ARCHIVES OF METALLURGY AND MATERIALS
Volume 51 2006 Issue 4

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CONTROLLED PRECIPITATION OF $CaCO_3$ SUB-MICRO CRYSTALS OF WELL-DEFINED STRUCTURE IN A MULTIPHASE SYSTEM

KONTROLOWANE WYTRĄCANIE W UKŁADZIE WIELOFAZOWYM SUBMIKROMETRYCZNYCH KRYSZTAŁÓW $CaCO_3$ O ZDEFINIOWANEJ STRUKTURZE

In this paper we present the new method that allows obtaining of super fine calcium carbonate particles in a (CO_2 – $Ca(OH)_2$ – H_2O) system. A new rotating disc reactor was employed as a processing unit to run this multiphase process. The device enables to control inter- and intraface mass and energy transfer as well as the macro- and micromixing effects in the reacting system.

The system can be controlled by the rate of discs revolutions speed and mixing conditions in the system, reagents contact area or gas flow rate. The influence of different parameters on the reaction kinetics and precipitated powders properties were investigated.

Crystallites and agglomerates morphology was examined with the Scanning Electron Microscopy (SEM). The testing with X-ray diffraction analysis confirmed that we have obtained a pure calcite, which is the most thermodynamically stable polymorph of $CaCO_3$.

Keywords: crystallite morphology, rotating disc reactor, precipitation, aggregates, calcium carbonate

W artykule przedstawiono nową metodę otrzymywania bardzo drobnych krystalitów węglanu wapnia w systemie (CO_2 – $Ca(OH)_2$ – H_2O). Do realizacji tego wielofazowego układu wykorzystano reaktor z wirującym dyskiem, co umożliwia wpływanie na procesy transportu masy i energii. Możliwe jest także wykorzystanie efektów makro- i mikromieszania.

Na zachowanie systemu istotny wpływ mają takie dające się kontrolować czynniki jak szybkość obrotowa dysków, powierzchnia kontaktu reagentów, czy wielkość przepływu gazu. W artykule pokazano wpływ poszczególnych czynników na szybkość reakcji.

Kształt i wielkość zarówno pojedynczych krystalitów, jak i aglomeratów badano z wykorzystaniem skaningowego mikroskopu elektronowego. Badania dyfrakcji rentgenowskiej potwierdziły, że w przeprowadzonych procesach otrzymywano czysty kalcyt, będący najbardziej trwałą termodynamicznie odmianą $CaCO_3$.

1. Introduction

The formation of $CaCO_3$ crystals was widely investigated because of its various applications as a filler or pigment in paper, food, pharmaceutics, plastics, printing ink and many others industries. Calcium carbonate crystallizes in three polymorphic modifications: calcite, aragonite and vaterite. The physicochemical properties of a material, such as density, solubility or stability strongly depend on the crystals crystalline structure. Therefore the production of a powder of a uniform particles is crucial from the industrial point of view. The crystallization process of $CaCO_3$ is very complicated. It was investigated mostly in a liquid-liquid system because of its simplicity in laboratory operation but the mechanism is still unknown. Many authors show the influence of pH, concentration of reagents, ionic strength, temperature, residence time or mixing conditions on the crystals internal structure, morphology, size or the way of aggregation [1, 2, 3].

Due to observed in nature template-controlled mineralization recent investigations are often focused on the effect of anionic surfactants [4, 5], uncharged polymers [6], polymer – surfactant mixtures [7] or fatty acids [8] on the formation of crystalline phase. Those processes are based on the mechanisms such as complexation, molecular recognition, local supersaturation. The presence of surface active agents such as anionic SDS during

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$CaCO_3$ nucleation and growth causes electrostatic interactions between SDS and calcium ions. Therefore polar groups of SDS act as active sites for CaCO3 nucleation. Wei *et al.* [4] observed that SDS affects calcite crystals morphology, preferentially induces calcite formation and inhibits the creation of different polymorphs.

The wet chemistry methods are very promising in production of relatively big quantities of functional solid materials, but elaboration of a good technique is still a challenge. One of the most important problems in precipitation from the solution is the control of mass and energy transfer. This is mainly due to high rate of crystals nucleation and aggregation. This problem can be solved by employing a rotating disc reactor for gas-liquid-solid process.

