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Investigation of different crystal habits without chemical additives in a three-phase reactor

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Abstract

A lot of powders with fine particle sizes and specific crystal habits are produced by precipitation processes, in which growth and morphology of the particles are controlled by a wide range of chemical agents. This study investigates alternative ways to limit crystal growth and influence crystal morphology. Experiments are carried out in an ultrasound levitator, where a single droplet can be suspended against gravity by an acoustic levitation force. The ultrasound leviator is a three-phase reactor, which allows the investigation of precipitation with applying specific shear forces at growing crystals within the droplet. The investigated system is calcium carbonate. By variation of physical reaction parameters as temperature and level of applied shear forces it is possible to obtain different crystal habits and morphologies. The morphology of calcium carbonate produced in the leviator can vary between prismatic, shell-like and spherical shape. Also the particle size distribution of the precipitated product is influenced. Increasing mechanical stress leads to a shift of the particle size distribution to smaller sizes.

Keywords: Crystallization; Fluid mechanics; Morphology; Particle formation; Precipitation; Product design

1. Introduction

Powders with particle sizes in the micron to sub-micron size range and specific crystal habits are desired in a wide range of industries. Precipitation is a common way to produce such particles. In these processes growth is often controlled by chemical agents and inhibitors and also chemicals are added to obtain desired morphologies (Kitamura, 2002; Cölfen, 2003; Reddy and Nancollas, 1976). This leads to complex controlling efforts. Moreover the chemical agents are often expensive. They may represent substances which cannot be tolerated as impuring the products and must therefore be separated. An alternative possibility to limit crystal growth is by introducing specific mechanical forces. Increasing mechanical stress leads to decreasing growth rates (Bhat et al., 1987; Herden and Lacmann, 1997; Sherwood and Ristic, 2001). As a result crystals growing under mechanical stress achieve smaller particle sizes. With increasing shear stress, which is a typical kind of mechanical stress attached during precipitation in a stirred vessel, steeper particle size distributions and less agglomeration can be obtained (Krammer et al., 2002; Andreassen and Thorsen, 2002).

It is a goal of this study to investigate parameters other than chemical additives which represent alternative possibilities to influence particle size and morphology. Experiments are carried out in an ultrasound levitator which enables to investigate the influence of temperature and mechanical forces on the precipitation. Especially the introduction of defined shear stresses on growing crystals is a unique possibility of this experimental set-up. The formation of calcium carbonate is the system investigated exemplary.

2. Experimental

Fig. 1 shows a picture of the experimental set-up. The core of the experimental set-up is the ultrasound levitator

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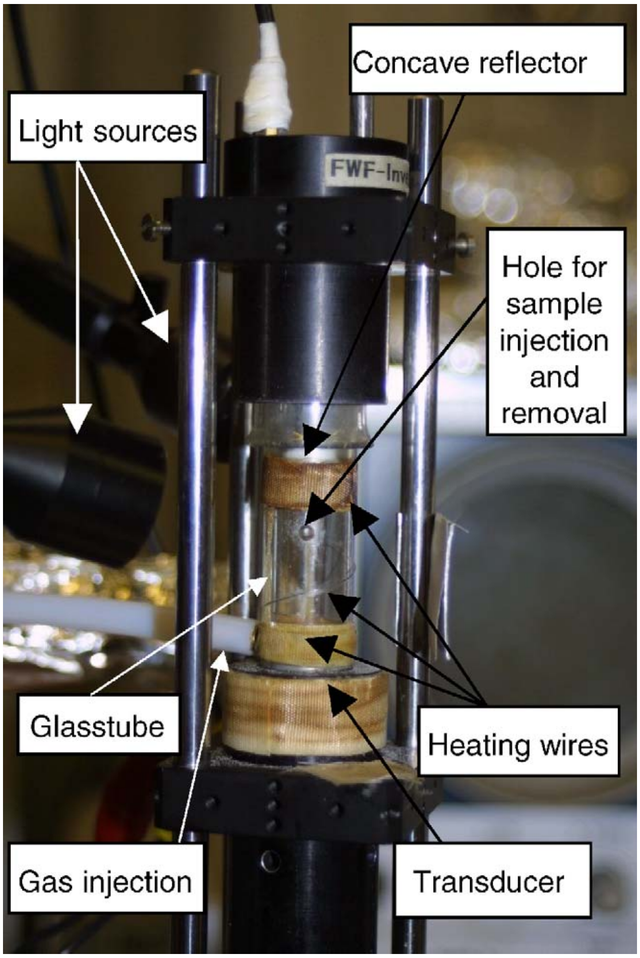

