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Property optimization of calcium carbonate precipitated in a high shear, circulation reactor

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ABSTRACT

Precipitated calcium carbonate (PCC) is a widely used mineral in a range of different applications. Its properties, such as morphology, particle size and surface area, determine its functionality and will have a large impact on the properties of the end product. This study examines the effect of different parameters in the PCC process on the pigment properties and the end-use properties in a paper filler application. The applicability of high shear, rapid solid/liquid mixing machine in lime slaking was examined and the properties of slaked lime prepared at different temperatures and concentrations were measured. For precipitation, a novel lab-scale reactor with a high shear mixer and circulation system was constructed. The precipitations were conducted at varying temperatures, slaked lime concentrations, carbon dioxide (CO_2) flow rates and mixing shear rates. The reactor had the rotational mixer in the CO_2 feeding zone, which broke up gas bubbles into different sizes by adjusting the rotation speed. This gave an additional parameter to control the particle size and specific surface area of the PCC particles. High precipitation temperature and calcium-to-carbonate ratio were found to favor the formation of scalenohedral PCC, which gave good optical performance and very low air permeability to paper. The rotation speed of 14,600 rpm was found to be optimal resulting in high optical properties together with good paper bulk. The use of a high shear mixer in the PCC process allowed an additional degree of freedom for engineering pigments with advantageous end-use properties.

1. Introduction

Calcium carbonate ($CaCO_3$) is an abundant, versatile mineral, which is widely used as a filler in several industrial applications such as paper, coatings, paints, rubber, lubricants and plastics. Besides filler material, it is also used in biomedical (drug delivery) and environmental applications (biosensors and water treatment) and by the chemical and food industries. It has many beneficial properties, such as high porosity, non-toxicity and biocompatibility, and can be produced with a range of properties [1].

Besides naturally formed ground calcium carbonate (GCC) crystals, $CaCO_3$ can be chemically synthesized (precipitated calcium carbonate, PCC). Two routes to form PCC are the solution method, i.e. liquid-liquid precipitation, and the carbonation method, i.e. gas-liquid method. In the former, soluble calcium and carbonate compounds are reacted. This approach is often used in laboratory experiments due to the ease of control of the process variables [2], whereas this work concentrates on the industrially important carbonation route. The raw material in carbonation is lime i.e. calcium oxide (CaO), which is formed by calcining limestone (GCC) around 900 °C:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

In the decomposition, carbon dioxide (CO_2) is formed, which means that the calcination reduces the mass of solid material by 44%. The slurry of slaked lime (calcium hydroxide, $Ca(OH)_2$) is formed by reacting lime with water in specific conditions and is thereafter bubbled with CO_2:

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3. \tag{3}$$

Crystals are defined as solids, in which the atoms are arranged in highly ordered, three-dimensional repeating periodic structure. The arrangement of atoms into the periodic lattice structure (Fig. 1) represents the internal structure of crystal and determines the particular polymorph, which can be identified with X-ray diffraction (XRD). Three common polymorphs of calcium carbonate are vaterite, calcite and aragonite. Different polymorphs have the same chemical

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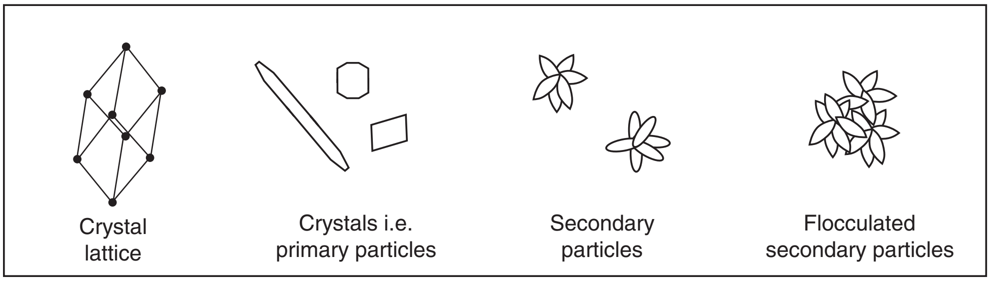

Fig. 1. The structural hierarchy of PCC particles [4,5].

composition, but they differ in physical properties. Thermodynamically, vaterite is the most unstable form while calcite is the most stable crystal form [3]. The lattice structure of crystal, faces present as well as their relative areas are responsible for the external appearance of the crystal, which is usually analyzed with specific surface area (SSA) measurement and scanning electron microscopy (SEM). Very often these crystals i.e. primary particles are strongly aggregated to form secondary PCC particles. The size of the secondary particles is typically measured with light scattering or sedimentation rate after a moderate amount of dispersion. In some cases, the secondary particles may further flocculate together often via electrostatic or van der Waals interactions. All levels of structure are important and it would be highly desirable to be able to enhance the control of the overall PCC hierarchy [4,5].

