A new process to produce high-quality PCC by the causticizing process in a kraft pulp mill

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ABSTRACT: A new process has been developed to produce high-quality precipitated calcium carbonate as a paper filler by using the causticizing process in a kraft pulp mill. The causticizing process converts green liquor into white liquor in the kraft pulp mill, producing calcium carbonate as a by-product. If the calcium carbonate (CCC) produced by causticizing could be extracted from the process and used as a papermaking material and if makeup quicklime for white-liquor generation were supplied, rotary lime-kiln operation could be reduced or eliminated, and the consumption of fuel oil and the resulting discharge of carbon dioxide gas could be reduced.

However, conventional CCC includes nonuniform particles with large diameters, which cause severe abrasion of plastic wire on paper machines and poor opacity of paper when it is used as a paper filler. To overcome these disadvantages, the challenge was to find a way to control the morphology of CCC produced from causticizing in the same manner as that of commercial precipitated calcium carbonate (PCC). In conventional causticizing, green liquor is mixed with quicklime to produce CCC and white liquor in two steps: slaking of quicklime with water, and causticizing of the slaked lime with sodium carbonate. When these two reactions were separated and precisely controlled, it was found that CCC was obtained in various forms such as rice-, spindle-, and needle-like particles, some of which demonstrated high opacifying ability and little plastic-wire abrasion when used as paper fillers. In particular, the needle-like aragonite CCC crystal produced in this way demonstrated higher opacity in papermaking than commercial aragonite PCC.

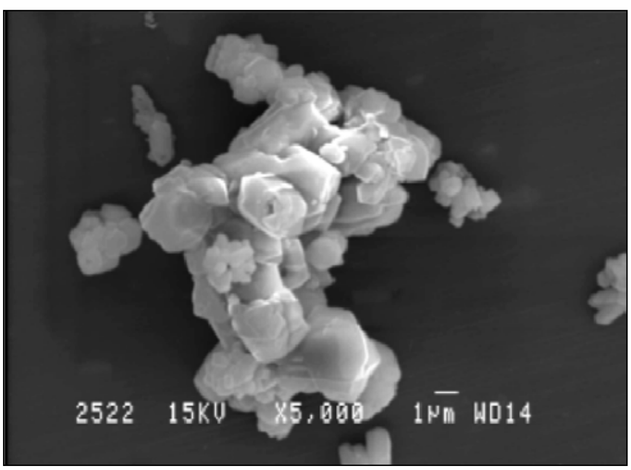
Based on these laboratory findings, the reactor was scaled up successfully to a mill-scale plant producing needle-like CCC at the Iwakuni mill of Nippon Paper Industries. This plant has been producing good-quality CCC for paper filler and good-quality white liquor for the last five years.

Application: An innovative process has been developed to produce high-quality precipitated calcium carbonate as a paper filler from the causticizing process in a kraft pulp mill. By using this process, rotary lime-kiln operation could also be reduced or eliminated, and the consumption of fuel oil and consequent discharge of carbon dioxide gas could be reduced.

With the recent growth of alkaline papermaking, precipitated calcium carbonate (PCC) has come to be used extensively as a paper filler because of its contribution to brightness and opacity and its low cost. Recent market demands for lighter-basis-weight papers and higher paper machine speeds require that paper fillers have higher opacifying ability and lower plastic wire abrasion.

PCC is produced primarily by the carbonation process, which involves bubbling boiler fuel gas containing carbon dioxide into a slurry of calcium hydroxide (slaked lime) in an agitated reactor. Many paper mills have installed on-site PCC manufacturing plants, which give papermakers more advantages in controlling paper quality and production cost.

Another manufacturing method for PCC is the causticizing reaction between sodium carbonate and calcium hydroxide used in the soda lime process and in kraft pulping [3]. Kraft pulping uses this reaction to convert green liquor to white liquor, with calcium carbonate produced as a by-product. Ordinarily, this causticizing calcium carbonate (CCC), known as "lime sludge" or "lime mud," is calcined in a rotary lime kiln and recirculated in the causticizing process. CCC is obtained at very low cost because it is a by-product of the preparation of white liquor. If CCC could be extracted from the process to be used as a papermaking material and replaced by quicklime from an outside supplier, the rotary lime-kiln operation could be bypassed. This would contribute to a significant cost saving of fuel oil for rotary lime-kiln operation and the consequent reduction of carbon dioxide gas emissions.



