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CONSTITUENTS OF CALCINED LIMESTONE AND THEIR RELEVANCE IN PAPER MANUFACTURING

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ABSTRACT

Quicklime and grit products produced by bench-scale calcining tests of commercial limestone were studied. The quicklime used in the paper industry consists mainly of CaO and $Ca(OH)_2$ which, on slaking, rapidly disintegrate into finely divided particles. The grit that remains after slaking mainly consists of Ca_2SiO_4, SiO_2, $Ca_2Al_2SiO_7$, various Ca–Al–K–Mg–Fe silicate mixtures, nondisintegrating $Ca(OH)_2$ and trace amounts of relict calcite, Fe_2O_3 and slow-reacting CaO. The constituents of the silicates are affected by the impurities of the limestone, whereas the amounts of the residual calcite, slow-reacting CaO and nondisintegrating $Ca(OH)_2$ are mainly controlled by the different conditions of calcination.

Keywords: quicklime, its constituents, paper.

SOMMAIRE

La chaux-vive et les particules abrasives produites lors du grillage de calcaires commerciaux à l'échelle du banc d'essai font l'objet de cette étude. La chaux-vive utilisée pour la fabrication du papier consiste principalement en CaO et $Ca(OH)_2$ qui, lors du grillage, se désagrègent rapidement en particules finement divisées. Les particules abrasives qui restent après le grillage sont constituées en majeure partie de Ca_2SiO_4, SiO_2, $Ca_2Al_2SiO_7$, divers mélanges de silicate Ca-Al-K-Mg-Fe, $Ca(OH)_2$ non-désintégrable, et traces de calcite résiduelle, Fe_2O_3 et CaO à réaction lente. Les constituants des silicates sont affectés par les impuretés du calcaire, tandis que les quantités de calcite résiduelle, CaO à réaction lente et $Ca(OH)_2$ non-désintégrable sont gouvernées principalement par les conditions du grillage.

Mots-clés: chaux-vive, ses constituants, papier.

INTRODUCTION

In the paper-making process, wood chips (lignin, cellulose) are cooked in a pulp-cooking liquor to remove lignin and to produce a cellulose fibre-rich pulp. The pulp is bleached and further treated to produce paper. Most of the quicklime (calcined limestone) consumed in the paper industry is used in the regeneration of cooking liquor, in the Kraft process. A small amount is used in the preparation of cooking liquor in the sulfite process and in the production of bleach. In the Kraft process (Jackson 1964, Boynton 1966), the cooking liquor is made of solutions of NaOH and Na_2S. After cooking, the waste liquor (black liquor) is separated from the pulp, evaporated, fired, and dissolved in water to produce a Na_2CO_3–Na_2S solution (green liquor). Lime is used to causticize this solution to regenerate, in turn, NaOH (caustic soda) for reuse in the cooking liquor:

$$Na_2CO_3 + CaO + H_2O \rightarrow CaCO_3\downarrow + 2NaOH$$

The $CaCO_3$ sludge is calcined to CaO for reuse in the above process. The calcined product is the so-called reburned lime. However, only approximately 90 to 96% of the lime is recovered; the remainder is made up by the addition of new quicklime. In the sulfite process (Britt 1964, Boynton 1966), the cooking liquor is prepared by reacting SO_2 with quicklime or other alkaline bases:

$$2SO_2 + CaO + H_2O \rightarrow Ca(HSO_3)_2$$

However, today this process uses little quicklime, and the trend is away from quicklime, as most bisulfite liquor is prepared from limestone or other alkaline bases such as MgO, NH_3, *etc.*; furthermore, the calcium bisulfite waste-liquor creates a costly waste-disposal problem, and the alkaline base cannot be recovered. In the bleaching of pulp (Boynton 1966), quicklime is used to produce calcium hypochlorite to provide a stable bleach:

$$Cl_2 + Ca(OH)_2 \rightarrow Ca(OCl)_2 + H_2$$

Other uses for quicklime in the paper industry include chemical coagulation or softening of plant-process water and pH control in treating pulp-mill-waste effluents.

