Application of In Situ Calcium Carbonate Process for Producing Papermaking Fillers from Lime Mud

Jung Soo Han, Dong Suk Kang, and Yung Bum Seo

ABSTRACT: A portion of the lime mud formed during the causticizing process in the recovery process of kraft pulping should be purged from the calcium cycle as waste before it is fed to the lime kiln; this ensures that the quality of the pulp and pulping chemicals is maintained. The discharged greenish-gray lime mud, which is often disposed as an industrial waste, has been transformed herein into a high-quality papermaking filler via the hybrid calcium carbonate (HCC) and post-HCC (pHCC) technology. Initially, the lime mud was heat-treated and then ground to small-size particles. The ground lime mud was preflocculated with calcium oxide by ionic polymers, and carbon dioxide was injected to the flocs to produce lime mud HCC (LHCC). To produce lime mud pHCC (pLHCC), only the ground lime mud was preflocculated first, calcium oxide was added next, and finally, carbon dioxide was injected to the flocs. The resultant products, LHCC and pLHCC, gave brightness as high as that of the ground calcium carbonate (GCC) in paper while a little higher brightness for pLHCC than for LHCC. They also enabled to increase bulk, stiffness, and tensile strength. Application of the LHCC and pLHCC technology to the lime mud could save waste disposal expenses and produce better-quality paper.

1. INTRODUCTION

Kraft pulping is the most commonly used wood pulping process in the pulp and paper industry for producing cellulose fibers; this is because of its capability to produce high-strength fibers. Energy recovery from black liquor incineration and closed-chemical recovery of the commonly used chemicals, such as sodium hydroxide (NaOH), enable a modern kraft pulp mill to become self-sufficient in terms of steam and electric energy supply, as well as chemical supplies. During the causticizing process in the chemical recovery system, sodium carbonate in green liquor reacts with slaked lime, which mainly comprises calcium hydroxide (Ca(OH)₂), to recover sodium hydroxide (NaOH) and precipitate the greenish-gray lime mud. The lime mud contains various nonprocess elements (NPEs), such as Ca, Mg, K, Mn, S, Zn, and Cu, which accumulate from the repetitive pulping and chemical recovery processes. A portion of the lime mud is purged from the closed-chemical recovery system to maintain the quality of the recovered chemicals by decreasing the amount of NPE and other foreign materials. The purged lime mud is an industrial waste, which must be responsibly discarded, albeit at an expense.

The utilization of the purged lime mud has been studied and reported extensively, especially for use as construction materials, landfill cover, bio-composite filler, CO₂ or SO₂ sorbent, etc. Meanwhile, for using lime mud as a papermaking filler, Said et al. washed the lime mud repetitively, dried, and ground it to obtain a 6% brightness improvement. The control of the causticizing step during the kraft pulping process produced precipitated calcium carbonate (PCC) of various shapes.

Low brightness is the main barrier for using raw lime mud as a papermaking filler. The color of the lime mud is usually dark green and is known to be formed by the interaction between a sulfur compound and aluminosilicate (main component of kaolinite) in the green liquor. For use as fillers during papermaking, the processed lime mud should have high brightness and contain minimal harmful substances.

Recently, new type of papermaking fillers known as the hybrid calcium carbonate (HCC) and the post-hybrid calcium carbonate (pHCC) were introduced. During the preparation of HCC and pHCC, ground calcium carbonate (GCC) was preflocculated with calcium oxide (HCC) and without calcium oxide (pHCC) using ionic polymers to construct soft...
flocs, respectively. For the pHCC, calcium oxide was added after formation of GCC flocs. Then, the newly formed PCC was attached to the surface of the flocs via an in situ PCC formation process. The resultant material is called the HCC and pHCC, respectively, and both of them increased the brightness, bulk, and tensile strength simultaneously and maintained the smoothness of the paper during the paper-making process. It was found that the pHCC was more rigid and brighter than HCC.

We had investigated the possibility of replacing GCC with lime mud during the preparation of HCC. In this paper, we investigated various aspects of lime mud HCC (LHCC) and lime mud pHCC (pLHCC) in detail by application of X-ray fluorescence (XRF) spectroscopy analysis, X-ray diffraction (XRD), NPE contents by energy-dispersive spectrometry (EDS) and thermogravimetric analysis (TGA), and by comparing paper physical and mechanical properties. By reusing the purged lime mud, we may save waste disposal costs and also produce a better-quality paper than the conventional GCC-containing paper.

