Application of Synthetic Mineral Microparticles with Various Metal Species

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ABSTRACT

Synthetic mineral microparticles (SMM) is a patented system which has been developed to promote drainage of water and retention of fine particles during papermaking. It is shown in patents that the SMM system can have advantages in both of drainage and retention, compared with montmorillonite (bentonite), which is one of the most popular materials presently used in this kind of application. Turbidity and gravity drainage time were measured using a Britt-Jar test with representative SMM formulations, in order to confirm the efficacy of SMM covering a wide range of compositions and discover effects of some key variables that have the potential to lead to unexpected advantages in terms of the effectiveness of the microparticles, when used in combination with a cationic polyacrylamide treatment of papermaking furnish. An iron silicate showed highest retention performance, as well as suitably fast drainage time relative to other metal silicate and bentonite. Zinc silicate improved retention and drainage. SMM synthesized from aluminum sulfate ($Al_2(SO_4)_3$) did not show a benefit in retention and drainage, relative to bentonite. SMM synthesized from aluminum chloride ($AlCl_3$) performed better in drainage and retention than bentonite when the Al/Si ratios were 0.76 and 1.00. It was found that when the Al/Si ratio and neutralization are considered, pH variation due to the change of Al/Si ratio can be a key factor to control the size of primary metal silicate particles and the degree of coagulation of the primary particles.

Keywords : *synthetic mineral microparticle, drainage, retention, sodium metasilicate, iron silicate, zinc silicate, aluminosilicate, Al/Si ratio*

1. Introduction

"Synthetic Mineral Microparticles"(SMM) is a patented system which can increase the rate of dewatering and promote the retention of fine particles more efficiently during the process of papermaking (1-3).

The SMM technology is protected by the following

• Department of Wood and Paper Science, North Carolina State Univ., Campus Box 8005, Raleigh, NC 27695-8005, USA
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US patents:

• US 6,184,258: Process for preparation of microparticles (1)

• US 5,989,714: Composition patent for microparticles (2)

• US 6,183,650: Water treatment by means of microparticles (3)

Of these three patents, US 6,184,258 shows the most basic invention. It is shown that highly effective microparticles can be synthesized by simple mixing a dilute solution of silicate ions and a dilute solution of aluminum ions. This capability is illustrated by the results in Table 1, which compares the Britt Jar first-pass retention achieved in the laboratory during initial testing with an SMM product prepared by adding aluminum sulfate solution to sodium silicate solution at an Al/Si ratio of 0.5. It is worth noting that the results in Table 1 were obtained without any effort to optimize the conditions of mixing, overall concentration of the mixture or detailed chemistry other than the ratio of the two major components of the SMM colloidal dispersion.

The filler retention performance of SMM microparticles was only moderately sensitive to the Al/Si ratio, as shown in Fig. 1. The furnish was 100 % softwood kraft with 20 % added filler. For tests involving water-washed clay filler, the furnish was first treated with 2 lb/ton of Percol®386 coagulant, followed by 1 lb/ton of Percol®175 cationic acrylamide copolymer retention aid, and finally 5 lb/ton of the microparticle on a dry basis. In the case of precipitated calcium carbonate (PCC, Albacar®HO) the additives were 1 lb/ton of Percol®175 retention aid followed by 5 lb/ton of microparticle. The highest retention was obtained at a critical Al/Si ratio. Fig. 2 shows confirmatory results for different pulp furnishes.
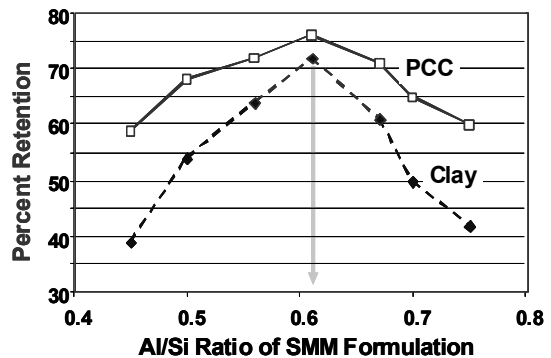

Fig. 1. **Effect of Al/Si ratio of SMM microparticles on filler retention results in a bleached kraft furnish.**

