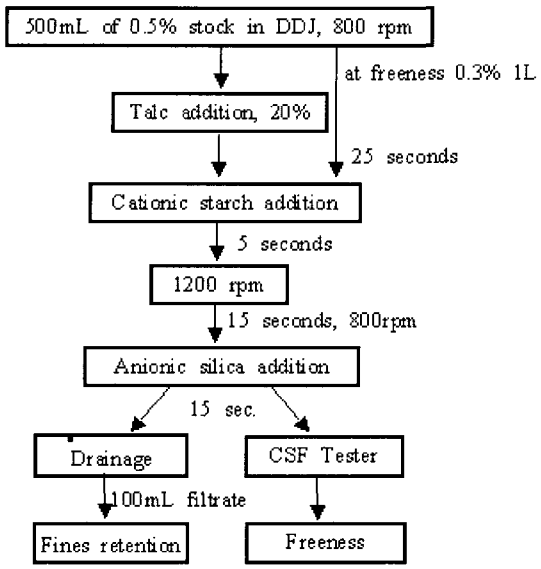


Fig. 3. Flow chart for measuring of fines retention and freeness.

While stirring the stock contained in a DDJ at 800 rpm, the cationic starch solution was added. Immediately after starch addition the stirring speed was increased to 1000 rpm, and agitated for 15 sec. After reducing the stirring speed to 800 rpm silica was added and stirred again for 15 sec. Handsheets with basis weight of 80 ± 1 g/m^2 were formed on a handsheet former, pressed and dried. Measurement of tensile strength and internal bonding strength was performed according to TAPPI Standard test methods. Formation was measured using a formation tester and expressed in NUI.

Table 2. Three combinations of starch and anionic silica tested

System	Cationic starch	Anionic silica
A	Potato starch	Structured silica
B	Corn starch	Structured silica
C	Corn starch	Silica-based microgel

3. Results and Discussion

3.1 Cationic starch

Influence of crosslinking treatment of cationic corn starches on fines retention and paper properties were investigated and compared with those obtained with cationic potato starches.

Fines retention obtained by using cationic corn or potato starches as a component of Compozil system are shown in Fig. 4. As shown in Fig. 4 (a), fines retention increased, reached maximum then decreased with the increase of starch addition. The fact that fines retention decreased when the amount of cationic starch was high suggests that nonadsorbed starch molecules, react with anionic silica to decrease the microfloc formation efficiency of colloidal silica particles.

A corn starch with the degree of substitution of 0.1 showed fines retention significantly lower than that obtained with lower DS starches when tap water was used. It means that the charge density of starches does not have a significant impact on fines retention, i.e., not the degree of substitution but the molecular weight of the cationic starch plays a vital role in fines retention in this case.

Fines retention obtained with the stocks at higher conductivity, i.e., 2000 μS/cm and 4000 μS/cm, are shown in Fig. 4 (b) and (c). As seen here the fines retention decreased as the conductivity increased. This indicates starch molecules contract due to charge neutralization at high conductivity and show low retention efficiency (10). It is eminent from Fig. 4 that the reduction of fines retention accompanying the increase of stock conductivity is minimal when a cationic corn starch with a high degree of substitution is used.