1. SEM photograph of conventional CCC.

However, conventional CCC includes massive, nonuniform particles with large diameters, as shown in the scanning electron micrograph (SEM) in **Fig. 1**. These particles cause serious problems of wire abrasion and poor opacifying ability when CCC is used as a filler for papermaking. The challenge was therefore to control the morphology of CCC by means of the methods used in commercial PCC manufacture. This approach succeeded in producing various shapes of calcium carbonate using the causticizing reaction, greatly reducing wire abrasion and improving opacifying ability. In particular, the needle-like aragonite crystal CCC that was produced demonstrated remarkably high opacifying ability. Based on these laboratory findings, the reactor size was scaled up successfully to a mill-scale plant producing the needle-like form of CCC in the Iwakuni mill of Nippon Paper Industries. This plant has produced good-quality paper filler. This paper reports the technical development and the advantages of this system.

EXPERIMENTAL PROCEDURE

Model experiment of causticizing reaction

A flask of 1L volume, including a water bath for heating, a tube pump for feeding solutions, and a stirrer, was used as a reactor for the model experiment of the causticizing reaction. Model green liquor (Na_2CO_3: 100g/l and Na_2S: 35g/l as Na_2O) and commercial quicklime were used as chemical inputs. As a control of the conventional causticizing reaction, green liquor was heated to 90°C and then quicklime was added with stirring at 400 rpm. The reaction time was 60 minutes. As a model experiment for the improved method shown in Fig. 2(b), the following two-step reaction was designed. In the first step, quicklime was added to the flask, which was filled with water and stirred at 400 rpm to achieve slaking. In the second step, green liquor was then added to the flask, and the causticizing reaction was carried out. The reaction temperature was varied from 50°C to 90°C depended on the trial [10,11]. After these reactions, the CCC was washed out with water and subjected to quality analysis.

Preparation of needle-like CCC

In the 1-L flask, 50 g quicklime was mixed with weak liquor at a quicklime concentration of 20% to 40% by weight to prepare lime milk. Then the slaked lime was causticized with green liquor (Na_2CO_3=100g/l, Na_2S=34g/l, NaOH=6g/ l, expressed as Na_2O) under the following conditions: green liquor loading rate of 0.22ml/min/g (quicklime), loading period of 60 min, temperature of 40°C to 95°C, and high-speed agitation. Secondary particles were produced by mixing additional slaked lime and green liquor into the primary particle slurry with mixing ratios of primary to secondary particles ranging from 1:1 to 1:4. For example, a mixing ratio of 1:4 means that the dry weight of secondary particles became four times as great as that of the primary particles by the additional reaction, which this report terms the “secondary reaction”. The reactor size was scaled up to 250 L for the pilot test and to 25 m^3 for mill-scale production.

Handsheet preparation

To hardwood bleached kraft pulp having a Canadian standard freeness of 300 ml, researchers added and stirred 0.2% of sizing agent (alkyl ketene dimer), 0.5% of aluminum sulfate, fillers, and 200 ppm of retention aid (polyacryl amide). Then handsheets (64g/m^2 of basis weight) with various filler contents ranging from 3% to 25% were prepared by varying filler dosage. To avoid the variation of paper properties caused by differences in filler particle size, the average particle size of produced CCC was adjusted to approximately 2 μm by a dispersing treatment with a sand mill.

Test methods

Wire abrasion was measured by the Japan Filcon abrasion tester with its polyester wire to evaluate wire-weight loss after the abrasion test (90 min and slurry concentration of 2%). Polymorphic forms of calcium carbonate were measured using an X-ray diffraction analyzer (RAD-C from Rigaku Ltd.). For the calculation of calcite and aragonite content, a peak at 2θ=29.4 was used to represent calcite content, and a peak at 2θ=26.2 was used to represent aragonite content in the calcium carbonate. These contents were quantitatively calculated by peak intensity ratios as in [11]. Technicians used a leaf tester (Miyamoto Machinery Inc.) to measure the drainage time of white liquor at a 20-mm thickness of lime-mud cake.