There are many technical approaches for conduction a multiphase precipitation. The first studies of the carbonation of lime process were conducted in a simple mechanically agitated vessel with a flat gas-liquid interface or in a bubble column by passing gas through a solution [9, 10, 11]. Juvekar *et al.* (1973) has established the mechanism of CO_2 absorption into a lime slurry according to which the gas absorption is accompanied by fast chemical reaction in the gas-liquid film. This highly enhances the absorption process and as a result the gas side resistance for the CO_2 transport to the liquid film is negligible [9]. Therefore it is possible to create high degree of supersaturation in the solution what is one of necessary conditions to precipitate small crystallites if we employ an adequate reactor. In the literature we can find descriptions of many types of multiphase contactors and their ability to control product properties, e. g. hollow fiber reactor [12], Couette-Taylor reactor [13], bubble column reactor [14] or spinning disc reactor [15].

The concept of the technique applied in this work is based on development of contact surface of gas and liquid reactants by formation of thin films of fluid at a surface of turning discs [16, 17]. The films are in contact with gas space which enables controlled transport of easily volatile or gaseous reagents. These reagents are absorbed by the falling film of the liquid reactant. The fluid in films is constantly renewed by discs rotation through the solution in the pocket (see Fig. 1).

Rotating disc reactor (RDR) enables to run multiphase processes with controlled reagent transfer from gaseous to liquid phase as well as in reverse direction. This device allows to conduct precipitation in a selective way, because the driving force for mass transfer is a difference of volatile reagents vapour pressure over liquid films. The mixing conditions during the multiphase process are controlled by discs revolution speed and hydrodynamics of bulk flow.

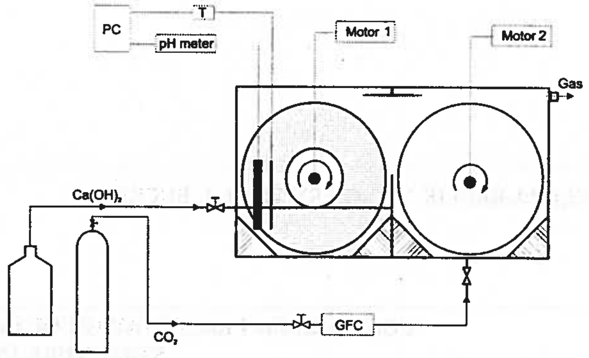

Fig. 1. Schematic representation of a rotating disc reactor

2. Experimental setup

In this paper the results for $CaCO_3$ precipitation in RDR are presented. The main goal was to investigate if it is possible to control the crystals size and morphology by changing mixing conditions in the system. The scheme of experimental set is shown in Fig. 1. Rotating disc reactor was designed and made in The Institute of Opencast Mining what was financed by The Foundation for Polish Science (Techne Programme). Gas – supplying system contains two pressure regulators for high purity gases and Mass Flow Controller GFC (Aalborg) calibrated on CO_2.

Precipitation experiments were performed under different values of discs rotation speed (30, 60, 120 and 200 revolutions per minute). The gas-liquid contact area was constant, equal to 0,24 m^2, volume of liquid phase was 2 dm^3 and volume of gas inflow to the reactor was 2 $dm^3\ min^{-1}$. The processes were performed under atmospheric pressure and the temperature of reaction solution was 25°C. The purity of CO_2 (from gas bottle, Linde) used in experiments was 99.9993%, $Ca(OH)_2$ powder was pure p. a. (POCH Gliwice, Poland). Sodium dodecyl sulfate (SDS) pure was from POCH, Gliwice. Glyoxal-bis(2-hydroxyanil) was pure p. a. for the detection of Ca (from Fluka), methanol was pure p. a. (Chempur, Poland). All the reagents were used without any further purification. The $Ca(OH)_2$ suspensions were prepared in a following way: 4 g of $Ca(OH)_2$ powder was placed in 2 l-volumetric flask and filled in with deionized water and then mixed. After two days suspensions were filtered and immediately used for experiment.

The reaction kinetics was observed by pH values and by calcium ions concentration changes determined with spectrophotometric analysis during the course of the reactions. The samples of reacting solution (2 ml) were sucked up with syringe equipped with filter (pore size 0.2 μm). The spectrophotometric method applied for determination of calcium ions concentration was based on glyoxal-bis(2-hydroxyanil) (GBHA) as a complexing agent. The analysis were performed in alkaline water-methanol solution with wavelength 516 nm (Genesys 10 UV Spectrometer, Thermo Spectronic). The concentration of samples were detected with the use of Standard Curve program. Calibration curve was created by measuring standard solutions absorbance of well known concentration. The crystals polymorph was detected with X-ray powder diffraction method (Bruker AXS D8 Advance).