Table 1. Performance of SMM in comparison with commercially available microparticles in four different fiber furnish environments

Microparticle Type	Britt Jar First Pass Retentions (%)							
	Furnish & Filler Type*							
	Kraft A		Kraft B		Groundwood A		Groundwood B	
No Microparticle	29	37	40	37	53	51	55	28
SMM	**57**	74	60	60	54	61	81	61
Bentonite	50	75	64	64	73	72	84	77
Colloidal SiO$_2$	27	35	40	32	50	51	52	30

Furnish: 1 % consistency with 20 % of added filler,
Pulp: Kraft A = 100 % softwood kraft; Kraft B = mixed kraft; Groundwood A and B are from different paper mills, Filler: PCC = Albacar®HO; Clay = Georgia water-washed;
Coagulant: Percol®368
Retention aid: Percol®175
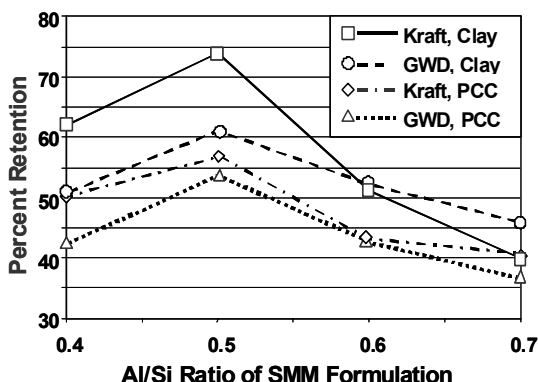Microparticels: SMM; Bentonite = Hydrocol®O; Colloidal silica = Nalco®8671.

Fig. 2. Effect of Al/Si ratio of the SMM additive for enhancement of filler retention in furnish already treated with cationic retention aid.

The purpose of this study was to confirm the efficacy of representative synthetic mineral microparticle (SMM) formulations, covering a wide range of compositions, and discover effects of some key variables that have the potential to lead to unexpected advantages in terms of the effectiveness of the microparticles, when used in combination with a cationic polyacrylamide treatment of papermaking furnish.

2. Experimental

2.1 Furnish

A mixture of 75 % bleached hardwood kraft and 25 % bleached softwood kraft pulp was disintegrated for 10 min and co-refined to about 400 ml CSF. Then 10 %, by total furnish mass, of Albacar®5970 scalenohedral precipitated calcium carbonate (PCC) was added. Sodium sulfate solution (Na_2SO_4) of 1M concentration was added to achieve approximately 1000 μS/cm electrical conductivity at a filterable solids level of approximately 0.5 %.

2.2 Synthetic conditions of SMM

Sodium meta-silicate ($Na_2SiO_3 \cdot 5H_2O$) is used as base ingredient with k molal concentration. The value

of x, the molar concentration of sodium meta-silicate ($Na_2SiO_3 \cdot 5H_2O$) in u gram mass of solution with k molal concentration is calculated by Eq. [1]. MW_s is the molecular weight of sodium meta-silicate.

$$x = \frac{k \cdot u}{1000 + MW_s \cdot k} \qquad \text{Eq. [1]}$$

The value of y, the molar concentration of metal ingredient in v gram weight of solution with l molal concentration was calculated by Eq. [2]. MW_m is the molecular weight of the metal ingredient.

$$y = \frac{l \cdot v}{1000 + MW_m \cdot l} \qquad \text{Eq. [2]}$$

The metal/Si ratio is given by $\alpha = (m \cdot y)/(n \cdot x)$, where m is the number of metal atoms in one molecule of metal ingredient and n is the number of Si atoms in one sodium meta-silicate molecule. The amounts of sodium meta-silicate and metal ingredient solutions were calculated by Eq. [3].

$$v = \frac{1000 + MW_m \cdot l}{m \cdot l} \cdot \frac{\alpha \cdot n \cdot k}{1000 + MW_s \cdot k} \cdot u \qquad \text{Eq. [3]}$$

Only sodium meta-silicate ($Na_2SiO_3 \cdot 5H_2O$) was used as base ingredient in this set of tests with 0.445 molal concentration. Added metal solution ingredients in different tests included 0.566 molal aluminum sulfate ($Al_2(SO_4)_3$), 0.566 molal aluminum chloride ($AlCl_3$), 0.500 molal zinc chloride ($ZnCl_2$), and 0.500 molal ferric chloride ($FeCl_3$).