RESULTS AND DISCUSSION

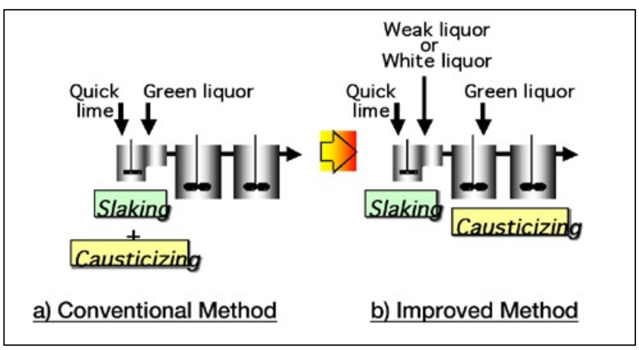
Morphology—control of CCC

In the conventional causticizing process shown in **Fig. 2(a)**, the green liquor is mixed with quicklime to produce caustic soda and calcium carbonate following the two reactions (1) and (2): slaking of quicklime with water in green liquor, and causticizing of the slaked lime with sodium carbonate in green liquor [1].

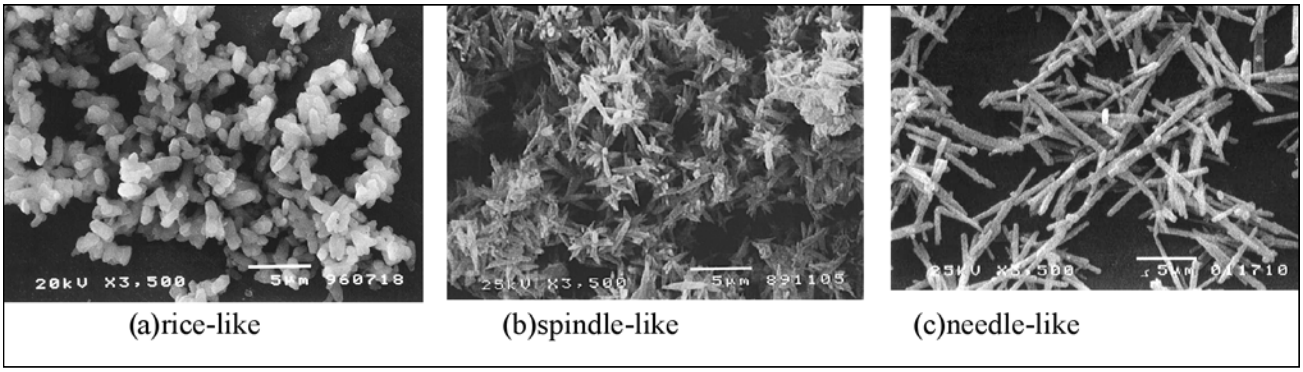
Slaking: $CaO + H_2O \rightarrow Ca(OH)_2$ (1)

Causticizing: $Ca(OH)_2 + Na_2CO \rightarrow CaCO_3 + 2NaOH$ (2)

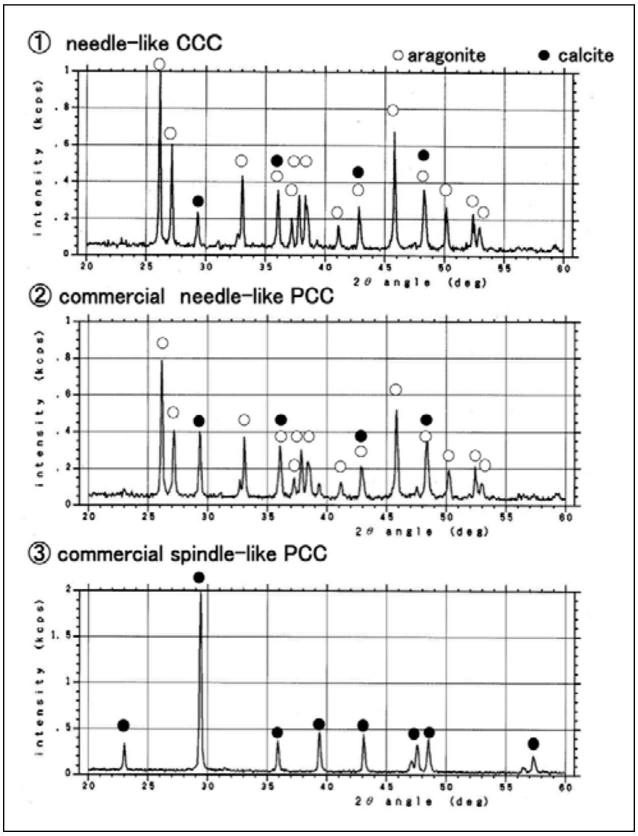
However, the timing of the change from slaking to causticizing is unclear because quicklime and green liquor are added to the slaker continuously and simultaneously. Several papers have reported that the slaking reaction is delayed in a solvent



