Chemical and Process Engineering 2021, 42 (1), 15–34
DOI: 10.24425/cpe.2021.137336

Production and formation modelling of $CaCO_3$ in multiphase reactions – A review

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The paper presents different approaches to the proper and accurate production and modelling (multiphase reaction) of $CaCO_3$ formation in the most popular, different types of reactors, i.e. continuous reactor (STR – stirred tank reactors, MSMPR – mixed suspension, mixed product removal; tube reactor), a bubble column reactor and a thin film reactor.

Many different methods of calcium carbonate production and their effect on the various characteristics of the product have been presented and discussed. One of the most important, from the point of view of practical applications, is the morphology and size of the produced particles as well as their agglomerates and size distribution. The size of the obtained $CaCO_3$ particles and their agglomerates can vary from nanometers to micrometers. It depends on many factors but the most important are the conditions calcium carbonate precipitation and then stored.

The experimental research was strongly aided by theoretical considerations on the correct description of the process of calcium carbonate precipitation. More than once, the correct modelling of a specific process contributed to the explanation of the phenomena observed during the experiment (i.e. formation of polyforms, intermediate products, etc.).

Moreover, different methods and approaches to the accurate description of crystallization processes as well as main CFD problems has been widely reviewed. It can be used as a basic material to formulation and implementation of new, accurate models describing not only multiphase crystallization processes but also any processes taking place in different chemical reactors.

Keywords: $CaCO_3$ production, $CaCO_3$ formation modelling, continues reactors, bubble column reactor, thin film reactor

1. INTRODUCTION

Although calcium carbonate formation and aggregation processes have been studied from many years (i.e. Bandyopadhyaya 2001; Cafiero et al., 2002; Chakraborty and Bhatia, 1996; Chen et al., 2000; Cheng et al., 2004; Colfen and Antonietti, 2005; Collier and Hounslow, 1999; Czaplicka and Konopacka-Łyskawa, 2019; Dindore et al., 2005; Feng et al., 2007; Jung et al., 2005; Kędra-Królik and Gierycz, 2009; Kędra-Królik and Gierycz, 2006; Kitano et al., 1962; Montes-Hernandez et al., 2007; Mullin, 2001; Reddy and Nancollas, 1976; Rigopoulos and Jones, 2003a; Rigopoulos and Jones, 2003b; Schlomach et al., 2006; Sohnel and Mullin, 1982), their mechanism which depends on the way of reaction conducting (i.e. Dindore et al., 2005; Feng et al., 2007; Jung et al., 2005; Kędra-Królik and Gierycz, 2010; Majerczak and Gierycz, 2016; Schlomach et al., 2006) is till now not fully understood. Calcium carbonate occurs in nature in

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three polymorphic modifications: rhombohedral calcite, orthorhombic aragonite usually with needle-like morphology and hexagonal vaterite with spherical morphology. The most needed from the practical point of view is the most stable thermodynamically calcite. Nowadays it has wide industrial applications such as plastics, rubber, paper making and medicine. One of its important applications area is connected with fabrication of new, functional materials where the fully controlled precipitation process (determination of many strictly defined parameters) must be applied. Therefore, the accurate information concerning the precipitation process is crucial.

Generally, we can define crystallization as a particle formation process by which molecules in solution or vapor are transformed into a solid phase (regular lattice structure), which is reflected on the external faces. So, describing crystallization both crystallographic and molecular factors have to be taken into account.

In the literature we can find two established mechanisms of crystals growth (Jones et al., 2005; Judat and Kind, 2004; Spanos and Koutsoukos, 1998). First, so called "the Ostwald ripening", involves the larger crystals formation from smaller crystals which have higher solubility than larger ones (the smaller crystals are a fuel for the growth of bigger ones). Second, revealed in recent years, is crystallization mechanism by aggregation, i.e. coalescence of initially stabilized nanocrystals which grow together and form one bigger particle (Judat and Kind, 2004; Myerson, 1999). This mechanism can be described either by calcium carbonate formation through oriented aggregation of nanocrystals (Collier and Hounslow, 1999; Myerson, 1999, Wang et al., 2006) or by self-assembled aggregation of nanometric crystallites followed by a fast recrystalization process (Judat and Kind, 2004; Myerson, 1999; Wang et al., 2006).

Crystals formation is a complex process in which we have to deal with three phase reaction and equilibrium, solid–liquid separation (suspension and sedimentation), change phase from liquid to solid or vice versa and generation or loosing of new particles. Moreover the crystal growth affecting both the shape, purity and structure of crystals (Colfen and Antonietti, 2005; Collier and Hounslow, 1999; Mullin, 2001) and the liquid and solid phases are subject to the physical laws of change: conservation of mass and momentum.

Independently of the way of process conduction, leading to formation of solid $CaCO_3$, each process needs its own modeling taking into account both particulate crystal characteristics and fluid-particle transport, as well as the conditions in the reactor. In the literature there are many different models and simulations (i.e. Bandyopadhyaya et al., 2001; Hostomsky and Jones, 1991; Malkaj et al., 2004; Quigley and Roger, 2008; Tobias and Klein, 1996; Wachi and Jones, 1991) done for different particular reactions.