Commercial quicklimes used in the paper industry generally contain (wt.%): CaO 95–98, MgO 0.3–2.5, SiO_2 0.2–1.5, Fe_2O_3 0.1–0.4, Al_2O_3 0.1–0.5, H_2O 0.1-0.9 and CO_2 0.4-1.5. According to the 1984 Annual Book of ASTM Standards, the available lime should be greater than 90%, the impurities ($SiO_2 + Al_2O_3 + Fe_2O_3$) less than 3% and, for hypochlorite production, Fe_2O_3 should be less than 0.3%. The reburned lime (the regenerated CaO), which contributes more than 90% of the total lime used in regeneration of Kraft cooking liquor, contains approximately (in wt.%) 90.4 CaO, 2.91 Na_2O, 1.62 MgO, 0.62 Fe_2O_3, 0.47 Al_2O_3, 0.72 SiO_2, 1.09 SO_3, 1.3 CO_2 and 0.48 P_2O_5 (Dorris & Allen 1985). The properties of the reburned lime have been reported by Dorris & Allen (1985); nevertheless, the constituents of the quicklime have rarely been examined in details. As part of an investigation to evaluate the sources of limestone and to obtain the optimum conditions of calcination for the production of quicklime used in the paper industry, the constituents of the quicklime were studied.

CONSTITUENTS OF QUICKLIME

A typical commercial limestone containing approximately 1.4 wt.% mineral impurity (quartz, clay minerals, chlorite and iron oxide) and 56.3 wt.% CaO, 0.3% MgO, 1.4% insoluble (in HCl solution) and 41.5% loss on ignition, was crushed and screened to grain sizes of 15, 30 and 45 mm. Approximately 600 g of sample for each test was calcined at 1000 or 1040°C in a muffle furnace for approximately 1.5 h, allowed to cool in the furnace for 4 h, removed, sealed and stored in a desiccator. In order to obtain a rapid evaluation of the properties of the calcined products for an optimization of the conditions of calcination, slaking (hydration) tests were performed using the ASTM (1984) standard procedure C110 within 2 days after calcining; the hydrated materials were washed and screened using a 150-μm sieve (100 mesh), and the grit contents (*i.e.*, the unreacted +150-μm fraction) determined. After slaking, the materials were dried at 40°C and the constituents studied.

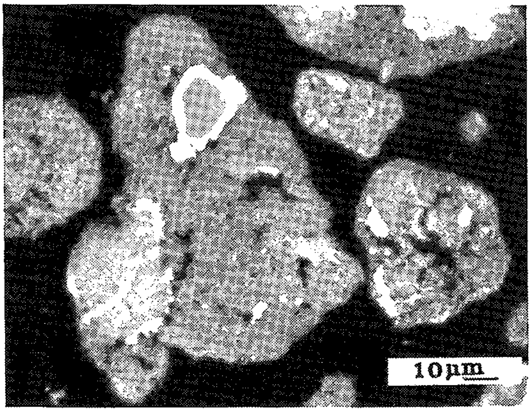

FIG. 1. Backscattered electron (BSE) image of hydrated lime, showing quartz grains with Ca_2SiO_4 rims, fine irregularly shaped Ca_2SiO_4 and $Ca_2Al_2SiO_7$ (bright) in matrix of $Ca(OH)_2$. Various degrees of compactness developed in $Ca(OH)_2$ (*i.e.*, dark grey, fine, loose aggregates at centre *versus* grey, large, compact aggregates at lower left).