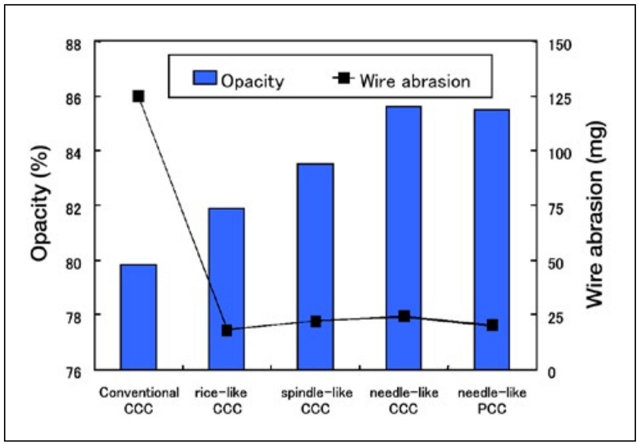
2. Schematic of improved causticizing process for morphology control of CCC.



3. SEM photograph of morphology-controlled CCCs.



4. Powder XRD spectra of needle-like CCC and commercial PCCs.



5. Wire abrasion and paper opacity of produced CCC (filler content 15%, basis weight 60 g/m²).

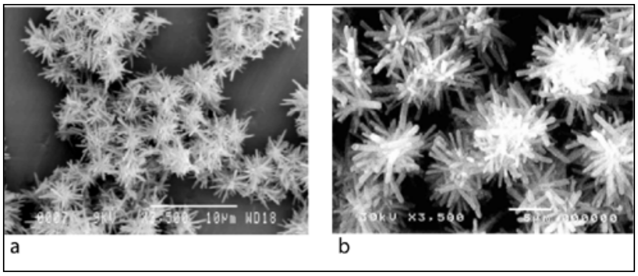
containing sodium carbonate and sodium sulfate, which are components of green liquor [2-4]. The second causticizing reaction may in fact start before quicklime has been slaked sufficiently. The two reactions therefore seem to take place very heterogeneously. This is considered to be the reason that the CCC particles produced are very heterogeneous in terms of particle shape and size, as shown in the SEM in Fig. 1.

For the improved process, we separated the two reactions, as shown in **Fig. 2(b).** In the slaker, quicklime was first slaked with weak liquor or white liquor to prepare lime milk, and then in the downstream causticizers, the slaked lime was causticized with green liquor to yield white liquor and CCC. By controlling the conditions of each reaction, various shapes of CCC in the form of rice-, spindle-, or needle-like particles could be obtained successfully, as shown in **Fig. 3**.

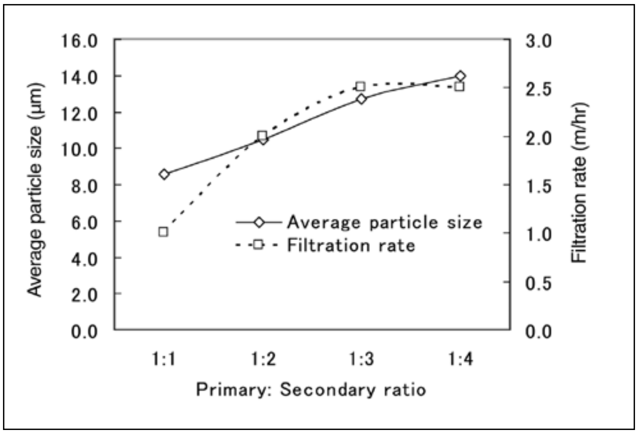
We found the important factors for morphology control to be slaking solution, activity of quicklime, lime slurry concentration, reaction temperature, loading time of green liquor, and agitation [11-13]. The most important in these factors was found to be a slaking solution in which the carbonate-ion concentration is relatively low. Instead of green liquor, weak liquor or white liquor was used as the slaking solution so that changes in the overall alkaline balance in the causticizing process could be avoided. In the experimental procedures, we describe the laboratory reaction conditions to produce needle-like CCC (see the authors' reports [11-13] and patents [5-8] for more details). When the temperature of the causticizing reaction was decreased, the shape of the needle-like CCC changed to a clustered shape consisting of smaller needles.