When the concentration of simple elec-

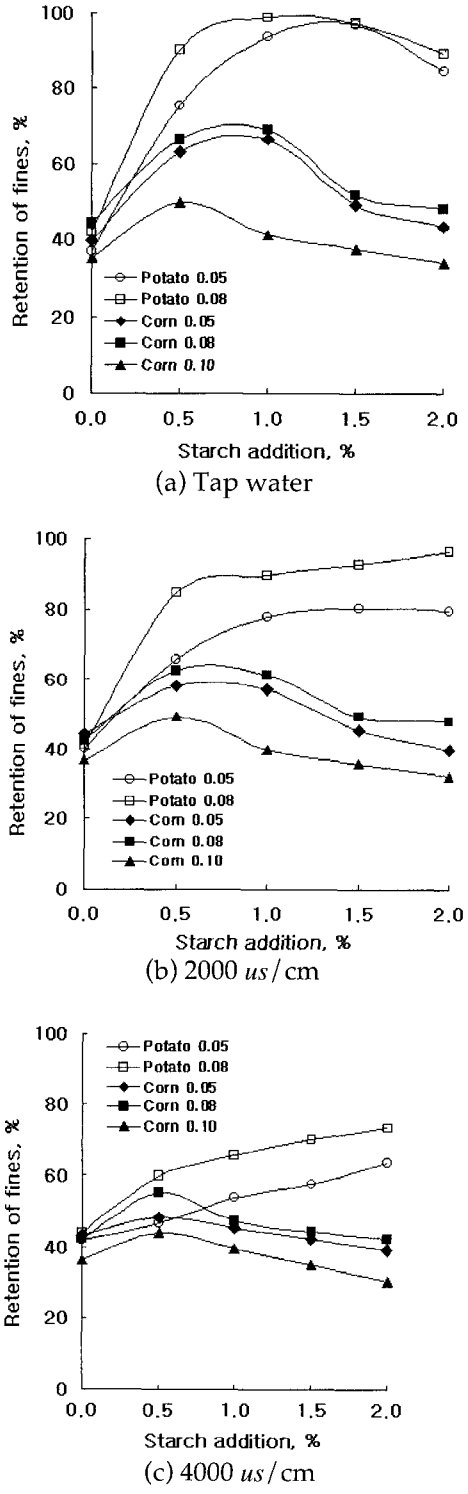


Fig. 4. Effects of cationic starch addition on fines retention.

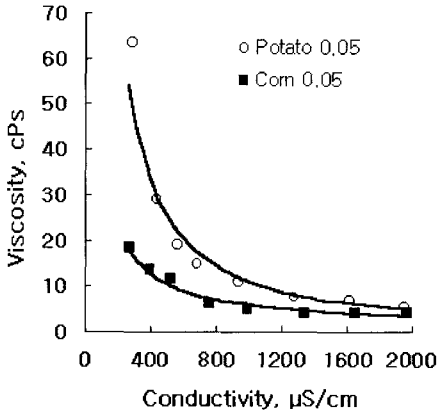
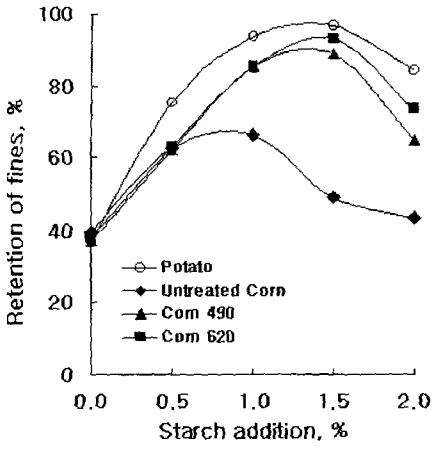


Fig. 5. Effects of conductivity on starch solution viscosity.

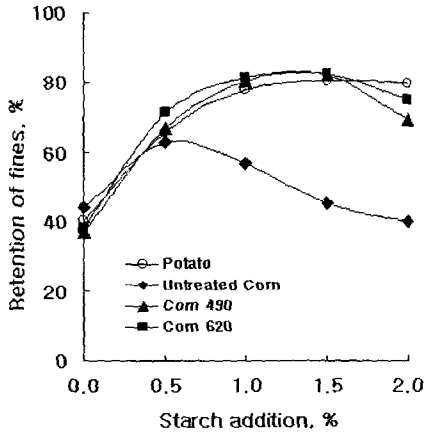
trolytes increases counter ions concentrate around the charged group to reduce repulsion. This means that at high conductivity the conformation of charged starch molecules changes to more compact one (1). This conformational change reduces the viscosity of starch solution as shown in Fig. 5.

High retention efficiency of high molecular weight potato starches (Fig. 4) suggested that it might be possible to increase the retention efficiency of the corn starches if their molecular weights are increased by crosslinking (8). Crosslinked corn starches were prepared to examine this hypothesis and their retention performance was examined with DS 0.05 corn starch (Fig. 6). As seen here fines retention increased with crosslinking treatment of corn starches. When tap water was used, potato starch still showed the highest retention (Fig. 6 (a)). The same results were obtained for crosslinked cationic starches with DS of 0.08 (Fig. 7). The effects of crosslinked starches on fines retention in highly conductive systems are illustrated in Fig. 6 (b) and (c). Fines retention decreased as conductivity increased, however, the retention performance of crosslinked corn starches was affected less

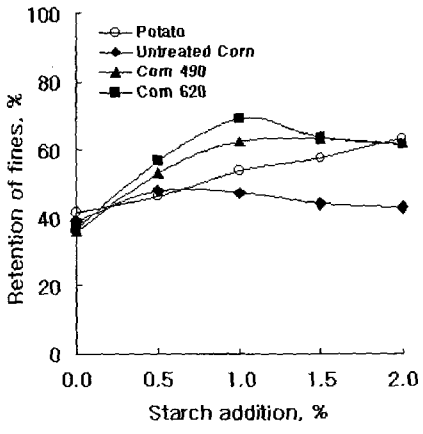
by conductivity increase than potato



(a) Tap water



(b) 2000 *us*/cm



(c) 4000 *us*/cm

Fig. 6. Effects of cationic starch addition on fines retention(DS 0.05).

starch probably due to the rigidity of starch molecules provided by the crosslinking treatment. At a conductivity of 4000 μS/cm crosslinked corn starches showed greater fines retention than the potato starch. It appears, however, excessive crosslinking impair the retention improvement since the flocculation ability of highly crosslinked starch molecules reduces.

