

OBTAINING CALCIUM CARBONATE IN A MULTIPHASE SYSTEM BY THE USE OF NEW ROTATING DISC PRECIPITATION REACTOR

K. Kędra-Królik and P. Gierycz*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland

Rotating disc reactor (RDR) was constructed to conduct gas–liquid–solid reactions with controlled reagent transfer from gaseous to liquid phase. The concept is based on continuous formation of thin liquid films at a surface of rotating discs where the mass transfer proceed in diffusion–convective way.

The reactor was employed to run precipitation reaction of CaCO_3 via carbon dioxide absorption in lime slurry. During each reaction pH changes and Ca^{2+} concentration in time were measured. Disc rotations and gas flows were changed during the experiment and their influence on the obtained CaCO_3 powders has been examined and fully discussed.

Keywords: calcium carbonate, gas–liquid–solid reaction, multiphase reactor, precipitation

Introduction

One of the most important tasks for precipitation processes is the preparation of functional solid materials. The crucial problem for producing of the well-defined size distribution particles, which is important in terms of the properties and performance of the product, is control of the local level of supersaturation.

The new rotating disc precipitation reactor [1] has been constructed to conduct reaction in such systems. The concept is based on continuous formation of thin liquid films at a surface of rotating discs where the mass transfer proceeds in diffusion–convective way.

The bottom half of each disc is partly immersed in one of reacting solutions, which are separated by a barrier so that the solutions are not mixed directly. As the discs rotate, the volatile reagent desorbs from the falling film of fluid, diffuses through an air gap and is absorbed by the falling film of the other fluid. The film of easily evaporated fluid is a donor stream and a second liquid film is the acceptor stream. The films are constantly renewed by discs rotation through the solutions in the pocket.

Rotating disc precipitation reactor allows to conduct gas–liquid–solid reactions with controlled reagent transfer from gaseous to liquid phase as well as in reverse and it can operate under batch or continuous mode. The gaseous reagent can be supplied from an outside source (gas cylinder) or be desorbed from the film of easily evaporated fluid in the reactor. The films formed on the discs are separated by an air gap what effectively enables a controlled transport rate of the volatile gaseous reagent from the donor to the ac-

ceptor stream. The driving force for mass transfer is a difference of volatile reagents vapour pressure over fluid films formed on discs. So the process proceeds in diffusion–convective way.

Experimental

Rotating disc reactor – the unit description

A schematic diagram of the rotating disc reactor (RDR) is shown in Figs 1a and b. All reactor elements have been constructed from the polycarbonate resin. The heart of the reactor is the system of 25 vertical discs mounted on a common axle enabling rotation. The electric drives assembled to the inverters provide a fluent revolutions control in range from 0 to 200 runs per minute. Discs (25 cm in diameter, 2 mm thickness) are placed one from another in the distance of 2 cm. In the unit there are two the same chambers with rotors. In the lower half of each chamber the liquid phase is placed. The space above is not split up into any parts (the gas phase space). Each chamber consists of 5 equivalent volume pockets, where the

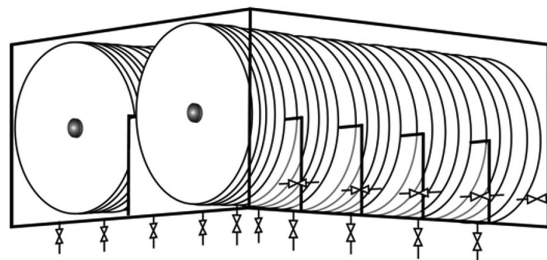


Fig. 1a Schematic diagram of rotating disc reactor

* Author for correspondence: gierycz@ichf.edu.pl

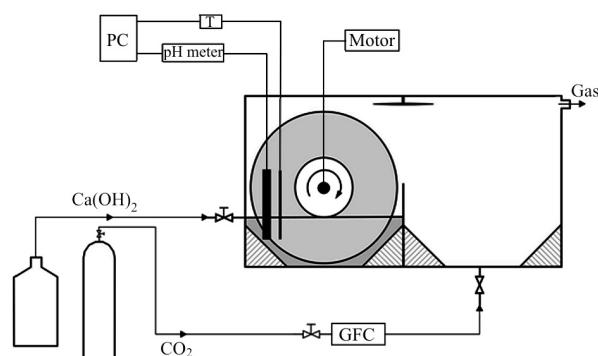


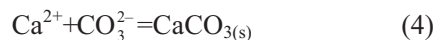
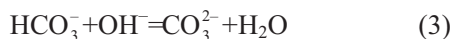
Fig. 1b Schematic diagram of experimental system for gas-liquid-solid reaction

solution can flow from one to another or not if the holes in partitions are plugged. The maximum volume of liquid in one pocket used in experiment is 2 L. The reactor is closed by a tight cover with two variable speed fans, which enhance convective flow of gaseous reactant inside the system.