The influence of discs rotation speed on crystals morphology, size and aggregation was examined with Scanning Electron Microscope (HITACHI S 5500 SEM/STEM with cold field emission gun). An acetone solution of obtained powders was prepared in ultrasonic bath, then applied to Si wafer and allowed to dry. Low energy Secondary Electron mode was employed for the observation. Low accelerating voltage (1-3 kV) allowed for successful observation of dielectric particles at relatively high magnifications (up to 80 000x) without excessive electrostatic loading and/or pronounced edge effects. Obtained images were quantitatively analysed using image analysis software "Micrometer" developed at Materials Science and Engineering Faculty of Warsaw University of Technology [18].

The multiphase process of carbon dioxide absorption into a calcium hydroxide slurry can be described by the following reactions:

$$CO_{2(g)} = CO_{2(l)} \tag{1}$$

$$CO_{2(l)} + OH^- = HCO_3^- \tag{2}$$

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \tag{3}$$

$$Ca^{2+} + CO_3^{2-} = CaCO_{3(s)}. \tag{4}$$

3. Results and discussion

First, let us consider the reaction rate dependence on discs rotation speed. Each process was stopped when pH value of reacting solution reached 7, when there was no doubt that whole amount of $Ca(OH)_2$ has been converted into $CaCO_3$. The typical neutralization curves obtained for different mixing conditions in RDR are shown in Fig. 2a and corresponding to them curves of calcium ions concentration changes are in Fig 2b. This two graphs fully describe the rate of $CaCO_3$ precipitation. The obtained results show that the discs revolution speed influences significantly the kinetics of the examined process. When discs rotate faster, the process goes with higher rate and the carbonation time from 12.9 minutes observed for 30 rpm is reduced to 7.66 minutes for 60 rpm, 5.25 minutes for 120 rpm and down to 4.08 minutes for 200 rpm. Corresponding to pH changes, the Ca^{2+} concentration in the solution decrease during first phase of precipitation, but during pH rapid drop phase it reaches a minimum and starts to increase. Then in the last phase of the process, $CaCO_3$ is redissolving due to the equilibrium in the CO_3^{2-} – HCO_3^- – CO_2 system.

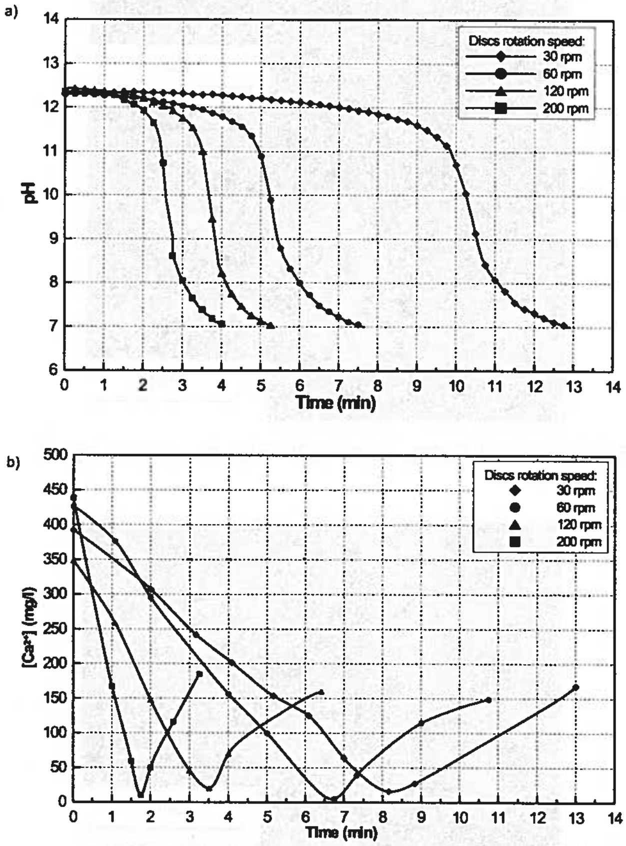

Fig. 2. Influence of discs rotation speed rate on carbonation time : a – pH changes, b – concentration of calcium cations changes in reaction time

The XRD analysis showed that obtained product is only one polymorph modification of calcium carbonate. It is pure calcite, which is the most thermodynamic stable of $CaCO_3$ polymorphs.