Turbidity of the DDJ filtrate is closely associated with fines retention (Fig. 8). Thus it would be possible to evaluate the retention performance by measuring the filtrate turbidity.

Fig. 9 shows formation indices of handsheets formed using corn starches with DS of 0.08 and a potato starch with a DS of 0.074 as a component of the Compozil system. NUI formation deteriorated as the addition of cationic starches was increased at low addition rates. When the addition rate of starches was increased further, the formation of handsheets improved again. Deterioration of the sheet formation was most eminent at addition rate of 0.5 % for a potato starch and at 1.0 % for corn starches. This indicates a potato starch shows greater flocculation ability because of its higher molecular weight.

3.2 Tensile and internal bond strength

Cationic starches function not only as a retention aid but also as a strength agent (11). The internal bond strengths and tensile strength increased as the starch addition increased (Figs. 10-11). As the crosslinking level of corn starches increased, higher internal bonding strength and tensile strength were obtained. Greater internal strength and strength were obtained with crosslinked corn starches than with potato starch in most cases.

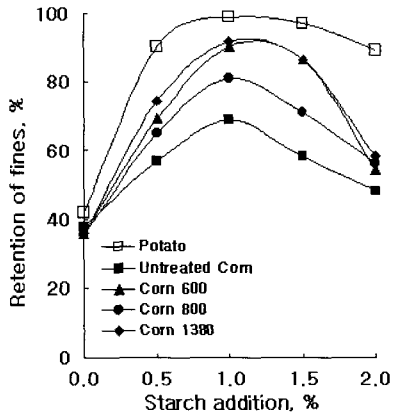


Fig. 7. Effects of cationic starch addition on fines retention(DS 0.08 - Tap water).

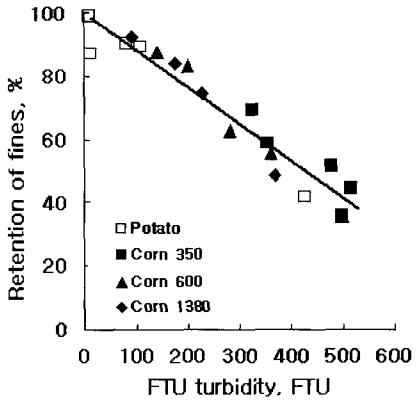


Fig. 8. Relationship between fines retention and FTU turbidity at tap water (DS 0.08).

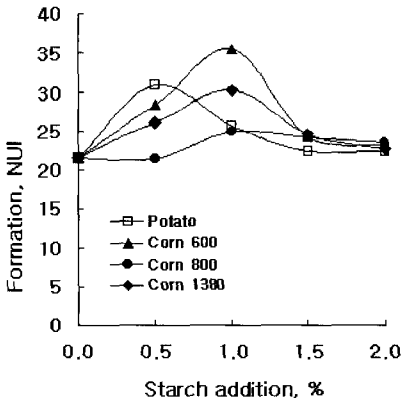


Fig. 9. Effects of cationic starch addition on formation (tap water, DS 0.08).

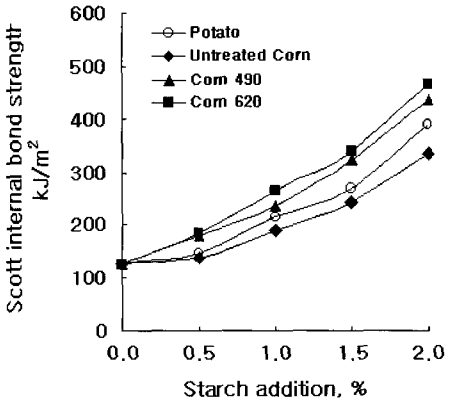


Fig. 10. Effects of starch addition on Scott internal bond strength.

