Development of a functional filler: swelling sericite

YUAN-SHING PERNG AND EUGENE I-CHEN WANG

ABSTRACT: Sericite is an indigenously produced mineral from eastern Taiwan. As a mineral of the mica family, it is a naturally swelling, layered material. It possesses a high degree of negative charge and high aspect ratio, making it suitable for use as a functional filler to strengthen the retention of fines and chemicals in the wet-end process. This study investigated the use and development of swelling sericite as a functional papermaking filler in both acidic and neutral sizing systems. The study included laboratory tests and on-machine tests on paper machines of different speeds (below 300 m/min, 500 m/min, and more than 1000 m/min). We studied the effects of adding sericite on wet-end performance and paper properties. In the neutral sizing system, when 3% of calcium carbonate was replaced with sericite, the sizing degree improved by 46%, ash content by 18%, bulk by 4%, and opacity by 1.5%; but brightness was lowered by 1.5% ISO. In the acidic sizing system, when 3% of clay was replaced with sericite, the sizing degree improved by 85%, ash content by 13%, bulk by 4%, and opacity by 1.2%. Brightness was lowered by 1.5%. Regardless of machine speeds, sericite addition in the on-machine tests not only enhanced first pass retention, but also lowered flow rates of retention aid, sizing agent, and filler. In the high-speed machine test, sericite helped to improve the thickness, formation, air permeation, and roughness of the products.

Application: This study could offer paper mills the choice of a new functional filler to stabilize the wet-end system and enhance retention of fines, fillers, and chemicals. Paper formation, thickness, air permeation, and smoothness could also be raised.

There are two types of naturally swelling, layered inorganic material: montmorillonite and sericite. In paper machine wet-end application, only bentonite (the main ingredient of which is montmorillonite) or montmorillonite are used in dual retention system as an enhancement agent [1-7]. As for its use as functional filler, there is a lack of pertinent reporting.

Sericite is a native mineral mined from eastern Taiwan. It is a lustrous layered powder composed mainly of silicone dioxide and aluminum oxide, with an empirical formula of $M^{2+}_{x/n}(Mg_6)(Si_{8-x})O_{20}(OH_4)$, having an average particle size of about 10-14 µm. Each powder particle possesses about 850 to 3500 strata of expandable layered structure [8]. **Figure 1** shows the typical scanning electron microscope (SEM) diagram of natural sericite. Typical sericite has a three-layer unit cell consisting of a SiO_2 tetrahedron–Al_2O_3 octahedron–SiO_2 tetrahedron. In between the layers, there are potassium ionic bonds holding the layers together. Kaolin clay, on the other hand, is a non-swelling, layered inorganic material with a two-layer unit cell of consisting of a SiO_2 tetrahedron–Al_2O_3 octahedron. In between the layers of kaolin clay are hard-to-break chemical bonds holding the layers together. Thus the particle is stable and non-swelling.

Table I compares the major physical properties of swelling sericite and traditional papermaking fillers (kaolin clay, calcium carbonate, and talc) [8, 9]. Sericite, similar to talc and clay, has a flaky structure; it has particle sizes roughly equal to clay and 10-12 times larger than that of calcium carbonate and talc. The particle charge determined by particle charge detector by Mütek (PCD) is three times that of the talc, and 25 times that of clay and calcium carbonate. The electrical conductivity of sericite is 1.3 times that of talc, and twice that of clay and calcium carbonate. It has hardness roughly equal to calcium carbonate, hence should not cause excessive abrasion to forming wires. It has optical properties similar to the other fillers, although the brightness is lower.

Because of the unique expandable layered structure, high negative charges, and high aspect ratio, sericite is a suitable candidate to serve as functional filler to assist in retention of fines and chemicals at the wet-end of papermaking. With regard to the wet-end addition, sericite not only can raise the first pass retention (FPR), but also raise retention of chemicals and filler. As for the paper properties, the flaky sericite can increase opacity and thickness of paper, and improve pinholes, air permeation and smoothness. With regard to printability, sericite can significantly lower the amounts of coating pigment and printing ink application; it can further resist ultra violet radiation and static electricity, functions particularly desirable to the operation of high speed printing machines.