Quality of the morphology-controlled CCC

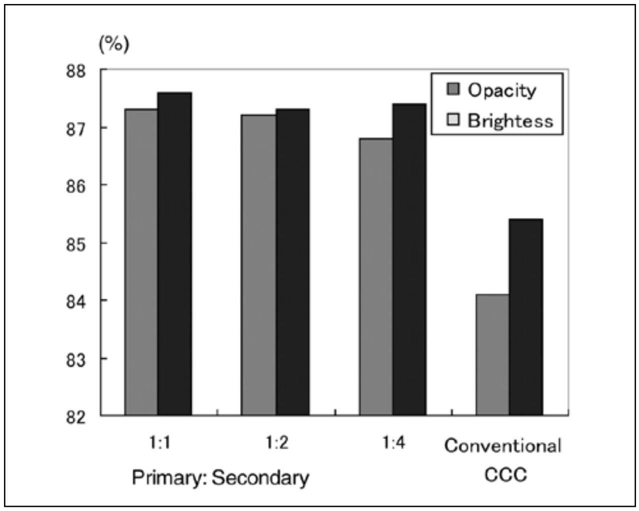
The polymorphic forms of CCC produced were investigated by the powder X-ray diffraction (XRD) method. The rice- and spindle-like forms of CCC were found to consist of calcite crystal, while the needle-like CCC was found to be aragonite crystal with a higher aragonite content than a commercial aragonite PCC, as shown in the XRD spectra in **Fig. 4**. Results for wire abrasion and paper opacity for the CCC produced are shown in **Fig. 5**. Morphology control improved



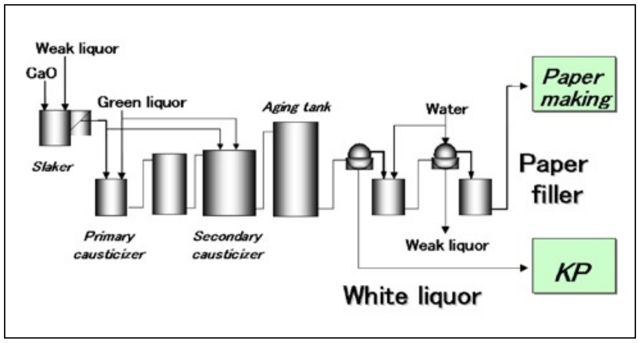
6. SEM photograph of primary (a) and secondary (b) particles of needle-like CCC.



7. Improvement of white liquor separation from CCC slurry by the secondary reaction.



8. Paper property change by the seconday reaction. (Handsheets basis weight: 64g/m², Ash content :15%)



9. A schematic figure of production flow of the mill plant for the needle-like CCC.

both these properties. In particular, the aragonite needle-like CCC was found to possess a remarkable opacifying ability as a filler, better than that of commercial aragonite PCC. The authors believe that aragonite crystal is relatively easy to produce by the causticizing process rather than by the carbonation process. It can be found in their other papers [11] that the high temperature and strong alkalinity of the causticizing process, which are very difficult to obtain in the carbonation process for making PCC, are preferable for formation of aragonite crystals.

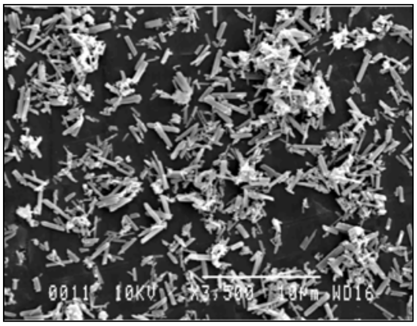
Improvement of white liquor separation from the CCC slurry

The next step was the scaleup of the reactor to industrial production size, but technicians encountered a problem with white liquor separation from the CCC slurry for the production of needle-like CCC.