Various ratios of metal to silicate were used, e.g. Al/Si = 0.5, 0.76, and 1.0 molar ratio, Zn/Si = 1.14, and Fe/Si = 0.76. When the metal ingredients are aluminum chloride ($AlCl_3$) and aluminum sulfate ($Al_2(SO_4)_3$), w ml of 1 M NaOH solution was calculated by Eq. [4] for the 25 % neutralization of Al^{3+}, and added to the reacted suspension during continuous stirring.
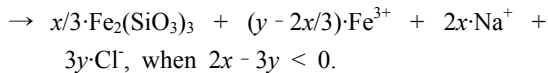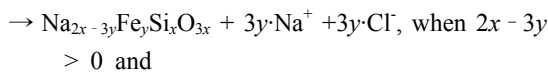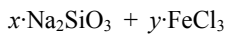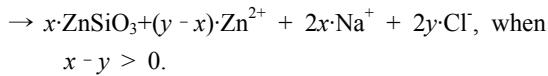
$$w = 0.75 \cdot n \cdot y \cdot 1000 \qquad \text{Eq. [4]}$$

where y is the molar concentration of metal ingredient, and n is the number of Al atoms in the metal-containing ingredient.

1 mM NaCl, based on the total mass of solution, was

added to adjust the salt concentration. Table 2 shows the grid of test conditions.

Based on the amounts of reagents, and assuming complete consumption of Si species, the reactions could be described by the following chemical equations

$x \cdot Na_2SiO_3 + y \cdot Al_2(SO_4)_3$

$\rightarrow Na_{2x-6y}Al_{2y}Si_xO_{3x} + 6y \cdot Na^+ + 3y \cdot SO_4^{2-}$, when $x - 3y > 0$ and

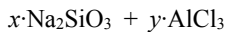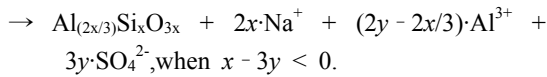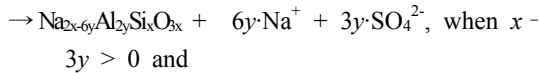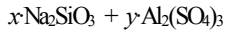$\rightarrow Al_{(2x/3)}Si_xO_{3x} + 2x \cdot Na^+ + (2y - 2x/3) \cdot Al^{3+} + 3y \cdot SO_4^{2-}$, when $x - 3y < 0$.

$x \cdot Na_2SiO_3 + y \cdot AlCl_3$

$\rightarrow Na_{2x-3y}Al_ySi_xO_{3x} + 3y \cdot Na^+ + 3y \cdot Cl^-$, when $2x - 3y > 0$ and

$\rightarrow x/3 \cdot Al_2(SiO_3)_3 + (y - 2x/3) \cdot Al^{3+} + 2x \cdot Na^+ + 3y \cdot Cl^-$, when $2x - 3y < 0$.

$x \cdot Na_2SiO_3 + y \cdot ZnCl_2$

$\rightarrow Na_{2x-2y}Zn_ySi_xO_{3x} + 2y \cdot Na^+ + 2y \cdot Cl^-$, when $x - y > 0$ and

$\rightarrow x \cdot ZnSiO_3 + (y - x) \cdot Zn^{2+} + 2x \cdot Na^+ + 2y \cdot Cl^-$, when $x - y > 0$.

$x \cdot Na_2SiO_3 + y \cdot FeCl_3$

$\rightarrow Na_{2x-3y}Fe_ySi_xO_{3x} + 3y \cdot Na^+ + 3y \cdot Cl^-$, when $2x - 3y > 0$ and

$\rightarrow x/3 \cdot Fe_2(SiO_3)_3 + (y - 2x/3) \cdot Fe^{3+} + 2x \cdot Na^+ + 3y \cdot Cl^-$, when $2x - 3y < 0$.