In this study, we purport to show the use of sericite as functional filler in the applications of both acidic and neutral sizing systems. A series of experiments ranging from bench-top scale to on-machine tests using paper machines of different speeds were carried out, and the effects of expandable sericite on papermaking wet-end and the physical properties of the products were examined and evaluated.

EXPERIMENTAL

Bench-top experiments

Maintaining a fixed filler load of 20%, we replaced calcium carbonate (in a neutral sizing system) or clay (in an acidic sizing system) with sericite in amounts ranging from 0%, 1%, 1.5%, 2%, 2.5%, 3%, 4.5%, and 6% to observe the effects on bulk, sizing degree, opacity, brightness, air permeation, and ash content of the handsheets.

	MAIN INGREDIENT			
	SERICITE	KAOLIN -CLAY	GCC	TALC
	SiO_2 54% Al_2O_3 31% K_2O 5%	Al_2O_3 45% SiO_2 39%	$CaCO_3$ 96%	SiO_2 62% MgO 31%
Crystalline structure	Monoclinic sys.	Triclinic sys. platy	Orthorhombic sys.	Monoclinic sys.
External appearance	Platy	Platy	Spherical	Platy
Specific surface area (g/m^2)	57	9 – 15	2 – 12	9 – 20
Hardness (Mohs)	2.2 – 2.4	1.5 – 2.0	2.5 – 3.5	1.0 – 1.5
Range of particle size (μm)	0.8 – 45.0	0.5 – 10.0	0.1 – 2.5	0.25 – 5.0
Average particle size (μm)	10.0 – 14.0	0.6	0.95	1.2
Specific gravity	2.6 – 2.7	2.58	2.65	2.7
Refractive Index	1.59 – 1.62	1.56	1.65	1.57
Reflectance (%) (457 nm)	70	82	98	97
Brightness (% GE)	65 – 75	80 – 86	86 – 96	73 – 80
pH	7 – 9	4 – 6	8 – 9	4 – 5
IEC[a] (meq/g)	5.0[b]	0.5 – 1.5	—	—
PCD (meq/g)	-48.4	-1.1	-1.9	-15.7
Conductivity (Mohm/cm)	92.6	48.3	44.8	72.5
Aspect ratio	40	5 – 15	—	—

a. IEC: Ion Exchange Capacities. b. Most mica minerals have values in the range of 1.6-2.0 meq/g

I. Comparisons of the physical properties of sericite and other traditional fillers [8, 9].

For the sizing degree variables, the amounts of sizing agent added were adjusted (in neutral sizing, alkyl ketene dimer (AKD) addition of 0.5%, 0.75%, and 1.0%; in acidic sizing, emulsified rosin addition of 1.0%, 1.25% and 1.5%) to observe the effect of sericite on different sizing degrees.

The experimental procedure for the neutral sizing series included dispersing wood pulp (5 g), adding calcium carbonate (20%-14%), adding sericite (0%-6%), applying AKD (0.5%-1.0%), adding cationic starch (0.8%), and finally adding cationic retention aid (300 mg/L). Then the pulp slurry was formed into handsheets in accordance with the TAPPI standard T205 sp-95. For the acidic sizing series, except that clay replaced calcium carbonate, and emulsified rosin replaced AKD, all the rest of procedures were identical.