The composition of the calcined product, recalculated from hydrated lime, is (wt.%): CaO 97.5, MgO 0.1, SiO_2 1.7, Al_2O_3 0.2 and Fe_2O_3 0.3. Under conditions of optimum calcination, weight loss due to calcination is 43%, calculated unslakable silicate residue is approximately 2.5%, grit content determined from slaking test is approximately 1%, the available lime determined using ASTM method C911 is 92%, and the slaking rate in terms of temperature rise (ASTM method C110) is approximately 50°C in 3 minutes. The calcined product, slaked lime (−150-μm fraction), and the grit were studied using optical microscopy, X-ray powder diffraction, scanning-electron microscopy and electron-microprobe analysis.

The calcined product consists of CaO, $Ca(OH)_2$ (presumably formed by hydration after calcination), and trace amounts of Ca_2SiO_4 larnite, $Ca_2Al_2SiO_7$ gehlenite, quartz, K–Al silicate, various Ca–Al–K–Mg silicate mixtures, Fe_2O_3 and occasional, relict cores of calcite and recrystallized $CaCO_3$ crystals. The −150-μm fraction, *i.e.*, largely the fraction obtained from the slaking tests, consists mainly of loosely aggregated $Ca(OH)_2$; however, trace amounts of the unslakable residues (*i.e.*, the silicates noted above, quartz and calcite) are also present. Figure 1 shows that quartz is present in coarse grains with Ca_2SiO_4 as a rim, and Ca_2SiO_4 and $Ca_2Al_2SiO_7$ are present as small irregular grains in the slaked lime. Various degrees of compactness occur in the $Ca(OH)_2$ aggregates, possibly resulting from agglomeration during sample preparation. The well-slaked fraction consists only of finely divided $Ca(OH)_2$ particles.

The grit (*i.e.*, the +150-μm fraction after slaking), constituting approximately 1 wt.% of the total quicklime, consists of mainly Ca_2SiO_4, $Ca_2Al_2SiO_7$, SiO_2, various Ca–Al–K–Mg–Fe silicate mixtures, and compact $Ca(OH)_2$ (Fig. 2). Trace amounts of relict calcite cores, slow-reacting CaO aggregates, and loose $Ca(OH)_2$ aggregates are also present. The details are shown in Figures 3 and 4; Ca_2SiO_4 occurs as a rim surrounding quartz grains and as small irregular grains, apparently produced from a reaction between calcite and quartz: $2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4 + 2CO_2$, which is common in the unslakable residues produced from limestones containing quartz as an impurity. $Ca_2Al_2SiO_7$ occurs as porous aggregates and as rims surrounding Ca_2SiO_4, various Ca–Al–K–Fe–Mg silicate mixtures and quartz. The silicate mixtures are mainly Ca–Al–K–Si, Ca–Al–Fe–Mg–Si, Mg–Ca–Al–K–Si, K–Al–Si, Ca–Al–K–Fe–Ti–Si, Mg–Al–K–Fe–Ti–Si and K–Ca–Al–Mg–Fe–Si, in terms of combinations of elements. Trace amounts of Fe_2O_3 inclusions are present in these mixtures. Most of the silicate mixtures are products of fusion of original mineral impurities, as is evident from their porous, irregular, sintered to semifused forms, and from the development of a reaction rim on residual grains.

A major amount of $Ca(OH)_2$, presumably CaO prior to slaking, is present in the grit (Figs. 2, 5). In contrast to the particles that rapidly disintegrate into finely divided particles (Fig. 1), most of the $Ca(OH)_2$ occurs as compact agglomerates (Fig. 2) and disintegrates in water very slowly. Although the slaking conditions, such as temperature, slaking medium, lime to water ratio, *etc.*, affect the nature of the grit, in the present study the slaking conditions were maintained the same for all the tests. However, some of the products of calcination consistently produced more agglomerates than the others after slaking. The agglomerates usually contain trace amounts of calcite, and underheated stones appear to contain more of these aggregates, possibly indicating incomplete calcination. Solid, angular grains of $Ca(OH)_2$ are found in some of the grit samples (Fig. 5). In contrast to other $Ca(OH)_2$ particles, which are powdery, white in color and become sludge in water (Fig. 1), these angular grains (presumably CaO after calcination) occur as solid, colorless, well-crystallized "fragments" (containing 70 wt.% CaO, probe analysis) that do not disintegrate in water, indicating extensive crystallization during slaking, possibly due to some degree of sintering during calcination.