2.3 Measurement of drainage and retention

2.3.1 Step-wise addition of additives

For each set of retention and drainage experiments, 500 ml of stock from the master batch was placed in the Britt Jar and agitated with an impeller at 800 rpm. Then 0.05 % (1 lb/ton, solids basis) of Percol®175 cationic acrylamide copolymer, on furnish solids from a 0.1 % solution, was added. After 30 seconds, the stirring rate was increased to 1,250 rpm for 30 seconds, and then immediately reduced to 800 rpm. Next the selected microparticle formulation was added, followed by 30 seconds more of agitation. Various levels of synthetic mineral microparticles, 0.25, 0.50, 0.75, and 1.00 % by solid basis of total furnish, were tested.

2.3.2 Turbidity Measurement to Evaluate Retention

An initial approximate 20 ml of filtrate was collected and discarded, because the fines and filler in this filtrate have high possibility of having been pressed through the screen by agitating motion of stirrer during the 1½ minute procedure. An aliquot of approximately 40 ml filtrate was collected in a 200 ml beaker and divided into two turbidity cuvettes (20 ml each). The turbidities of these two filtrates were

Table 2. Test conditions

Test No.	Metal Solution Ingredients	Ratio Metal Ion to Si	Shear, rpm	Salt	Neutralization
1	$Al_2(SO_4)_3$	0.76	500	None	None
2	$AlCl_3$	0.76	500	None	None
3	$ZnCl_2$	1.14	500	None	None
4	$FeCl_3$	0.76	500	None	None
5	$Al_2(SO_4)_3$	0.76	1500	None	None
6	$AlCl_3$	0.5	500	None	None
7	$AlCl_3$	1.0	500	None	None
8	$AlCl_3$	0.76	500	None	25 %
9	$ZnCl_2$	1.14	500	1 mM NaCl	None
10	$ZnCl_2$	1.14	1500	1 mM NaCl	None
11	$Al_2(SO_4)_3$	0.76	1500	1 mM NaCl	25 %
12	$Al_2(SO_4)_3$	0.50	1500	1 mM NaCl	25 %

evaluated based on the tenth appearance of digital output (about 3 seconds) after placement in the device. The cuvette was gently swirled and the turbidity was evaluated again.

In analysis of turbidity data, it will be assumed that a lower turbidity of filtrate implies a higher retention of particles. To account for the increase of turbidity due to microparticles, blank tests were done. 500g of water was placed in the Britt Jar. The same amounts of SMMs, synthesized in each conditions, and bentonite were addedinto the blank water. The turbidities of each filtrate was measured in the same way.

2.3.3 Gravity drainage time

After taking the turbidity samples, 200 ml of the slurry was placed in a filtration device, supplied with a 200 mesh screen of circular cross-section and a diameter of 3.9 cm. The time required for the water to drain from 200 ml to 150 ml was measured and recorded as the "gravity drainage time." Another sample was measured for the second value.

3. Results and Discussion

3.1 Effect of metal species

Fig. 3(a) shows the results of turbidity to evaluate
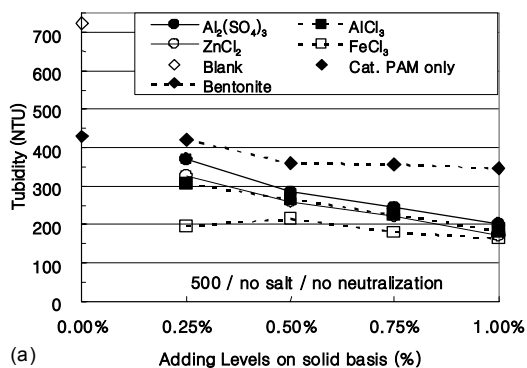
retention performances of each type of microparticle. The iron silicate, synthesized by adding the solution of ferric chloride ($FeCl_3$) to sodium meta-silicate solution, had the highest performance in the retention of fines and PCC through the all levels of addition. Zinc silicate and aluminosilicate synthesized by adding solution of either zinc chloride ($ZnCl_2$) or aluminum chloride ($AlCl_3$) showed similar retention performances. All species of SMMs performed better than bentonite through all addition levels. The retention performances of zinc silicate and two kinds of aluminum silicates were improved linearly according the increase of addition level of SMM.