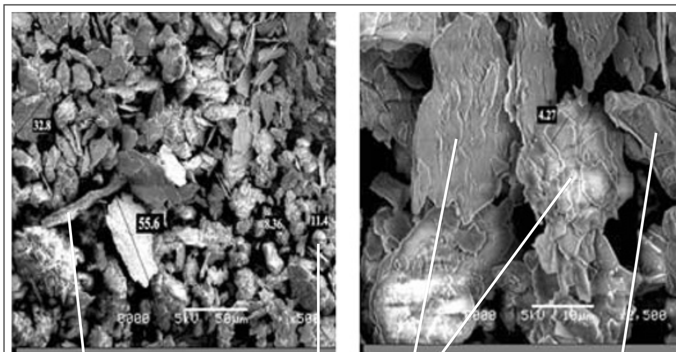
The raw materials, filler and chemicals used in the above experiments have the following specifications:

- Wood pulp: BHKP manufactured by the Taiwan Pulp and Paper Co., having a freeness of 500 mL CSF.
- Sericite: Mined and refined by the Sunshine Mineral Co., average particle size about 10 μm.
- Calcium carbonate: GCC 75F, Omya Inc.
- Kaolin clay: Indonesian clay
- AKD: Hercon® TD15, Hercules Taiwan Co.
- Emulsified rosin size: Hi-Phase®, Hercules Taiwan Co.
- Cationic starch: T-500, Tse-mao Co.
- Cationic retention aids: DM-543, C-PAM, Chi-you Co.

The handsheets, with a target basis weight of 60 g/m^2, were tested for grammage and thickness (TAPPI standard T205 sp-95, T410 om-98, T411 om-97), sizing degree (Stoeckigt sizing degree, TAPPI standard T433 cm-84), opacity (TAPPI standard T519 om-96), brightness (TAPPI standard T452 om-98), air permeation (TAPPI standard T460 om-96), and ash content (TAPPI standard T413 om-93).

On-machine experiments

Once we determined the effects of applying sericite on papermaking wet-end and handsheet properties, we planned a series of on-machine tests using paper machines of different operating speeds. Those included a low speed machine (less than 300 m/min), mid-speed machine (ca. 500 m/min), and high speed machine (greater than 1000 m/min). To maintain the stability of product quality, parameters such as the flow rates of sizing agent, retention aid, and filler were adjusted automatically. The main objective here is to compare the retention rates and sizing degrees, whereas physical properties of the paper produced are used only for reference purposes.



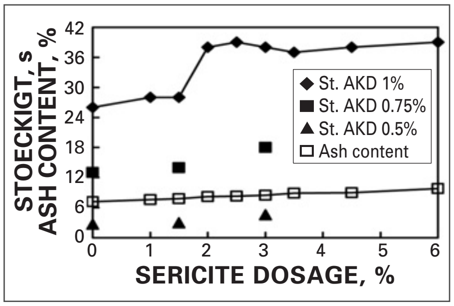
1. Typical SEM diagrams of the nature sericite.

RESULTS AND DISCUSSION

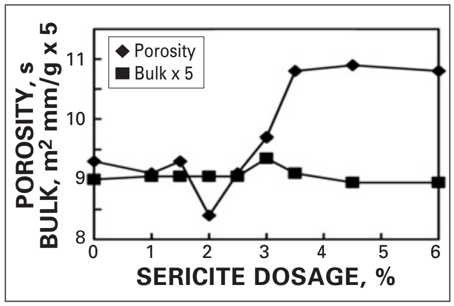
Bench-top experiments

Neutral sizing system. Using a fixed filler loading of 20% and 1% AKD application, we added sericite to replace calcium carbonate in steps (0%-6%), completing nine sets of experiments in this series. To observe the effects of sericite on sizing degrees, we adjusted the AKD amounts to 0.5%, 0.75%, and 1.0%, in six sets of experiments.

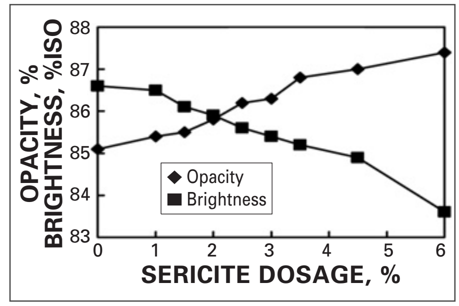
Figure 2 shows the effects of sericite addition and AKD amounts on the sizing degrees and ash contents of the handsheets. When sericite addition was more then 2%, the sizing degree increased by 46%, and remained steady; it did not fluctuate with further increases in sericite addition. This phenomenon suggests that once sericite addition exceeded a critical level, the mineral could effectively adsorb AKD molecules and enhance retention of the size chemical. In the series with different levels of AKD application, we observed the same trend.