Fig. 1. Side view picture of the ultrasound levitator and auxiliary equipment.

(UL), where a single particle or droplet can be suspended against gravity. The UL has a working frequency of 57 kHz. The UL consists of a glass tube of 12 mm inside diameter, a piston transducer at the bottom and a concave reflector at the top of the tube. The ultrasound transducer generates a cylindrical sound field standing between transducer and reflector. The glass tube representing the reaction chamber is heated by a single heating wire, which also heats transducer and reflector. For the reason of not influencing the sound field there is no regulation of the temperature but a constant voltage is used to keep constant temperature during experiments. The reaction temperature is adjusted before starting. The reaction gas is provided by a mass flow controller and enters the levitator at a small hole in the lower part of the glass tube. There is another hole in the glass cylinder to introduce sample droplets with a small syringe through which the gas exits the levitator. The levitated droplet is observed by a long range microscope and a CCD camera and its pictures are recorded (not shown in Fig. 1). To evaluate mechanical forces acting in the droplet the sound pressure level is measured by a piezosensor located in the reflector. This sensor is connected to an oscilloscope.

Table 1
Experimental conditions

Experiment number	Gas temperature [°C]	Droplet temperature [°C]	Residence time [min]	Effective sound amplitude [Pa]
31-1	34.5	20.5	5	2270
24-1	37.5	22	5	2700
24-2	37.5	22	5	4500
24-3	45	25	5	2337
24-4	45	25	5	3888
31-4	48.5	26.5	5	2430
1-3	51.5	28	5	4600

For performing experiments commercially available lime is added to deionized water at surplus at ambient conditions. Before and during this procedure nitrogen is bubbled through the water to minimize the possibility of a reaction with carbon dioxide of the surrounding atmosphere. After allowing a settling time a 1 ml syringe is filled with the suspension and a droplet of clear liquid is inserted in the levitator. The starting concentration of calcium hydroxide is between 0.06 and 0.09 mass% for all experiments. The reaction gas is pure carbon dioxide with a flow rate of 22 ml/min at standard temperature and pressure. After a predefined residence time the droplet is taken out of the levitator using an empty syringe and put on an electron microscope sample holder, where it is drying under a nitrogen purge gas at ambient temperature. With a residence time of 5 min only particles of calcium carbonate were observed optically. Thus all calcium ions were converted to calcium carbonate. Table 1 gives a list of experiments with its corresponding conditions.

The actual droplet temperature is measured with a teflon isolated 0.08 mm type K thermocouple in separate temperature calibration experiments. It is also calculated using Sherwood and Nusselt relations. Thermal and mass related Biot numbers are much smaller than 1 for any working conditions, which means that temperature and concentration gradients within the droplet can be neglected. Definitions of Bi_m, Bi_{th}, Nu and Sh are given in the nomenclature.

3. Gas–liquid–particle mechanics

The UL is a three-phase reactor which allows the investigation of containerless precipitation under the influence of defined mechanical forces acting on growing crystals. A droplet is positioned locally stable at an acoustic standing wave. The sound pressure of this standing wave causes an acoustic levitation force, which deforms the droplet into a rotational ellipsoid. The acoustic field causes toroidal vortices within the droplet (Yarin et al., 1999) producing shear forces which can be calculated from the stream function.