The average particle size of the CCC produced is much smaller than that of ordinary lime mud, as can be seen in **Fig. 6(a)**, and therefore white liquor separation from the CCC slurry becomes significantly more difficult. Because the main purpose of the causticizing process is to produce white liquor, the production of CCC must not negatively influence the operation of that process. To overcome this problem, both mechanical devices to aid liquid separation and modifications to improve reaction conditions were investigated. As a result, the authors developed the following two-step causticizing process. In the first step, the primary particles of needle-like CCC are produced as described previously, and in the second step, a certain amount of slaked lime and green liquor are added continuously to the primary particles. By this additional reaction, the primary particles grow and aggregate into secondary particles, as shown in **Fig. 6(b)**. This results in improved white liquor filtering characteristics, as shown in **Fig. 7**; however, additional dispersion treatment with a sand mill becomes necessary to adjust the size of the secondary particles and make them suitable for papermaking. We found the optimal reaction ratio of secondary versus primary causticizing to be 1:3 to 1:4, which balanced white liquor separation efficiency (Fig. 7) and the impact of filler quality on paper properties (**Fig. 8**).

Development and operation of a mill scale plant to make needle-like CCC

These laboratory research findings were used to scale up to a mill-scale plant in the Iwakuni mill of Nippon Paper, which is an integrated mill producing pulp and various kinds of paper products such as coated paper, printing paper, and computer printer paper. This mill-scale plant started operation in 2000 to manufacture needle-like CCC. A schematic of



10. SEM photograph of the needle-like CCC produced by the mill plant and weakly dispersed by a sand mill.

		Conventional CCC[1)] (non-uniform)	Needle-like CCC		Commercial PCC (needle-like)
			primary	secondary[1)]	
(Powder Properties)					
Polymorphic forms		**calcite**	**aragonite**		**aragonite**
Ave.particle size	(μm)	2.1	2.6	1.2	1.5
Surface area	(m^2/g)	3.5	8.6	7.8	8.5
Brightness	(%)	95.5	97.5	97.2	97
Wire abrasion	(mg)	121	12	20	19
(Paper properties)					
Basis weight	(g/m^2)	64.0	63.2	63.6	64.9
Filler content	(%)	18.9	18.8	17.2	18.3
Density	(g/cm^3)	0.62	0.57	0.6	0.59
Opacity	(%)	85.4	89.8	89.4	89.1
Light scattering	(cm^2/g)	559	756	717	68.8
Brightness	(%)	84.2	86.6	86.1	85.7

1)These were dispersed by a sand mill before measurements.

I. Comparison of powder and paper properties between CCC and commercial PCC.

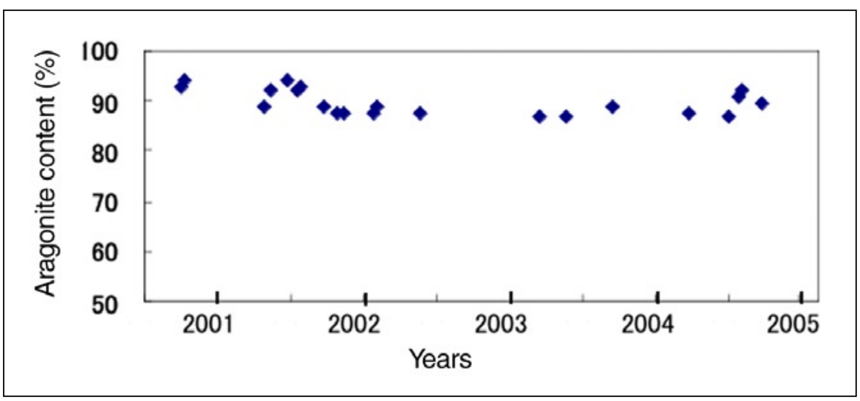
the production flow in the mill-scale plant is shown in **Fig. 9**. Note that, in the CCC process, the source of carbonate ion is sodium carbonate in green liquor instead of carbon dioxide gas as in the carbonation process. **Fig. 10** shows an SEM photograph of the CCC produced by the mill-scale plant after mild dispersion by a sand mill, showing that the final CCC product consists of small needles having an aspect ratio similar to commercial aragonite PCC.