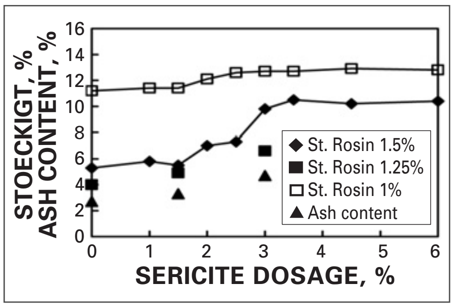
2. Effects of sericite addition on sizing and ash content of sheets in a neutral sizing system.



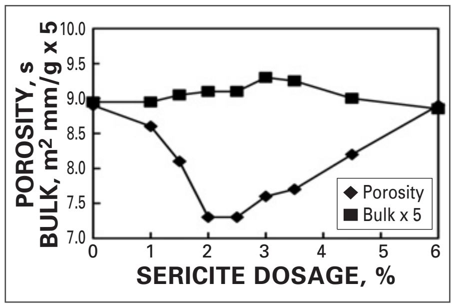
3. Effects of sericite addition on porosity and bulk of sheets in a neutral sizing system.



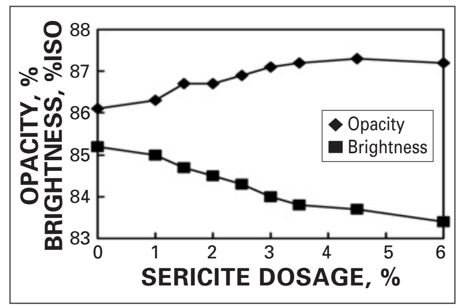
4. Effects of sericite addition on brightness and opacity of sheets in a neutral sizing system.



5. Effects of sericite addition on sizing and ash content of sheets in an acidic sizing system.



6. Effects of sericite addition on porosity and bulk of sheet in an acidic sizing system.



7. Effects of sericite addition on brightness and opacity of sheet in an acidic sizing system.

With regard to filler retention, tests show that ash content increases with increasing sericite addition, and there is a linear correlation between the two. When sericite was added at 3%, the ash content of the handsheets increased 18%, compared to handsheets using only calcium carbonate. These results suggest that the expandable layered structure of sericite, with its highly negative charges, has the capability of effectively adsorbing fines and filler particles in between the flake strata. AKD sizing agent is also effectively retained with the help of sericite.

Figure 3 shows the effects of sericite addition on air permeation and sheet bulk. Air permeation of the sheets decreases with increasing sericite, as the platy mineral covers the sheet surface. At 2% sericite, air permeation dropped to a minimum. Subsequent additional sericite helps raise air permeation; at a 3.5% replacement level, air permeation improved 16%. Sheet bulk at 3% sericite increased about 4%. Other levels of addition, however, do not affect sheet bulk to any significant extent.

Figure 4 shows the effects of sericite addition on opacity and brightness of the sheets. Opacity increases with the level of sericite addition, showing a linear correlation. Opacity increases about 1.5% at 3% addition of sericite. Apparently, the light scattering coefficient of the mineral, coupled with increased retention of filler and fines, helps to raise opacity. However, because sericite has distinctly lower brightness than calcium carbonate, as sericite replaces calcium carbonate, the brightness of the sheets drop. The correlation is also linear with the amounts of addition.

Therefore, in a neutral sizing system, replacing a portion of ground calcium carbonate with 3% sericite raises the sizing degree 46%, ash retention 18%, bulk 4%, and opacity 1.5%. The only drawback is a lowering of brightness by 1.5%. If the main objective is to improve air permeation, then a 10% improvement results at 2% sericite addition.