In recent years, there are two ways of calcium carbonate production: without and with organic additives. The precipitation of $CaCO_3$ conducting without any additives (i.e. Cafiero et al., 2002; Chakraborty and Bhatia, 1996; Chen et al., 2000; Cheng et al., 2004; Rigopoulos and Jones, 2003a; Sohnel and Mullin, 1982) does not give an easy opportunity to control of precipitation process or to modify product properties. Such possibilities are given by methods with organic additives (Bandyopadhyaya, 2001) but unsolved problem remains purity of the obtained powder.

The aim of this paper is to present the different approaches to the proper and accurate production and modelling (multiphase reaction) of $CaCO_3$ formation in most popular, different types of reactors, i.e. continuous reactor (STR – stirred tank reactors, MSMPR – mixed suspension, mixed product removal; tube reactor), bubble column reactor and thin film reactor.

2. MODELLING

The behavior of real crystallization processes is determined by the interaction of multiple process phenomena, which all have to be modelled for a full description of the process. Over the past decades, different tools have been developed to solve many typical chemical engineering problems for standard fluid phase processes. Also for more complex processes, where the solution of Navier–Stokes equations (Ferziger and

Perić, 1996) or population balance for crystallization processes (Randolph and Larson, 1988) is needed, the commercial simulation tools are available.

However, not every kind of crystallization process models can be solved with the available tools. In many cases, the particular crystallization process needs a specific treatment taking into account process parameters, hydrodynamic conditions, crystallizer construction, etc. Moreover, the separate problem, which has to be considered, is connected with the accuracy of the simulation. The accurate calculations are time consuming and the accuracy is strongly connected with the way in which the simulation is performed. So, modelling of a particular crystallization process it is necessary to take into account both the appropriate physicochemical description of the process and the proper way of simulation performance.

Generally, in the case of crystallization it is necessary to solve the conservation equations, which enables to predict results of operation performed in defined equipment (Spiegelman, 2004), and together with the population balance (conservation equation for particle numbers), basing on particle formation (nucleation, growth, agglomeration, breakage, etc.) (Jones et al., 2005), allows for prediction of particle size distribution in the specified crystallizers. It is necessary to remember that for not well-mixed systems, the velocity derivatives, in addition to crystal growth, have to be included to the equation.

The population balance which is a partial integrodifferential equation, can be normally solved by only numerical methods, except for some simplified cases. Different numerical discretization schemes for solution of the population balance (Kumar and Ramkrishna, 1996; Nicmanis and Hounslow, 1998; Ramkrishna, 2000) and compute correction factors to preserve total mass are widely described in the literature (Hostomsky and Jones, 1991; Rigopoulos and Jones, 2003a; Wojcik and Jones, 1998; Wuklow et al., 2001).

Very useful tool for solving all transport processes equations via computer simulation is Computation Fluid Dynamics (CFD). In the case of crystallization, CFD involves the numerical solution of conservation continuity, momentum and energy equations coupled with constitutive laws of process rate (kinetic) together with the population balance accounting the solid particles formed and destroyed during crystallization. So, the CFD model solution comprises both the flow properties and a particle size distribution what leads to the formation of conservation equations which enable to predict results of operation performed in specific equipment.

Attempts to generate a theoretical model-based description of the interaction of fluid dynamics and crystallization face the multi-scale nature of this interaction. Usually, the population balance is represented by a partial differential equation of particle size and time and the mass balance, in most cases, is expressed as ordinary differential equations. On the other hand, the growth and nucleation kinetics of particles are often based on empirical correlations.

The main problem connected with a numerical simulation is a problem of discretization of the all coordinates (Euclidean space, particle size, time). Discretization significantly affects the accuracy, the computational costs and even convergence properties of numerical algorithms. Therefore, the selection of the proper discretization grids has to be carefully considered in the context of the characteristic scales of the modelled phenomena.

One of the most important flow phenomena is turbulence. If it is present in a certain flow it appears to be the dominant over all other flow phenomena. That is why successful modelling of turbulence greatly increases the quality of numerical simulations. Although, all analytical and semi-analytical solutions of simple flow cases were solved at the end of 1940s, there are still many open questions on modelling of turbulence and properties of turbulence it-self. Till now, no universal turbulence model exists yet.

Usually, for the fluid flow calculation, the Euclidean space is divided into a number of CFD grid cells with elementary volumes. The size of these cells is above the Kolmogorov turbulence scale (order of magnitude

10^{-4}) but small enough to well resolve the convective flows and energy transport within the unit (Ferziger and Perić, 1996). Such discretization is sufficient to resolve the most of the phenomena occurring in mass crystallization but needs to be improved in the case of reactive crystallization processes where micromixing phenomena play the significant role. The time coordinate of the CFD problem is also discretized using small time steps (seconds) to resolve fast fluctuations.