2. EXPERIMENTAL SECTION

2.1. Materials and Handsheet Preparation. Lime mud, GCC (2.1 μm in mean diameter), and PCC (2.0 μm in mean diameter) were donated by Moorim P&P, located in South Korea, which produces market pulp and printing paper. Calcium oxide was purchased from Korea Showa Chemicals Co. Meanwhile, cationic polyacrylamide (PAM) (C-PAM, MW 5–7 million g/mol +5 mequiv/g) from CIBA Specialty Chemical Korea was used as a retention aid during papermaking at 0.1% based on the dry weight of the handsheet. To make the handsheets, we used a mixture (20:80) of commercial softwood bleached kraft pulp (a mixture of hemlock, Douglas fir, and cedar) and hardwood bleached kraft pulp (a mixture of aspen and poplar) as the wood fiber furnish. These wood pulps were mixed and refined together in a valley beater until the freeness had reached 500 mL of cerebrospinal fluid (CSF) (TAPPI T227 om-99). After mixing with fillers, we produced 80 g/m² basis weight handsheets with ash contents of 30 and 40%. We made the handsheets with exact ash contents by trial and error (30.0% ± 0.3 g, 40.0 ± 0.5%). We ensured the ash contents by heating the samples in the furnace at 525 °C, and measured the remnant. The ash content (TAPPI 211 om-02), bulk (TAPPI T411 om-97), tensile strength (ISO 1924), Bekk smoothness (TAPPI T479 cm-99), and Gurley stiffness (TAPPI T543 om-00) of the handsheets were measured according to the standard methods.

2.2. Preparation of the Lime Mud Filler. To prepare the lime mud filler, we initially treated the raw lime mud at 525 °C for 4 h in a furnace. The heat-treated lime mud (LMHT) was ground (Attrition mill, Oishi Machine Co. Ltd., Japan) to the size of less than 2 μm (>83.7%). To prepare LHCC50 and LHCC70, 25 g of this heat-treated and ground lime mud (LMHTG) was mixed with 14.0 and 32.8 g of calcium oxide, respectively, and each was added to 500 mL of deionized water. To prepare the preocculated floccs, 0.02% cationic PAM, the same PAM used as the retention aid, and 0.02% anionic polymer (Perform SP7200, MW 0.5 million g/mol −5.0 to −3.0 mequiv/mol Hercules) were added by weight sequentially to the mixtures, while stirring at 2000 rpm. As soon as the floccs were formed, carbon dioxide was injected, while stirring at 300 rpm at 30 °C, to form in situ PCC required to produce the LHCC50 (LMHTG/new PCC = 50:50) and LHCC70 (LMHTG/new PCC = 30:70), respectively. We think the newly formed PCC were attached among the lime mud.

We also prepared pLHCC, where the preocculated floccs of the LMHTG only were made using the same ionic polymers as LHCC, calcium oxide was added later to the floccs, and carbon dioxide was injected to the mixture to produce pLHCC50 and pLHCC70, respectively. It was expected the newly formed PCC were attached more on the surface of the floccs and less inside the floccs. Another set of comparative fillers was made by mixing the LMHTG and commercial PCC at ratios of 50:50 and 30:70 (denoted as LMHTG/PCC50 and LMHTG/PCC70, respectively. The diagram for the preparation of fillers is presented in Figure 1.

![Diagram of the filler preparation method.](https://dx.doi.org/10.1021/acsomega.0c05688)

Figure 1. Diagram of the filler preparation method.

2.3. Evaluation of the Properties of the Raw and Modified Lime Mud. The elemental compositions of the raw and modified lime mud were determined by X-ray fluorescence (XRF) analysis (ZSX Primus IV, Rigaku, Japan). The micrographic images of the fillers were taken by a field emission scanning electron microscopy (FE-SEM. S-4800, Hitachi, Japan). The surface chemical compositions of the fillers were determined by an energy-dispersive spectrometer (EDS, energy-dispersive X-ray microanalysis (EDXMA)). X-ray diffraction (XRD), Bruker AXS D8 advance, Germany) with a Cu Kα radiation source (40 kV and 40 mA) was used to evaluate the crystalline phases of the fillers. Thermogravimetric analysis (TGA) was done on the powdered fillers using a thermogravimetric analyzer (TGA/DSC1/1600 LF, Mettler- Toledo, Switzerland) by heating them from 30 to 1000 °C at 10 °C/min in atmospheric air.