Acidic Sizing System. At a fixed filler loading of 20% and emulsified rosin size addition level of 1.5%, we replaced kaolin clay with sericite stepwise (0%-6%) through a set of nine experiments. For the size addition variable, we adjusted the rosin amounts to 1.0%, 1.25%, and 1.5%, to observe the effects of sericite on sizing degrees in six sets of experiments.

Figure 5 shows the effects of sericite and emulsified rosin addition amounts on the sizing degree and ash content of the handsheets. When sericite addition exceeds 3%, sizing degree increases 85%. It then remains steady, even with further increases in sericite addition. We observed the same trend in the series with different rosin additions. The observed phenomenon is similar to that of the neutral sizing system. Hence, when sericite addition exceeds a critical concentration, the mineral can effectively adsorb rosin size and increase retention of chemicals. The acidic system is dominated by cationic ions, which complement the high degree of negative charge on sericite particles and produce a synergistic effect, contributing to an even more marked sizing effect. As for filler retention, the ash content increases with increasing sericite addition. When sericite addition exceeds 3%, the ash content increases 13% and keeps steady without further change.

Figure 6 shows the effects of sericite addition on air permeation and bulk of the handsheets. When sericite addition is between 2% and 3.5%, air permeation improves 18%, as compared with pure kaolin clay-filled sheets. Beyond this range, however, the effect of sericite on air permeation is not significant. The effect of sericite on sheet bulk is similar to that of the neutral sizing system. When 3% sericite is added, the bulk increases by 4%, but there is no apparent change at other levels of addition.

Grammage, g/m²	60	60	80	80	100	100	120	120	147	147
Sericite, %	0	7.12	0	6.51	0	4.68	0	3.46	0	3.86
Retention aid flow rate, mL/min	1520	1220	1520	1249	1500	1250	1500	1333	1690	1250
FPR, %	76.4	79.1	75.4	80.3	77.1	82.4	88.9	90.6	85.6	91.7
Size flow rate, mL/min	930	365	480	380	525	430	500	435	500	390
Stoeckigt size, sec	8	10	25	25	38	42	73	84	92	95

II. On-machine sericite trial results on a low speed machine.

Grammage (g/m²)	60	60	70	70	80	80
Sericite (%)	0	2.56	0	2.56	0	2.85
Retention aid flow rate (mL/min)	2300	2242	2480	2400	2343	2150
FPR (%)	56.7	72.7	66.3	72.1	71.1	73.5
Size flow rate (mL/min)	1013	894	1095	936	921	794
Stoeckigt size (sec)	5.7	6.8	8.8	7.8	13.1	12.5

III. On-machine sericite trial results on a mid-speed machine.

Figure 7 shows the effects of sericite addition on sheet opacity and brightness. Opacity increases with increasing sericite addition, showing a linear correlation. At a sericite addition level of 3%, opacity increases 1.2%, whereas sheet brightness drops with sericite addition. The change is also linear.

In summary, in an acidic sizing system, when sericite replaces kaolin clay at a 3% level, the sizing degree can be raised 85%, ash retention 13%, bulk 4%, and opacity 1.2%. The only drawback is a lowering of brightness by 1.5%.

On-machine tests

Low speed machine (operating at less than 300 m/min). We opted for a fine paper mill producing roughly 50 ton/day of wood-free paper for the low speed, on-machine trial. The machine typically runs at 200 m/min and trims at 2.75 m. The mill uses an acidic sizing system. The trial grammages were 60, 80, 100, 120, and 147 g/m². We added sericite to the system, replacing 3.5%-7.1% of the kaolin clay filler. **Table II** shows the experimental results. Because the flow rates of sizing agent, retention aid, and filler were adjusted automatically, we only examined the retention rates and sizing degrees, with and without the sericite addition. The results indicate that with sericite, the retention aid flow rate dropped 11%-26% and the FPR increased 2%-7%. As for the sizing system, within the range of water resistance (increasing from 0% to 25%), the flow rate of size decreased 13%-60%. If we assume a positive linear correlation between the flow rate of retention aid and the FPR, then sericite could raise FPR by 13%-35%.