The results of gravity drainage experiments are depicted in Fig. 3(b). Aluminum silicate synthesized from aluminum sulfate performed slightly better in drainage than bentonite at the higher addition level. Zinc silicate performed slightly better in terms of drainage at the 0.50 % addition level, under the same conditions of synthesis (500 rpm, no salt, no neutralization), though it should be noted that the metal/Si ratios were not held constant (Al/Si = 0.76, Zn/Si = 1.14, Fe/Si = 0.76).

Considering the results of both graphs, it is summarized that the SMMs synthesized by addition of metal species; aluminum chloride ($AlCl_3$), zinc chloride ($ZnCl_2$), and ferric chloride ($FeCl_3$),
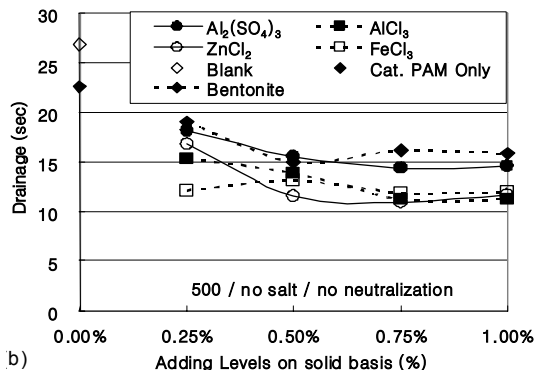

(a)

(b)

Fig. 3. Effects on filtrate turbidity and drainage times after replicate batches pulp-PCC suspension were treated with microparticles resulting from addition of metal solutions to sodium silicate solution under the following constant conditions: 500 rpm, no salt added, no neutralization; (a) results of turbidity measurements; (b) gravity drainage times.

performed better than bentonite for retention and drainage.

3.2 Effect of stirring speed

Results in Fig. 4(a) show that an agitation speed of 1500 rpm produced results, in drainage, that were superior to 500 rpm during preparation of synthetic mineral microparticles in low addition levels, 0.25 and 0.50 %. Through the all of addition levels, both of 500 and 1500 rpm system performed better than bentonite.

Tentatively it is proposed that the higher performance of the material produced at 1500 rpm is due to a smaller primary particle size, which is equivalent to saying that the surface area per unit mass was higher, compared to the material produced at a lower speed of agitation. A higher surface area would explain why the microparticles produced at 1500 rpm were able to achieve relatively large retention effects at the lowest levels of microparticle addition considered. It is proposed that the higher hydrodynamic shear creates a larger number of nucleation events, leading to a higher number of primary particles, which consume the available precipitating ions before they have grown as large as those produced under lower agitation. However, a smaller primary particle size does not in any way rule out the possibility of primary particles becoming fused

together into gel structures. Past work has shown that more highly structured microparticles (chains, elongated clusters, *etc*.) can provide enhanced retention performance, when used in combination with a high-mass cationic polymer treatment (5). This hypothesis is consistent with the observation that under pH 7, the microparticles formed at the higher agitation speed showed higher retention performance.

Part (a) of Fig. 4 also shows that the retention performance of SMM produced at 1500 rpm did not change when the amount added was increased above 0.25 % on a solids basis. Such behavior is highly desirable in a microparticle product, since there is no evidence of a reversal of the retention effect upon overdose of the microparticle. To explain this effect, retention aid systems basedon high-mass acrylamide copolymers are well known for their largely irreversible behavior. Polyelectrolyte complex structures formed between highly structured microparticles and extended loops and tails of retention aid polymers would not be expected to easily become detached. Thus, any attachments mediated between polyelectrolyte-covered fibers and fines, upon initial addition of the structured microparticle additive would be expected to persist as higher incremental amounts of the microparticle are added (6-9).
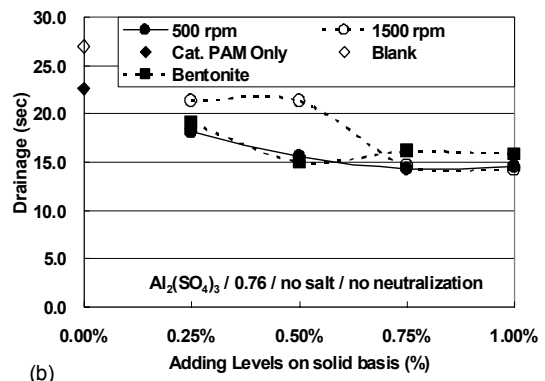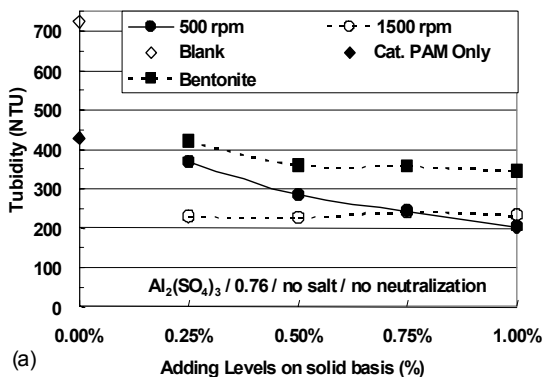