3. RESULTS AND DISCUSSION

3.1. Composition of the Raw and Modified Lime Mud. Table 1 shows the compositions of the raw and modified lime mud expressed as oxides, as determined by XRF. The weight loss percentage (WL%) was determined at 1000 °C by TGA, where all of the calcium carbonates were turned to calcium oxide already. The WL% of the pLHCC70 was higher than that of the others. This was because it contained 70% pure calcium oxide already. The WL% of the others was lower as expected. The elemental compositions...
of the lime mud, the heat-treated ones (LMHT), and the heat-treated and ground ones (LMHTG) except pLHCC70 seemed to be identical when their mean values and standard deviations were considered.

The results of the EDS surface elements analysis are shown in Figure 2. Heat treatment did not change the NPE contents (Mg, Al, and Si) in the lime mud. However, the GCC had a low sodium and sulfur content since it did not undergo kraft pulping process. Two lime mud samples had higher contents of sulfur. It was reported that the green-gray color of the raw lime mud was from the reaction of sulfur compound and aluminosilicate. The element, Au was not from the process, but from the FE-SEM coating material.

### 3.2. Morphology and Physical Properties of the Raw and Modified Lime Mud

The LMHTG heat-treated at 525 °C for 4 h and ground to less than 2 μm is shown in Figure 3a, and it was transformed to the LHCC using the HCC technology (Figure 3b). The pLHCC, which is the same as LHCC except that in the preparation stage, the preflocculated flocs consisted of only LMHTG, is shown in Figure 3c. The LMHTG had many small particles while the pLHCC50 and LHCC50 had fewer small size particles, and their mean sizes were much larger than that of the LMHTG.

The XRD analysis results of the raw and modified lime mud are shown in Figure 4. Lime mud dried at 105 °C, (a), was also identified as calcite. The other modified lime muds such as LMHT, pLHCC50, and LHCC50 were all identified as calcite.

We measured the lightness ($L^*$) in the CIE color system of the raw lime mud and its modified forms (Figure 5). From this figure, we observe that the lightness of the raw lime mud was less than 70; however, heat treatment at 525 °C raised it to over 80, and the grinding process to exceed 90. We know that the surface of the raw lime mud was in contact with the green liquor and dried without washing. The organic chromophore on the surface of the raw lime mud was removed by heat treatment. Meanwhile, grinding of the lime mud exposed its inner part to result in increasing its lightness. We believe that the inner part of the lime mud was lighter than the surface because the inner part was in the form of calcium carbonate crystal (calcite). The coating of the lime mud flocs with newly formed PCC via the in situ calcium carbonate process (LHCC50, LHCC70, pLHCC50, and pLHCC70 in Figure 5) increased the lightness further. We then compared the role of the in situ calcium carbonate process to the simple mixing of the LMHTG and commercial PCC (LMHTG/PCC50 and LMHTG/PCC70 in Figure 5) at the same weight composition. We found that the in situ calcium carbonate process (LHCC and pLHCC) resulted in higher lightness. Furthermore, the lightness of the LHCC seemed to be slightly...
lower than that of the pLHCC. We believe it is because in the in situ calcium carbonate formation process, newly formed PCCs were attached more on the surface for pLHCC case than for the LHCC case.

3.3. Paper Physical Properties. The most important factor that determines the utility of the lime mud in printing paper as a filler is its impact on the paper brightness. Figure 6a shows that the ISO brightness of the paper containing LHCC70 and pLHCC70 was higher than that containing the commercial GCC. In Figure 5, LHCC70 and pLHCC70 still gave lower lightness than GCC when compared as fillers, but higher brightness when they were inside the papers (Figure 6a). We measured the lightness (CIELAB L*) of the fillers when they were not the component of the papers. We believe

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Figure 3. Morphology of the raw and modified lime mud: (a) GCC, (b) heat-treated and ground lime mud (LMHTG), (c) LHCC50 that contains 50% LMHTG, and (d) pLHCC50 that contains 50% LMHTG.