Mid-speed machine (operating at about 500 m/min). We selected a mid-speed machine at the same mill, with a daily capacity of 150 tons of wood-free paper, a speed of 500 m/min, and trim of 3.55 m, for this series of the trial. This machine also uses an acidic sizing system. The trial grammages were 60, 70, and 80 g/m². Sericite was added to replace 2.6%-2.9% of the kaolin clay. **Table III** shows the results of the trial. Because of the relatively low FPR of the blank (57%-71%), adding sericite could maintain FPR steadily at a 72%-74% level. At this significantly higher retention level improvement, the flow of retention aid decreased 2.5%-4.0%. As for the sizing degree, working from the original water resistance and then adding sericite, the flow rate of sizing agent could be reduced by 12%-15%.

High speed machine (operating at greater than 1000 m/min). The trial on the high speed machine was carried out in a different mill. The machine produces wood-free paper at a 1173 ton/day capacity. It uses neutral sizing system, runs at 1390 m/min, and trims at 9.77 m. The trial grammage was 60 g/m². We replaced 2%-4% of the precipitated calcium carbonate (PCC) filler with sericite during the experiments. **Table IV** shows the results of the trial. Adding sericite lowered the amounts of retention aid and bentonite in the dual system by 8% each, while the FPR increased 15%. As for sizing, when maintaining a constant level of water resistance (0%-25% increase), the amount of sizing agent needed was reduced by 10%.

Notably, the thickness of the sheet will first increase with increasing sericite addition, and then drop with further increases. The decrease in thickness does not appear to be related to increased ash retention. This result is similar to the observation of the bench-top study. The sheet formed on the high speed machine, with sericite addition, also has superior surface properties. Formation, air permeation, and roughness all improved. Each 2% addition of sericite causes a 1% ISO drop in brightness.

Reaction mechanism

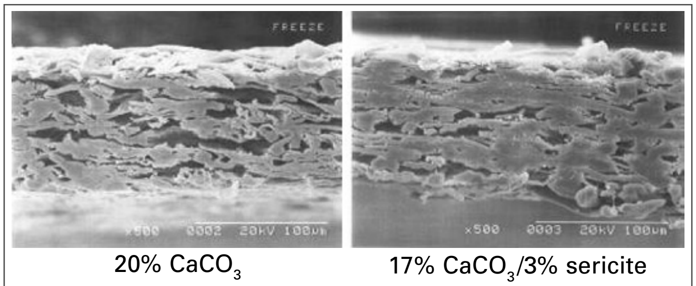
Asselman and Garnier [6] proposed that the flocculation mechanism of bentonite is to transfer deactivated bridging polymer on the fiber surface to freshly activated polymer ends through high shear force. When bentonite is added to the system, the montmorillonite particles contained therein can effectively flocculate the chemicals, fines, and fillers with higher bond strengths.

The main role of sericite as functional filler in the retention system is to provide a strong link between fibers and polymers, chemicals, fines, and fillers. The effects probably derive from the platy nature of sericite's structure, which has negative charges on the plate surfaces and positive charges on the edge of the plates [8]. During dispersion of the mineral in water, mechanical agitation will cause part of the sericite strata to defoliate and the inter-ply distances generally expand. When the distances are greater than the diameters of most long-chain polymers, the charge characteristics will enable effective adsorption of fines and chemicals. We speculate that during drainage, and coupled with a high aspect ratio, the sericite plates will form irregular, three-dimensional (3-D) cross-stacked networks at sufficient concentrations. Then, because of the ionic forces and Van der Waal's forces, the networks will entrap and adsorb fines and filler particles to increase retention. This proposed mechanism may be confirmed by the SEM diagrams of handsheet cross sections. **Figure 8** shows the SEM diagram of a handsheet cross section. This proposed mechanism is summarized in **Figure 9**.