Fig. 4. Effects of the variations of stirring speeds, while holding other condition unchanged – Al$_2$(SO$_4$)$_3$, no salt added, no neutralization; (a) is the graph of the results of turbidity measurements and (b) shows the gravity drainage times.

Drainage rate results in Part (b) of Fig. 4 show an inverted order of effectiveness, compared to Part (a). The SMM formed at a lower rate of agitation approximately matched the performance of bentonite, whereas the higher agitation rate yielded microparticles that were less effective at addition levels below 0.75 %. These results suggest that the latter particles have a higher degree of structure, an attribute that tends to favor retention performance over drainage performance (5).

3.3 Effect of Al/Si ratio

A change in Al/Si ratio causes the pH to change, due to the high acidity of dissolved aluminum ions in aqueous form. The behaviors of silica and aluminum are complicated. High Al/Si ratio causes low pH synthetic conditions. Low pH decreases the amount of hydroxyl ion (OH^-), in aqueous solution. The hydroxyl ion is essential for deprotonation from silanol groups on the silica (10). As a result of this, condensation of silica is limited, and the growth of silica particles is prevented. Under these circumstances, the primary particles remain small and the relative surface area of particle is large. On the other hand, when the pH decreases into the range of 3.5 – 5, polymerized aluminum species are formed by the hydrolysis of

Al-ions (11-14), and act as bridge ions to coagulate small size of primary particles (15).

As illustrated by the results in Fig. 5, there appears to be an optimum Al/Si ratio relative to retention and dewatering benefits of the synthetic microparticles. When we consider this fact, in Fig. 5, we can suppose that 0.76 and 1.0 Al/Si ratios are around the optimum value, which is supposed to be between 0.76 and 1.0, because the data of these 2 ratios have similar resultscaused by small primary particle and coagulation of primary particle to high structure.

3.4 Effect of salt

Fig. 6 shows no big change in the retention performance of $ZnCl_2$ as a function of changes in either salt addition or stirring speed. Zinc silicate showed a linear dependence of retention performance on the increase of added amounts of microparticle. Considering drainage time, the most rapid drainage was achieved in the case of the zinc silicate that was formed in the absence of salt and with agitation at 500 rpm.

3.5 Effect of neutralization

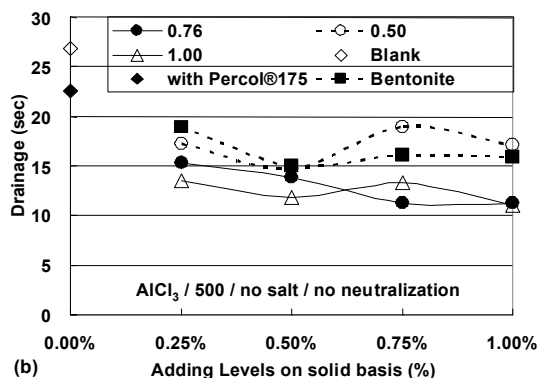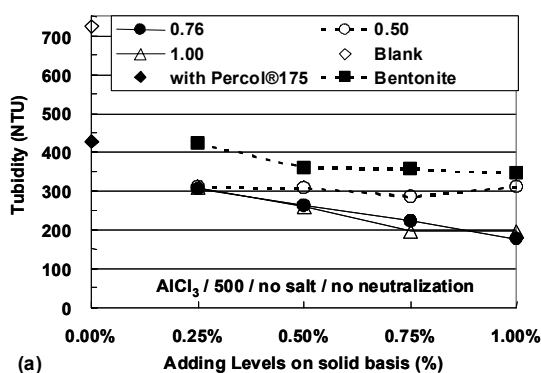As shown in Fig. 7, partial neutralization of the aluminum chloride solution with NaOH before its