Calcium carbonate precipitation in RDR

Calcium carbonate is precipitated by the use of RDR via carbon dioxide absorption in lime slurry. This process was the subject of many investigations and is widely described in the literature (e.g. [2–5]).

The reaction in liquid phase goes in contact with continuously flowing gaseous carbon dioxide. This forms a constant surface area of gas-liquid interface and the carbonation reaction of lime water involves gas, liquid and solid phase. The reactions occurring during the process can be described in the following way:



In described system the film of calcium hydroxide solution is formed on the rotating discs surface. The gas contacts the liquid film on the covered discs when it is diffusing across air gap. Carbon dioxide is absorbed into $\text{Ca}(\text{OH})_2$ solution and if supersaturation is achieved it reacts with hydroxide anions. This process initiates the nucleation crystalline phase of calcium carbonate. The nucleation is followed by the crystal growth but with the liquid film, where the nucleation proceeds, the crystallites return back to the solution inside the pocket either by drainage or rotation of the discs. Some are redissolved, while some grow to dimensions that are sufficient to serve as seeds for the formation of the solid phase. Those seeds return back with liquid film to be re-exposed to the air gap reach in

carbon dioxide on subsequent rotations. This makes the system self-controlled, because as the growth of the seed particle achieves the appropriate dimension, its density also grows sufficiently such that the particles can be separated from the system by sedimentation [1].

Materials and methods

The calcium hydroxide suspension was prepared by dispersing of calcium hydroxide powder of 4 g (pure p.a.) from POCH Gliwice, Poland in 2 dm³ of redistilled water from MiliQ-Plus System. Two days later the suspension was filtered and immediately used for the experiment. Carbon dioxide (5.3 purity) was taken from Linde Company.

To observe dynamic behavior of precipitation process during the course of each experiment the pH values were registered every 5-second and regular samples were taken for calcium ion concentration [Ca^{2+}] analysis. All the experiments were carried out under atmospheric pressure in a single middle pocket of reactor at the temperature equal to $18^\circ\text{C} \pm 2$. The volume of $\text{Ca}(\text{OH})_2$ suspension used in majority of the experiments was 2 L.

The carbonation of lime slurry was always conducted until pH reached 7. At this time, all amount of calcium hydroxide was completely converted into CaCO_3 . Then the calcium carbonate particles were de-watered, dried in temperature 60°C and sealed from contact of air.

The reactor was washed after each experiment with 10% HCl solution to get rid of any particles of CaCO_3 and then rinsed with distilled water.

Finally, after obtained the dry powder the particles size and morphology were examined. The crystals size was analyzed with Zeta Plus instrument (Brookhaven Instruments Co.) which applies dynamic light scattering technique for determination of effective diameter of particles and multimodal size distribution. For the measurements, suspension of 10 mg of CaCO_3 powder in 10 mL NaCl 10^{-3} M solution was prepared. The fraction of polymorphs was determined with X-ray powder diffractometry method.

Results and discussion

The experiments were carried out under different ways of contacting calcium hydroxide suspension with a gaseous reagent in RDR. Figure 2 shows crystals effective diameter dependence on discs rotation speed for different gas flow rates. The best results of CaCO_3 crystals size in function of discs rotation speed were obtained for 1 and 2 L $\text{CO}_2 \text{ min}^{-1}$ in flow, what agree with other results [6] concerning CaCO_3 crystals size investigations. The reason is that an in-