Table I shows the quality of the needle-like CCC produced by the mill plant. Brightness, opacity, and wire abrasion of the CCC are comparable to commercial PCC. In particular, the primary particles are of better quality than the secondary particles in terms of opacity, brightness, and paper bulk. In the future, the authors intend to use the primary particles rather than the secondary particles as the main reaction product. There is therefore a need to identify other white-liquor separation systems that can extract and wash out even the primary particles efficiently.

This mill-scale plant has produced both white liquor and needle-like CCC successfully, as shown in Fig. 9. A high aragonite content of around 90% in the needle-like CCC has been consistently observed for five years, as shown in **Fig.11**.

The mill production cost of the needle-like CCC was assessed. Variable costs of CCC production consist of payments for raw materials, operators' wages, and utilities such as electricity, steam, and water. The CCC is produced by the causticizing reaction of quicklime and green liquor. Only the quicklime was taken into account as a raw material cost because the green liquor circulates in the causticizing process. The cost of quicklime was assumed to be approximately 3/4 of the total production cost. Therefore, we calculated the CCC production cost to be approximately 4/3 times as much as the cost of the quicklime.

In addition, the CCC process is advantageous and cost-effective because it can reduce fuel-oil consumption for operation of the rotary lime-kiln. The authors have found that the amount of fuel oil necessary for calcining lime sludge in the kiln is 90 liters/ton of $CaCO_3$ [9]. This oil consumption was reduced when CCC was extracted from the causticizing process and used as a paper filler. Hence, the CCC process is expected to reduce the lime-kiln operating cost by more than 20%, depending on the price of oil. Therefore, the use of CCC is recommended to improve mill profitability.



11. Progress of the mill production of the needle-like CCC.

CONCLUSIONS

1. We found that various particle shapes (rice-, spindle-, and needle-like particles) can be obtained for causticizing calcium carbonate (CCC) by separating and precisely controlling the two reactions of slaking and causticizing.
2. In particular, the needle-like aragonite crystal CCC that was produced demonstrated remarkably good opacifying ability when used as a paper filler.
3. To improve white liquor separation from needle-like CCC, a secondary causticizing process has been devel-

oped in which the CCC particles aggregate and grow larger, resulting in improved white liquor filtering characteristics.

4. Findings from the laboratory reactor have been successfully used to design a mill-scale plant to co-produce white liquor and needle-like CCC. This plant has been running for five years, producing white liquor and a paper filler of good quality and low cost.

In summary, a new process has been successfully developed that uses the causticizing process in a kraft pulp mill to produce a high-quality calcium carbonate material, similar to precipitated calcium carbonate, for use as a paper filler. This process has the potential to reduce fuel-oil consumption and carbon dioxide emissions because rotary lime-kiln operation can be reduced or even eliminated. **TJ**

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INSIGHTS FROM THE AUTHORS

To meet today's market demands for high-quality, low-cost, environmentally friendly paper products, the industry needs new production technologies for paper fillers that offer these benefits.

This work presents the first process that produces both white liquor for kraft pulping and high-quality calcium carbonate filler particles. In addition, with purchased quicklime makeup, it reduces or eliminates the need for lime kiln operation, with its associated fossil fuel consumption and generation of carbon dioxide gas.

The most difficult aspect of this research was achieving good control of the morphology of the calcium carbonate particles. After considerable investigation, this was achieved by separating and precisely controlling the slaking and causticizing reactions.

We found the aragonite crystal of calcium carbonate easier to produce by the causticizing process than by the carbonation process that is commercially used. We discovered that the high temperature and strong alkalinity of the causticizing process, which are difficult to attain in the carbonation process, are preferable for formation of aragonite crystals.

This information could be very useful for integrated kraft pulp and paper mills seeking to reduce their energy consumption and greenhouse gas emissions while obtaining a valuable by-product from the causticizing process. It is planned to expand this process into other mills in Japan and thence worldwide.

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