Fig. 5. Effects of variations of Al/Si ratio, while holding other conditions constant – AlCl₃, 500 rpm, no salt added, no neutralization; (a) is the graph of the results of turbidity measurements and (b) shows the gravity drainage times.
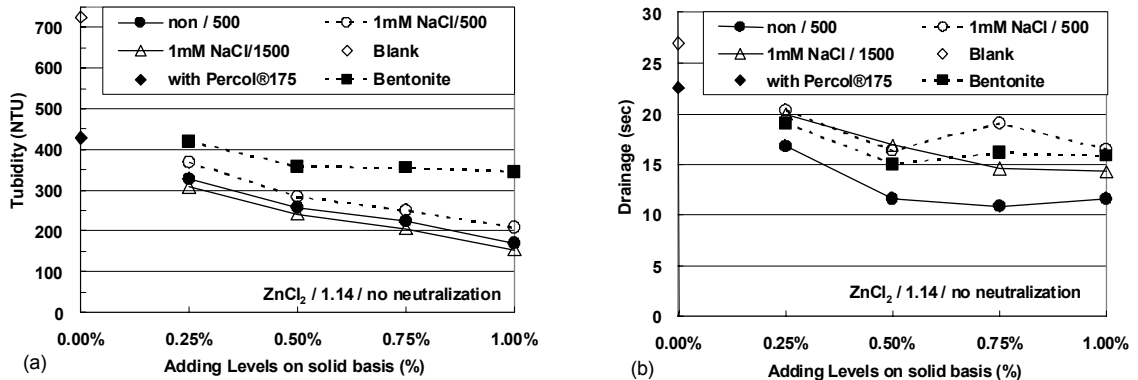
Fig. 6. Effects of variations of salt and stirring speed under the same other conditions – ZnCl₂, no neutralization; (a) is the graph of the results of turbidity measurements and (b) shows the gravity drainage times.

addition to the sodium metasilicate solution rendered the microparticle product less effective in terms of both retention (Part a) and dewatering (Part b). When the Al/Si ratio was 0.76, neutralization moves the pH from 3.79 to 6. When pH is lower than 5, there are some aluminum ionic species, e.g. $Al_{13}O_4(OH)_{24}^{7+}$ and $Al_2(OH)_2^{4+}$, which can act as coagulants in SMM suspension. When the pH is 6, there is no cationic Al-ion species that can act as a coagulant. As a result of this, the micropaticles tend to remain more in a dispersed sol state, instead of forming a gel structure as shown in Fig. 8. In paper slurry, the higher gel

structure, which consists of the smaller microparticles, shows higher performance in retention and drainage (8). This phenomenon is confirmed well by the lower turbidities and faster drainages in Fig. 7.

4. Conclusions

Turbidity and gravity drainage time were measured using a Britt-Jar test with representative synthetic mineral microparticle (SMM) formulations, in order to confirm the efficacy of SMM, covering a wide range of compositions, and discover effects of some key
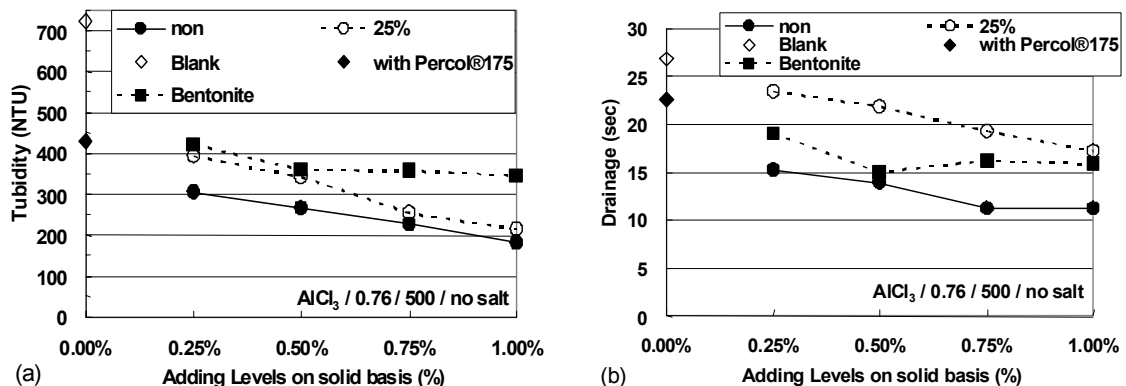