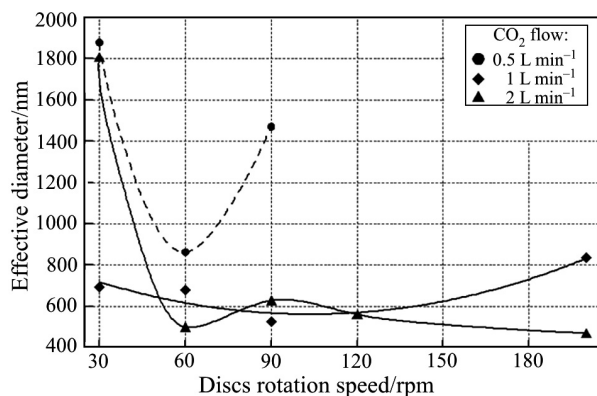


Fig. 2 Discs rotation speed influence on CaCO_3 crystals size for different gas flow rate

crease of gas flow rate will increase the mass transfer rate between the gas and liquid in the RDR reactor. However, in the case of $1 \text{ L CO}_2 \text{ min}^{-1}$ inflow there is one minimum (around 90 rpm) on the curve describing discs rotation speed influence on CaCO_3 crystals size (Fig. 2) whereas for the $2 \text{ L CO}_2 \text{ min}^{-1}$ inflow the local minimum is around 60 rpm but further decreasing of the crystal size is observed above 180 rpm.

Further investigation have been performed for these two different inflows. First of all the influence of discs rotation speed rate on the kinetics of CO_2 absorption into lime slurry was examined. The rotation

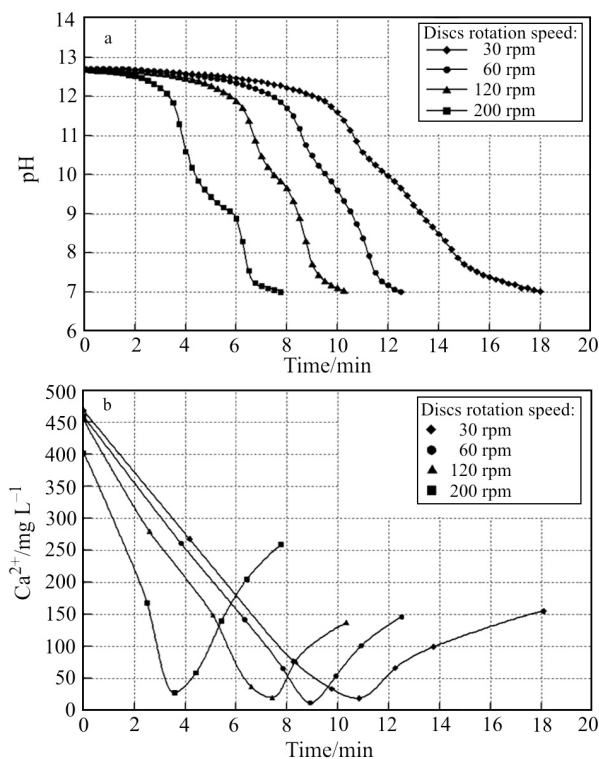


Fig. 3 Influence of discs rotation speed on carbonation time for $1 \text{ L CO}_2 \text{ min}^{-1}$ flow rate: a – pH changes, b – calcium ions concentration curves during the reaction course

rates were changed, ranging from 30, through 60, 120 and 200 discs revolutions per minute. Typical plots of pH and $[\text{Ca}^{2+}]$ changes in the reaction course are shown at Figs 3a and b (for 1 L min^{-1} gas flow rate) and Figs 4a and b (for 2 L min^{-1} gas flow rate).

The obtained results show that the carbonation reaction goes faster with higher discs rotation and gas flow. Calcium ions concentration curves during the reaction course reached their minimum faster for higher (2 L min^{-1}) gas flow rate what is caused by the faster carbonation. Most of CaCO_3 precipitation occurs for pH in the range of 11–12.8. After that pH value drops down rapidly and Ca^{2+} concentration, after reaching minimum, starts to increase what indicates on CaCO_3 redissolving.

The effective diameter of particles and multimodal size distribution was determined by the use of dynamic light scattering method. The obtained results for 2 L min^{-1} gas flow and different values of disc rotation are shown on Fig. 5.

The best results (the smallest particles) have been obtained for disc rotation of 200 rpm (418.6 nm) and 60 rpm (515.6 nm). The curve describing discs rotation speed influence on CaCO_3 crystals size (Fig. 2) for the $2 \text{ L CO}_2 \text{ min}^{-1}$ can be used for adjusting the process parameters needed for precise defined diameters (from 40 to 1600 nm) of CaCO_3 crystals precipitated in RDR.