The driving force for crystallization to occur is supersaturation. The controlling factors, which determine the crystal form, include the temperature, supersaturation, stirring rate, pH and use of additives or solvents [6]. Crystallization can be done in a continuous or in a batch process [7]. In the continuous process, the reaction volume is kept constant by continuously feeding the reactants into a crystallizer and simultaneously removing the product, whereas in the batch process, the product is withdrawn after completing the precipitation [8]. If the reactant is continuously added to the batch reactor and/or the product removed in time, the process is called semi-batch.

The industrial importance of PCC is immense. The global production of filler grade PCC was 14 Mt (2011) the paper industry being the biggest consumer [9]. In 2014, the worldwide consumption of PCC in paper was around 6.5 Mt. There are several reasons why the use of PCC in paper is so popular. Limestone is available in vast deposits (around 10% of sedimentary rocks) with high purity [10]. High quality PCC can be produced on-site at an integrated paper mill. By adjusting the reaction conditions, a range of useful crystal morphologies and sizes can be formed to meet the paper grade requirements [11–16]. For on-site production, CaO is delivered to the mill in a dry form and flue gas from the pulp mill calciner or power plant is used as a source of CO_2. Transport of lime to the mill instead of calcium carbonate gives a roughly 40% savings in logistics costs per ton of PCC since the CO_2 does not need to be shipped. An additional advantage of the PCC process is that no major side products are formed in the carbonation reaction and the amount of rejects is very low. These factors make the overall production cost and value proposition of PCC very attractive.

The range of industrially important crystal morphologies is somewhat more limited than the range that can be produced in laboratory conditions. One of the reasons for this is that traditional PCC batch reactors, while robust and stable, have a limited control window. In addition to crystal engineering, control of the pigment aggregation level would be very useful. Paper manufacturers have attempted to control the aggregate structure by preflocculating filler but the methods have often faced challenges in controlling the floc size and resistance to shear [15,17–20].

If the PCC crystal structure, as well as the aggregate structure, could be easily controlled, it would provide the quality advantage in crystal engineering. In this paper, the applicability of novel high shear mixing devices in lime slaking and PCC carbonation was tested. The target of slaking study was to examine the suitability of high solid content slaking process and find out if particles with high surface area can be produced by a fast hydration of lime. The variables of the slaking process, i.e. temperature and solid content, were examined to optimize the properties of $Ca(OH)_2$ used in the precipitations. The PCC reactor was equipped with the recirculation system and a rotational, high shear mixer placed in CO_2 feeding zone. This enabled the dispersion and control of gas bubble sizes by adjusting the rotation speed. Since the dissolution of CO_2 is a rate limiting step in the overall carbonation reaction [21], this is a useful way to control crystal growth kinetics and the properties of PCC. The precipitation process was monitored by means of custom-built measuring and recording system. In addition to rotation speed, broad range of different precipitation variables, such as initial temperature, concentration of $Ca(OH)_2$ and flow rate of CO_2, was examined. Since $CaCO_3$ is a very important and extensively used pigment in papermaking due to its ability to improve several paper properties [14,22,23], the behavior of the precipitated pigments as a filler in paper was also studied.

2. Experimental

2.1. Materials

Lime, i.e. calcium oxide (CaO) was provided by Lhoist, Ltd. (La Mède, France). Pure carbon dioxide from AGA, Ltd. (Finland) was used in the precipitations. Deionized water was used in all experiments. Particle size distribution of $Ca(OH)_2$ was measured in ethanol (Etax A) from Altia, Plc. (Finland). Part of the prepared pigments was used in paper sheets to examine their effect on paper properties. Bleached pine and birch kraft pulps, which were used as a fiber raw material in sheet preparation, were obtained from Stora Enso Varkaus mill (Finland). Kemira, Ltd. provided the retention aid for the experiments (cationic polyacrylamide, grade K3400R). As a reference, scalenohedral PCC (grade Syncarb FS-240 from Omya AG, Switzerland) was used in the sheet making.

2.2. Synthesis of $CaCO_3$

Production of $CaCO_3$ consisted of two steps. First, lime was reacted with water by mixing it for 10 min to form slaked lime. The slaking was performed in a high shear, semi-batch machine (IKA® magic LAB® with the module CMS), which is designed for rapid and homogenous mixing of solid and liquid. The components were fed to the machine at different inlets. Due to the vacuum at solid inlet, lime was sucked directly to the mixing chamber of the machine. The effects of initial water temperatures from 30 °C to 50 °C and lime-to-water ratios from 1:8 to 1:3 on the properties of slaked lime particles were examined.

In the precipitation step, slaked lime was carbonated with CO_2 gas inside the laboratory-scale reactor, whose set-up is presented in Fig. 2. The reactor was filled with the slurry of slaked lime ($1\ dm^3$), which circulation in the reactor was switched on before starting to feed CO_2 gas. The gas flow rate was adjusted with a rotameter and gas was fed directly above the high-shear rotational mixer, which enabled dispersion of gas