Fig. 7. Effects of neutralization under the same other conditions – AlCl₃, Al/Si=0.76, 500 rpm, no salt added; (a) is the graph of the results of turbidity measurements and (b) shows the gravity drainage times.
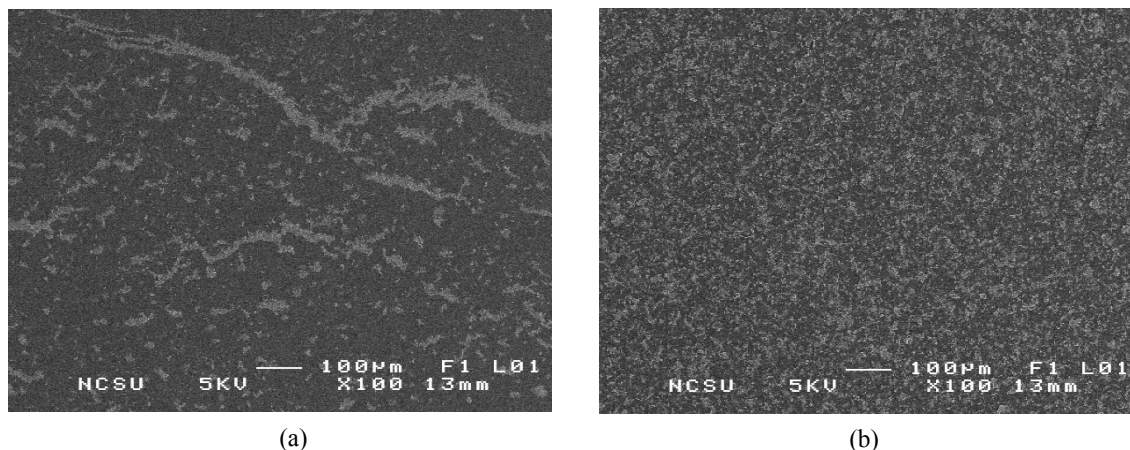
(a)   (b)

Fig. 8. SEM pictures of SMMs synthesized under the conditions AlCl₃, Al/Si=0.76, 500 rpm, no salt added with (a) no neutralization and (b) 25 % neutralization with 1M NaOH.

variables that have the potential to lead to unexpected advantages in terms of the effectiveness of the microparticles, when used in combination with a cationic polyacrylamide treatment of papermaking furnish.

An iron silicate showed highest retention performance, as well as suitably fast drainage time relative to other metal silicate and bentonite. Zinc silicate improved retention and drainage. SMM synthesized from aluminum sulfate ($Al_2(SO_4)_3$) did not show a benefit in retention and drainage, relative to bentonite. However, these three compositions have SO_4^{2+}, Zn^{2+}, and Fe^{3+}, which are not regarded by papermakers as welcome species, due to the environmental concerns. SMM synthesized from aluminum chloride ($AlCl_3$) performed better in drainage and retention than bentonite when the Al/Si ratios were 0.76 and 1.00. For these reasons, $AlCl_3$ is a more desirable metal species to synthesize SMM suspensions than others.

In the results of retention and drainage at different stirring speed, the higher speed (1500 rpm) was proposed to produce small primary particles, whereas the lower speed (500 rpm) was expected to form a higher degree of structure in SMM suspension. However, it was found that when the Al/Si ratio and neutralization are considered, pH variation due to the change of Al/Si ratio can be a key factor to control the size of primary metal silicate particles and the degree of coagulation of the primary particles. These effects appear to be due to the distribution of Al-ion species and different ionic behavior on the surface of silica through the pH variation.

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