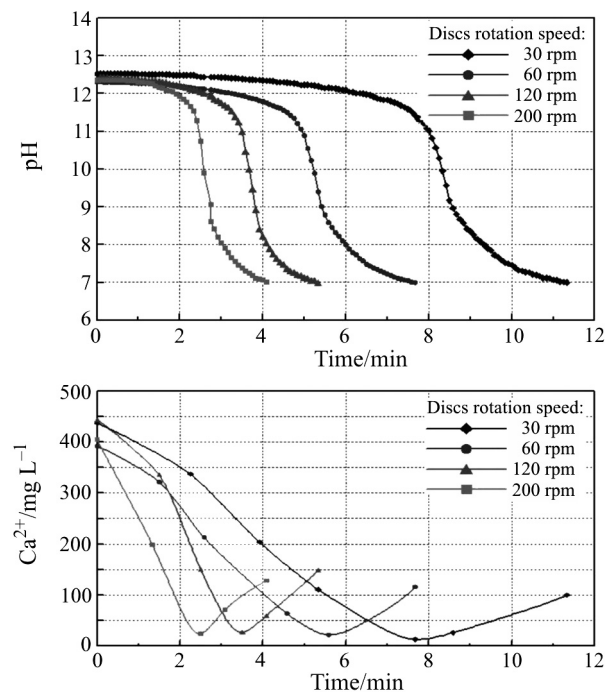


Fig. 4 Influence of discs rotation speed on carbonation time for $2 \text{ L CO}_2 \text{ min}^{-1}$ flow rate: a – pH changes, b – calcium ions concentration curves during the reaction course

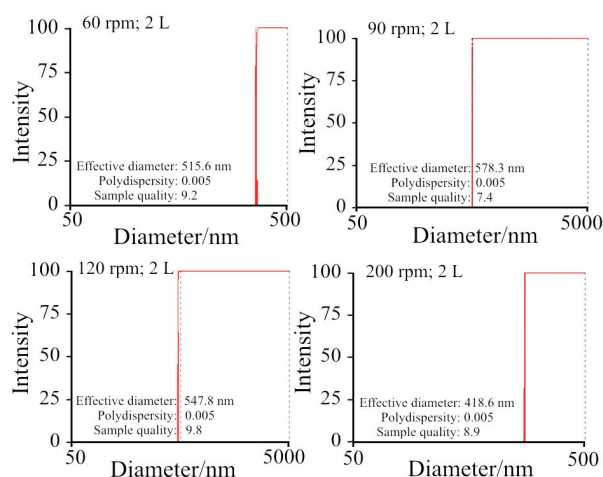


Fig. 5 Multimodal size distribution and effective diameters of CaCO_3 crystals precipitated in RDR under different conditions

Changing the gas inflow e.g. from $2 \text{ L CO}_2 \text{ min}^{-1}$ to $1 \text{ L CO}_2 \text{ min}^{-1}$ and properly adjusting the process parameters (Fig. 2) one can obtain the CaCO_3 crystals with well defined diameter in the range of: 580 to 820 nm.

That is why, using different process parameters (gas inflow, discs rotation speed, pH) for the CaCO_3 precipitation on RDR the size of obtained CaCO_3 crystals can be fully controlled in the approximate range from 1600 to 400 nm.

It is important to notice that the polydispersity index for all measured samples was close to zero (0.005) what indicates that obtained CaCO_3 samples were monodispersed.

The obtained crystal powders were checked also on existence of different polymorphic modification of calcium carbonate. The result showed that in all cases the obtained crystals are pure calcite which is the most thermodynamic stable polymorphic modification of calcium carbonate.

Conclusions

The obtained results confirm effectiveness of the employed method for precipitation of small (below $0.6 \mu\text{m}$) calcium carbonate particles with very narrow size distribution.

The rate of disc rotation speed, as well as rate of gas inflow, can precisely control the kinetic of calcium carbonate and mass transfer, therefore the proposed method allows to obtain particles with defined value of diameter.

The obtained results evidentially show that the RDR can be employed for the controlled process of obtaining well-defined, stable CaCO_3 crystals. The question is how far the size of particles can be decreased. At this moment the CaCO_3 crystals can be obtained in the stable, fully controlled process, with the diameter size not smaller than 400 nm.

It is very important to notice that the crystals obtained by the use of RDR exist in their most thermodynamic stable polymorphic modification of calcium carbonate form i.e. calcite.

The new RDR was constructed to conduct any of gas–liquid–solid reactions with controlled reagent transfer from gaseous to liquid phase. That is why it can be also successfully applied for other reactions of this type i.e. reactions where the mass transfer proceeds in diffusion–convective way.

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