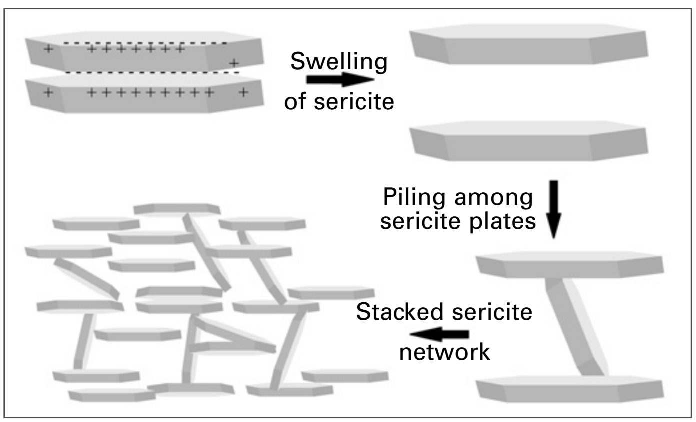
Before the concentration of sericite is sufficient to form crisscross networks, the largely flat pigment plates will cause a drop in air permeation of the paper. Upon formation of the 3-D networks, and with the platy nature of the topmost sericite layers, smoothness and bulk of the sheets improve. As the average particle size of sericite is much greater than that of the calcium carbonate, excessive amounts of sericite will probably harm air permeation and sheet bulk. These effects may be confirmed by the SEM micrographs of the frontal surfaces of the handsheets. **Figure 10** shows SEM

Sericite (%)	0	2	4
Retention aid addition (ppm)	240	220	230
Bentonite addition (ppm)	2500	2300	2300
FPR (%)	57.1	65.3	66.5
Size addition (%)	1.05	0.95	0.95
Cobb value (g/m^2)	22.0	23.2	22.0
Cobb value (g/m^2)	22.0	23.2	22.0
Thickness (µm)	77	79	78
Air permeation (mL/min)	701	557	494
Roughness BS	110	98	97
TS	123	120	127
Formation index	25.8	38.1	34.9
Brightness (% ISO)	91.8	90.7	89.7
Ash content (%)	12.8	13.2	13.0

IV. On-machine sericite trial results on a high speed machine (grammage = 60 g/m^2).



8. Typical SEM diagrams of the lateral view of handsheet.

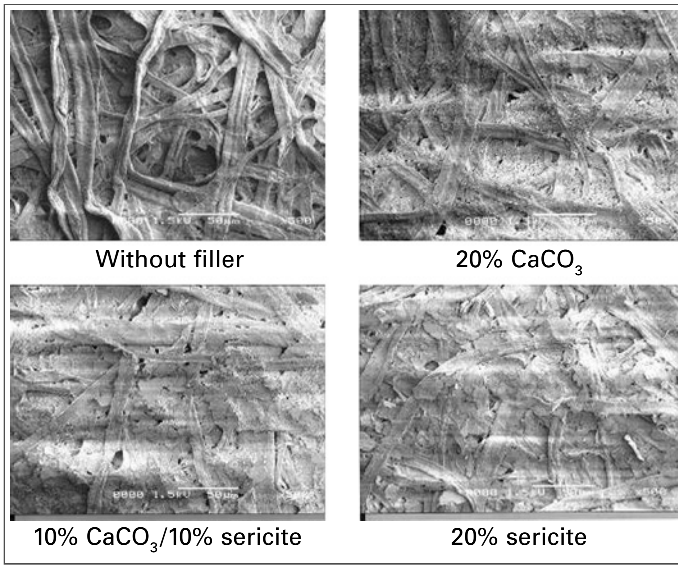


9. A proposed sericite reaction mechanism.

micrographs of the handsheet without filler, with 20% $CaCO_3$, with 10% $CaCO_3$/10% sericite, and with 20% sericite, respectively. The hypothesis of a 3-D edge-surface stacked sericite network will lead to the further prediction that sericite addition will help dewatering efficiency of wet webs at the forming and pressing sections of paper machines. That is conducive to lowering steam input or raising machine speed.