DISCUSSION

Some information concerning the properties of quicklime are discussed further under the following subheadings.

Recrystallization of calcite

In commercial operations, high-calcium limestone is crushed and screened to sizes approximately 1 to 6 cm, and calcined in rotary kilns at approximately 1000 to 1400°C for 2 to 3 h to produce quicklime according to the reaction: $CaCO_3 + \text{heat} \rightleftharpoons CaO$ (quicklime) + CO_2. The release of CO_2 from carbonate during calcination increases the porosity and, consequently, the specific surface-area and the chemical reactivity of the calcined product. The above reaction is reversible, as CaO and, particularly, $Ca(OH)_2$ have strong affinity for CO_2; consequently, the quicklime can readily revert to calcium carbonate, producing recrystallized calcite by adsorbing CO_2 from the air, particularly when moisture is present. Thus, recrystallized calcite is commonly observed in the calcined products.

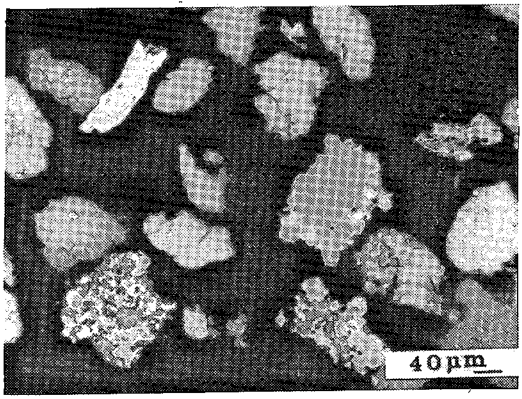

FIG. 2. General view of grit, showing quartz with Ca_2SiO_4 rim, irregularly shaped Ca_2SiO_4 and $Ca_2Al_2SiO_7$ (bright), Mg–Al–K–Fe silicate (fibrous, bright) and compact $Ca(OH)_2$ aggregates (light grey, subrounded). BSE image.

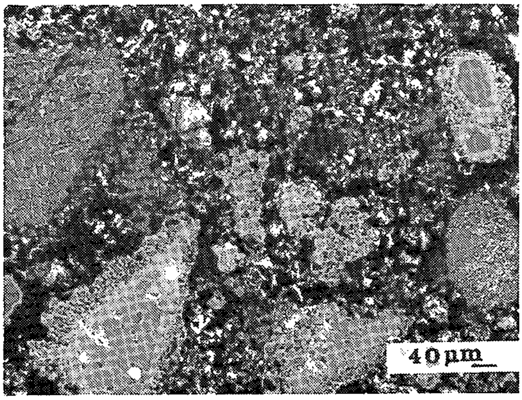

FIG. 3. General view of unslakable residue, showing quartz grains with Ca_2SiO_4 rim (left), $Ca_2Al_2SiO_7$ (irregular, porous; centre), various Ca–Al–K–Fe–Mg silicate mixtures with $Ca_2Al_2SiO_7$ and Ca_2SiO_4 rims (lower part of photograph).

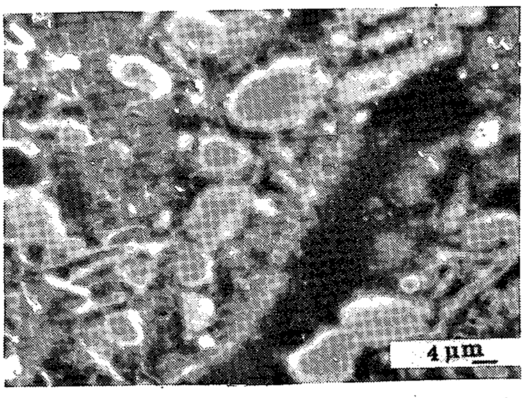

FIG. 4. SEM micrograph of unslakable residue, showing quartz grains with Ca_2SiO_4 rims, indicating the reaction $2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4 + 2CO_2$.