SEM observations showed that disk rotation speed influenced not only the kinetics of the reaction, but also obtained crystals size, shape and aggregation. As one can see from Fig. 3 (30 rpm) and Fig. 4 (120 rpm), increase in rotation speed led to decrease in single crystallite size obtained during complete reaction. This corresponds to change in mean equivalent diameter from 320 to 190 nm. Shape of single crystallites is similar in both cases (mean elongation factor defined as maximum diameter to equivalent diameter ratio in range of 1.31-1.33). Smaller single crystallites obtained at higher rotation speed show greater tendency to form big aggregates. The crystallites in observed aggregates are strongly bounded and densely packed.

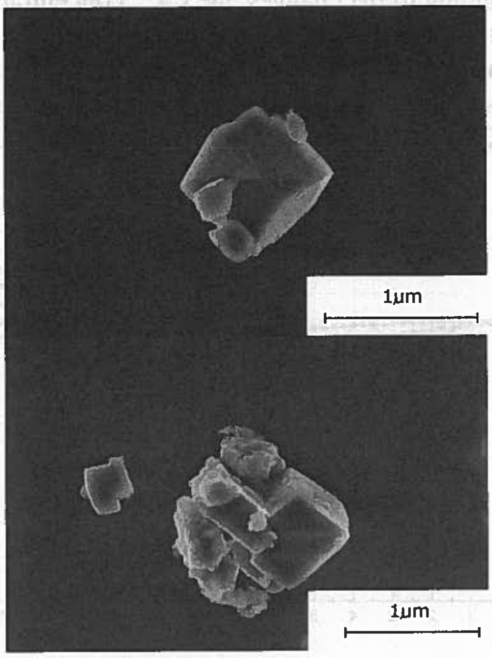

Fig. 3. Obtained $CaCO_3$ for low (30 rpm) disc rotation speed

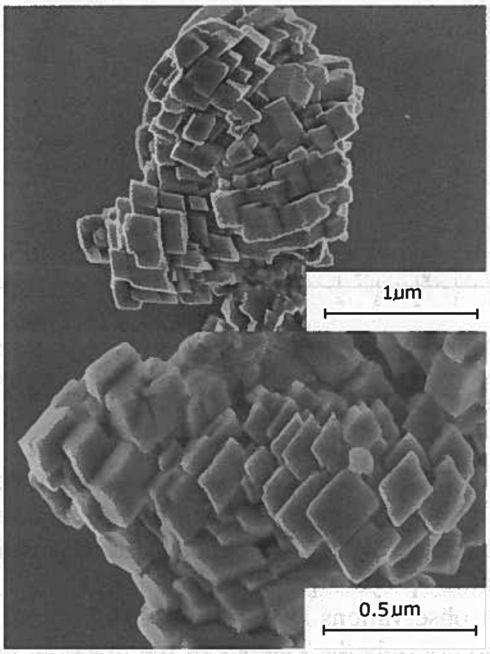

Fig. 4. Obtained $CaCO_3$ for high (120 rpm) disc rotation speed

The size and shape of the crystallites, as well as aggregation behaviour, do not change significantly during the reaction progress. Fig. 5 presents aggregates obtained after 1.5 minute of reaction occurring at 120 rpm. Slightly rounded edges of observed crystallites could be result of crystallization-redissolving processes occurring intensively in presence of a relatively high concentration of substrates. As one can notice from Fig. 2, after 1.5 minutes of process at 120 rpm, pH value was still well above 12 and Ca^{2+} concentration in the solution above 200 mg/l.

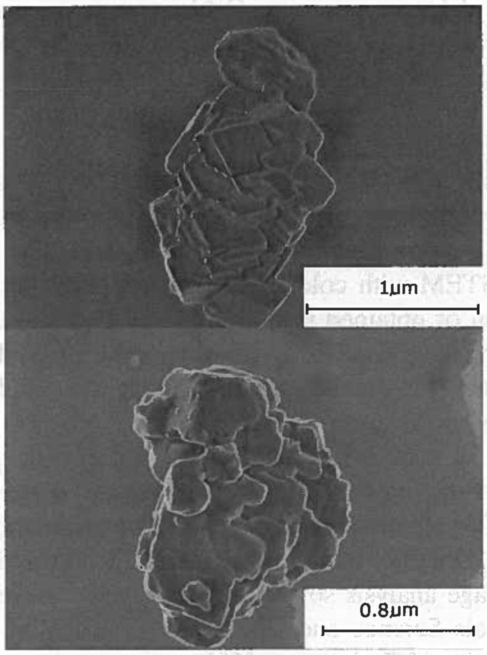

Fig. 5. $CaCO_3$ crystallites obtained during first phase (after 1,5 minute) of the process. 120 disc revolutions per minute