CONCLUSIONS

As a functional filler, sericite has been proven, through bench-top and on-machine trials, to effectively raise FPR and retention of chemicals, regardless of the acidic or neutral sizing systems. In a neutral sizing system, when sericite replaces GCC at 3% level, the sizing degree, ash content, bulk and opacity of the handsheets increase 46%, 18%, 4%, and 1.5%, respectively.



10. Typical SEM diagrams of the front surface of handsheet.

Only brightness decreases (1.5%). In an acidic sizing system, however, the same level of kaolin replacement by sericite results in increases in sizing degree, ash content, bulk, and opacity of 85%, 13%, 4% and 1.2%, respectively. Again, the brightness is lowered by 1.5%. Regardless of machine speeds, the on-machine trials suggest that partial sericite replacement of traditional fillers not only increases FPR, but the necessary flow rates of retention aid, size, and filler are also reduced. The high-speed machine trial provides encouraging improvements in thickness, formation, air permeation and roughness of the sheets as well. **TJ**

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from Sunshine Mineral Company (Taiwan) and part of mill trials in the Long Chen Paper Co., Ltd. (Taiwan.)

LITERATURE CITED

1. Anon. "The Hydrocol system," Allied Colloids/Ciba Inc., Basel, Swiss, 2001.
2. Swerin, A. and Odberg, L., *Nordic Pulp Paper Res. J.* 8(1): 159(1993).
3. Gerli, A., Oosterhof, F., and Keiser, B.A., "An inorganic nanosize particle–Part of a new retention/dewatering system under commercial development", p. 264-269 SPCI symposium, Stockholm, Sweden. (1999).
4. Clemencon, I. and Gerli, A., *Nordic Pulp Paper Res. J.* 14(1): 23(1999).
5. Asselman, T. and Garnier, G., Colloids Surf. A 168(2): 175(2000).
6. Asselman, T. and Garnier, G., *J. Pulp Paper Sci.* 27(8): 273(2001).
7. Liu, W., Ni, Y. and Xiao, H., *J. Pulp Paper Sci.* 29(5): 145(2003).
8. Tsai, M.S. "A study of mineral pressing process and economic evaluation of sericite and pyrophyllite in the Shiang-Yang area, Taitung." NSC75-0405-E006-21 rep. Taiwan, 1989.
9. Scott, W.E., Abbott, J.C., and Trosset, S. *Properties of paper: an introduction.* TAPPI PRESS, Atlanta, Georgia, USA, 1995, p. 137.

Received: December 21, 2003
Revised: March 24, 2004
Accepted: February 24, 2004

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the June *Solutions! for People, Processes and Paper* magazine (Vol. 87 No. 6).

INSIGHTS FROM THE AUTHORS

Sericite is a swelling, layered inorganic mineral of the mica family that is mined in eastern Taiwan. It has similar properties as those of bentonite and is potentially useful in the wet-end and coating processes of papermaking application. This study represents the first step in developing the material for papermaking purposes. We hope to establish a whole spectrum of data demonstrating its applicability.

The most difficult part of this study was trying to modify the variables under the fully automated paper machine conditions to achieve the goals of the study, without significantly disturbing the operation of the machine and the product quality. After much communication with the production line supervisors and selection of appropriate ranges of adjustments for the variables and the sequence of trials, we managed to obtain useful on-machine trial results.

Paper mills and chemical suppliers could use the results of this study, in conjunction with the adjustment of wet-end chemistry, to achieve a more stable wet-end system and further enhance the retention of fines, chemicals, and fillers, while improving paper formation, air permeation, smoothness, and sheet bulk.

—Yuan-Shing Perng

Perng is with Da-Yeh University, Department of Environmental Engineering, 112 Shan-Jiau Rd., Da-Tsuen, Chang-Hwa, 51505, Taiwan; email ysperng@mail.dyu.edu.tw. Wang is with the Taiwan Forestry Research Institute, Division of Wood Cellulose, 53 Nanhai Rd., Taipei 100, Taiwan; email iwang@serv.tfri.gov.tw.

Perng