Figure 4. XRD results of the raw and modified lime mud. (a) Lime mud dried at 105 °C, (b) lime mud heat-treated at 525 °C for 4 h (LMHT), (c) lime mud HCC50 (LHCC50), and (d) lime mud pHCC50 (pLHCC50).
that the higher brightness of the paper containing LHCC70 and pLHCC60 was due to the large bulk difference between LHCC70- and pLHCC70-containing paper and GCC-containing paper (see also bulk difference in Figure 7c). The ISO brightness of paper depends on the degree of reflectance of visible light at 457 nm wavelength. Therefore, more scattering of the visible light increases brightness. High-density paper transmits more and scatters less visible light than low-density paper. High-bulk paper should make higher light scattering and higher light reflectance. Therefore, we believe the fact that LHCC70 and pLHCC70 gave higher brightness in paper than GCC did despite similar lightness, due to their ability to increase the bulk of paper and to make space between wood fibers for scattering more visible light.

Simply mixing the commercial PCC and LMHTG could not yield a brightness as high as that of GCC (see the LMHTG/PCC case in Figure 6a). The efficiencies of the development of paper brightness for the three different fillers were compared as shown in Figure 6b. For the same amount of LMHTG, pLHCC always gave the highest brightness followed by LHCC. LMHTG/PCC had the lowest brightness.

3.4 Physical Properties of Papers Containing Modified Lime Mud Fillers. The application of the HCC and pHCC technology to lime mud not only enabled us to improve the brightness of the lime mud-containing paper but also improved its essential physical characteristics. Breaking length, which is a measure of the tensile strength after compensating the basic weight differences, has been improved by more than 20% in the LHCC- and pLHCC-containing papers compared to those of the GCC-containing papers at two different filler contents (30 and 40% in Figure 7a). The mixed fillers (lime mud/PCC) yielded an even lower breaking length than GCC. Furthermore, the stiffness and bulk were significantly improved by more than 40% in the LHCC- and pLHCC-containing papers (Figure 7b,c). Simultaneous improvement of tensile strength and bulk was unusual; however, we have explained the mechanism in detail elsewhere. In the micrographs of the LHCC (Figure 3c) and the pLHCC (Figure 3d), they had no small-size filler particles, but GCC (Figure 3a) had plenty. Those small size particles may be located between wood fibers and prevent hydrogen bond formation. The more the small size filler particles, the less the hydrogen bonding between wood fibers. More hydrogen bonding increases tensile
strength. For the LHCC and pLHCC cases with almost no small size filler particles, the increase of hydrogen bonding overwhelmed the effects of tensile strength decrease caused by the increase of paper bulk. We believe that is why the LHCC- and pLHCC-containing paper gave a higher tensile strength than the GCC-containing paper.

However, the surface contour of the papers containing LHCC and pLHCC should be rough due to their large size.
and their smoothness should be lower. In fact, despite their large sizes, LHCC and pHCC are deformable under wet pressing pressure.\textsuperscript{10} Figure 7d shows that the smoothness values of the LHCC- and pHCC-containing papers were approximately equal to those of the GCC-containing papers.

\section{4. CONCLUSIONS}
We investigated the possibility of utilizing the disposed lime mud from the kraft pulping process for manufacturing high-quality papermaking fillers via the in situ calcium carbonate formation process. The raw lime mud was initially dark greenish, turned to a lighter gray by heat treatment at 525 °C, and became brighter by grinding to a diameter of less than 2 \(\mu\)m. Prefloculation of the mixture of this lime mud and calcium oxide using ionic polymers and subsequent application of the in situ calcium carbonate process further rendered the lime mud much brighter. The modified lime mud was referred to as LHCC. The pHCC, which was the same as LHCC except adding calcium oxide later to the lime mud flocs in the preparation process, yielded a slightly higher lightness than the LHCC. Both LHCC and pHCC showed potential to yield higher brightness in paper than the commercial papermaking GCC did and much higher breaking length, bulk, and stiffness without losing smoothness. Turning lime mud into a high-quality paper filler material using LHCC and pHCC technology could enable the calcium cycle in the kraft pulping process to be more a sustainable, cleaner, and profitable process. Otherwise, the lime mud would have to be discarded at an expense.

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\subsection*{Notes}
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