Another way for crystals morphology changing is addition of some substances which can affect crystals nucleation, growth and aggregation process, e.g. surfactants. The preliminary investigations of the influence of small amount of sodium dodecyl sulfate (SDS) on $CaCO_3$ formation in RDR were conducted under 120 rpm of disc rotation speed. To prevent formation of surfactant micelles the SDS concentration was [10^{-3} mol l^{-1}] what is below its CMC. According to Wei *et al.* (2005) SDS gradually changes calcite morphology from typical rhomboedral through surface-coursed calcite for low concentration below CMC to hollow spheres for high concentration where micelles are formed. The crystals diameter obtained in the system without micelles was about 3-4 µm [4].

Obtained morphology of the products precipitated in RDR is shown on Fig. 7. In the presence of surfactant aggregates are much weaker bounded, and loosely packed. Also regularity of shape of single crystallites was affected by the surfactant presence. The observed mean equivalent diameter was 170 nm while elongation factor reached mean value of 1.42. The obtained size of single crystallites was much smaller than precipitated by mixing aqueous solutions of $CaCl_2$ and Na_2CO_3 [4].

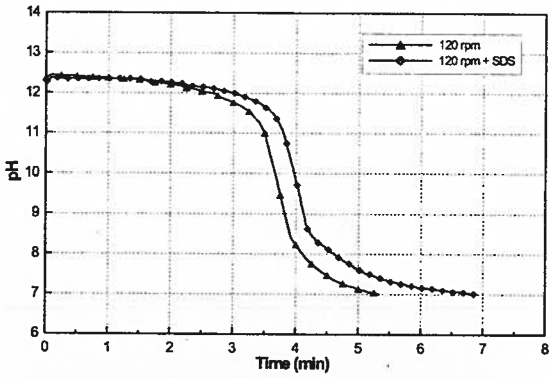

Fig. 6. Influence of addition of SDS on precipitation $CaCO_3$ kinetics

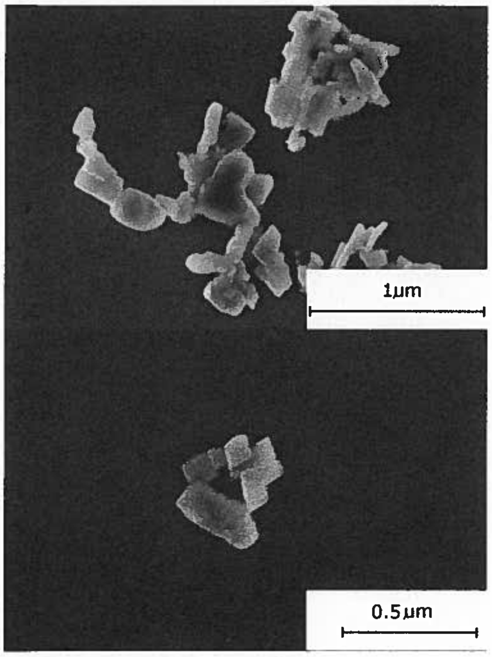

Fig. 7. $CaCO_3$ crystallites obtained in the presence of surfactant during the process. 120 disc revolutions per minute

The Fig. 6 shows the preliminary results of kinetic analysis. In the system with SDS reaction goes with a little lower rate and carbonation time is 1.7 minutes longer than in pure CO_2 – $Ca(OH)_2$ – H_2O system. Although the effect of SDS on the crystals size and morphology is evident, the kinetics results should be confirmed in future investigations.

4. Concluding remarks

Rotating disc reactor method allowed for obtaining of very fine calcium carbonate particles. Obtained crystallites size and agglomerates morphology depend on discs revolutions speed. The higher discs rotation speed causes precipitation of smaller crystallites and the particle mean equivalent diameter decreases from 320 nm to 190 nm.

Addition of surfactants led to changes in crystallites morphology and decreased intensity of aggregation process. The mean equivalent diameter of crystallites precipitated without SDS is smaller than in pure system (170 nm). The elongation factor is about 0.1 higher what indicates the big change in particles shape.

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Received: 10 September 2006.