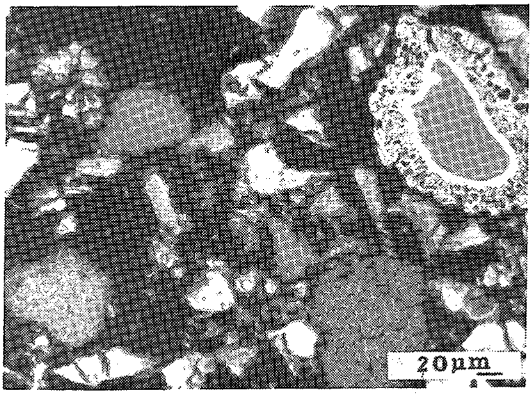

FIG. 5. BSE image of grit, showing solid, angular, well-crystallized $Ca(OH)_2$ "fragments". Also shown are partly disintegrated $Ca(OH)_2$ aggregates (dark, loose) and quartz with Ca_2SiO_4 (solid) and $Ca_2Al_2SiO_7$ (porous) rims (upper right).

Impurities and available lime

In general, the value of quicklime for paper manufacturing can be evaluated from the amount of available lime for reaction with water: $CaO + H_2O \rightleftharpoons Ca(OH)_2$ + heat, and also from its ability to disintegrate in water (*i.e.*, rapid slaking) to form a suspension of finely divided $Ca(OH)_2$ particles. The amount of available lime is mainly affected by the purity of the original limestone and calcination conditions. The impurities, mainly SiO_2, Al_2O_3 and Fe_2O_3 in terms of chemical components, may react with CaO to form calcium silicate and calcium–aluminum silicate during calcination and consequently reduce the amount of available lime. The amount of impurities in limestone also affects the specific surface-area of the quicklime, because only carbonates contribute to the development of specific surface-area during calcination. Other impurities in the quicklime include the cores of relict calcite and recrystallized calcite.

Calcination condition and specific surface-area

The rate of slaking is mainly affected by the specific surface-area of the quicklime (Libby 1983), which in turn is affected by the duration and temperature of calcination. Soft-burned lime is softer, porous and very reactive; hard-burned lime is denser, stronger, but has a lower surface-area and is less reactive and slow slaking; dead-burned lime is more sintered, or even glazed, has low surface-area and is essentially unreactive with water and carbon dioxide.

Consequently, the changes of slaking rate and amount of available lime in quicklime produced from a particular limestone are commonly indications of improper heating, *i.e.*, overheating or underheating. Thus the amount of grit, available lime and slaking rate were used to guide the testing conditions in order to obtain a condition of optimum calcination for the limestone.

In summary, the quicklime used in the paper industry consists mainly of CaO and $Ca(OH)_2$, which disintegrate rapidly into finely divided $Ca(OH)_2$ particles after slaking. The unslakable residues, obtained under standard slaking conditions, are mainly Ca_2SiO_4, SiO_2, $Ca_2Al_2SiO_7$, various Ca–Al–K–Mg–Fe silicate mixtures and trace amounts of Fe_2O_3, residual calcite and slowly reactive (hard-burned?) CaO. In addition to the unslakable residues noted, a major amount of $Ca(OH)_2$ is also present as compact or solid aggregates in the grit (+150-µm fraction). The proportion of the $Ca(OH)_2$ aggregates in the grit can be affected by the slaking conditions, but where these conditions are maintained, the proportion of aggregates also indicates the degree of improper heating.

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