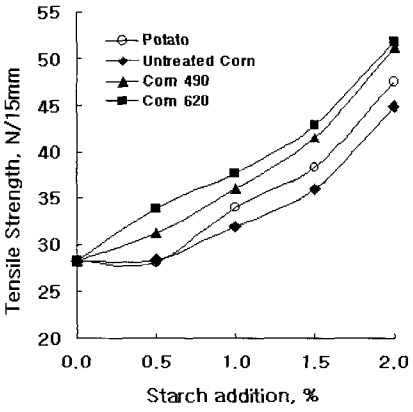


Fig. 11. Effects of starch addition on tensile strength.

3.3 Anionic silica

Silica microgels were prepared by reacting sulfuric acid and sodium silicate solutions. The microgels prepared in this experiment showed higher charge density than the reference product. Fig. 12 clearly shows that the highest charge density was obtained when product pH was controlled to 9. Decrease of the charge density as pH decreases lower than 9 shows that silanol groups changes into non-ionized form at low pH (12).

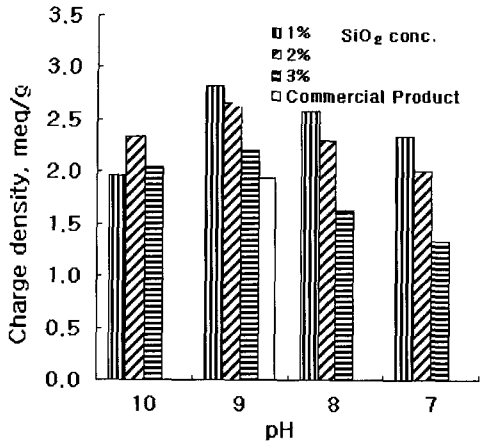


Fig. 12. Effects of SiO_2 concentration on the charge density of silica microgels (1N H_2SO_4).

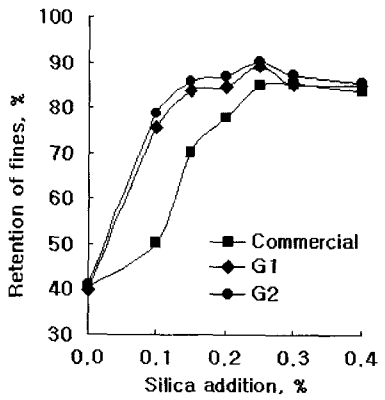


Fig. 13. Effect of anionic silica products on fines retention.

3.4 Fines retention, turbidity and freeness

Influence of two highly charged microgels prepared in this experiment, G1 and G2, on fines retention, freeness and turbidity was examined when they were used as a component in Compozil system along with 1.0 % of C-600 cationic starch. Charge density of G1 and G2 were 2.90 meq/g and 2.648 meq/g, respectively. The conductivity and calcium hardness of the stock were adjusted to 1000 μS/cm and 100ppm, respectively.

As shown in Figs. 13-15, G1 and G2 showed higher 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 probably because the charge density of prepared microgels were higher than that of the commercial product.

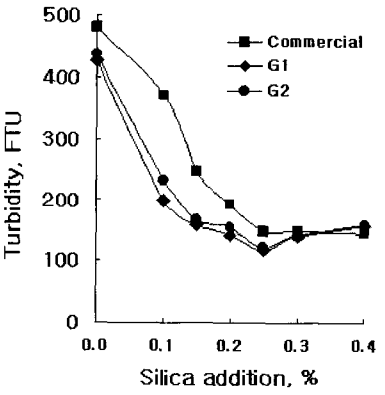


Fig. 14. Turbidity as a function of the addition rate of anionic silica products.

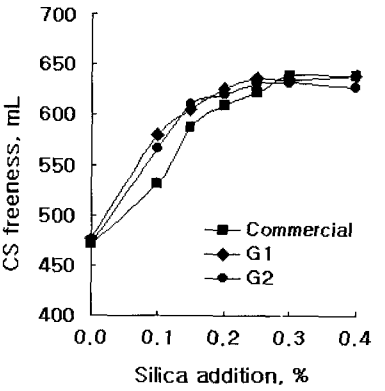


Fig. 15. Effect of anionic silica products on freeness.

4. Conclusions

In this study the effectiveness of crosslinked cationic corn starches and anionic silica products made from sulfuric acid

and sodium silicate solutions as components of Compozil system has been evaluated. It was shown that improvements both in retention and strength could be achieved by employing crosslinked cationic corn starches. Crosslinked cationic corn starches showed better retention properties when used in highly conductive systems because of their molecular rigidity. Silica-based microgels with better performance in retention and drainage than a commercial colloidal silica have been successfully produced through a reaction of sulfuric acid and sodium silicate solutions.

Acknowledgement

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