The particle size coordinate (the population balance equation) has to be also discretized. There are many methods available to perform this discretization (Hill and Ng, 1995; Hounslow et al., 1988; Hounslow, 1990; Ramkrishna, 2000) but in all cases, the most important is the proper evaluation of the size of CFD cell with the appropriate number of particles. If the CFD cells are too small or have too low number of particle the statistical requirements of the population balance is not fulfilled. This may result in an incorrect solution. The next problem connected with the discretization is necessity of solution of several dozens of the equations in each CFD grid cell what would certainly result in prohibitive computational cost and possibly introduce convergence problems. Therefore, some means of model reduction must be employed to allow a numerical simulation. Moreover, all these methods have been developed with a focus on the way of the systems mixing.

Generally, CFD models can be implemented to "well-mixed" and "not well-mixed" systems. Assumption of well-mixing is commonly used for the modelling of crystallization processes, what simplifies the simulation and reduces its time. Such approach can be accepted in the case of theoretical calculations and small, laboratory scale crystallizers.

Crystallization systems frequently show also high levels of supersaturation around the points where it is generated (cooling surfaces, evaporation interfaces, etc.) causing suspension significant local density variations (Sha and Palosaari, 2000). Consequently, crystallization rates locally vary throughout the crystallizer even in case when no reactive crystallization occurs. Therefore, assumption of uniform conditions throughout the reactor volume cannot be accepted.

Moreover, many crystallization processes are directly affected by the local fluid dynamic state. One of the most important factors is the shear rate which strongly influences both the frequency and the efficiency of particle collisions (agglomeration (Hounslow et al., 2001)) as well as particle-impeller collisions (Gahn and Mersmann, 1999) which are depended on the relative velocity of the particle and local streamlines around the impeller blade.

The mixing problem increases as the scale of operation increases. Typically, fluid dynamics phenomena occur in 'micro-scale' (CDF grid), a much smaller scale compared to crystallization phenomena which are usually considered on the 'macroscale' (unit). To solve the problem one can compute the population balance in each CFD grid, accounting for the full locality of the crystallization kinetics or use the scale of spatial resolution for the population balance. The first approach is not recommended because it can violate the statistical assumptions used for the formulation of the population balance equation and needs a long, time consuming calculations (computational costs). The second method enables for selection of some compartments, representing a certain region in the crystallizer, which can be treated as homogenous (well-mixed) and well described by CFD. Such approach can be a compromise between one single, well mixed unit and the over-detailed system. The use of this model requires the exchange of information between the two scales of calculations: "inner" inside the compartment and "outer" between the compartments.

Taking into account these assumptions some compartmental mixing models (Wei and Garside, 1997) for modelling precipitation processes based on the engulfment theory (Baldyga and Bourne, 1984a, 1984b, 1984c) has been elaborated. Also, several mesomixing and micromixing models have been proposed to describe the influence of mixing on chemical reactions on the meso- and molecular scale (Baldyga et al., 1995; Villermaux and Falk, 1994).

This very complex problem for most popular, different types of reactors, i.e. batch, tube and thin film reactor as well as bubble column can be generally simplified.

The batch (or semi-batch) precipitation process can be described by closed-form solution of population balance equation, which has not taken into account aggregation and breakage (easier simulation). In the case of tube reactor to integration of simulation of crystallization and fluid dynamics the Method of Moments can be successfully applied. The used method allowed for reconstructing the solids fraction profiles on the fine CFD grid, while preserving the full information on particle size distribution on the coarser compartment scale. The technique is well established and has moderate computational costs.

The thin film reactor can be described by the model which takes into account both kinetics of the multiphase reaction and crystals growth rate. Results of such calculation agreed very well with the experiment and the model described properly the change of precipitation rate from bulk liquid to the film region and showed that the higher supersaturation leads to smaller mean crystal size, since the nucleation rate is more sensitive to the level of supersaturation than the growth rate.

The gas-liquid precipitation process in the bubble column can be modeled by integration the population balance, reaction kinetics and hydrodynamic principles. The model well described the precipitation of $CaCO_3$ by CO_2 absorption into lime and can be recommended for the analysis and scale-up of industrial-class equipment. It can give also some explanations for the experimental results. It showed that the crystal mean size increase after the pH drop is due to the disappearance of the smaller crystals by dissolution, the secondary nucleation takes place because a new wave of nucleation-growth is induced by the existing crystals and crystal agglomeration starts to take place at relatively high pH and proceeds to a considerable extent because the aggregates are less frequently disrupted than in stirred tanks.

Below, a wide review of different methods and approaches to the accurate description of crystallization processes as well as main CFD problems has been presented. It can serve as a basic material for formulation and implementation of new, accurate models describing not only multiphase crystallization processes but also any processes taking place in different chemical reactors. Combined population balance and kinetic models, computational fluid dynamics and mixing theory enable well prediction and scale-up of crystallization and precipitation systems but it is necessary to remember that each process (performed in the properly defined reactor) needs always its own modeling.

3. CONTINUOUS REACTOR

Process parameters of a reactor (i.e. temperature, pressure, flow rate), way of a crystallization proceeding (i.e. continuous process) as well as reaction conditions (reagents concentrations, pH, additional substances) have a great influence on the mechanism of calcium carbonate precipitation. Therefore, the morphology of the obtained $CaCO_3$ particles (e.g. rhombohedral calcite, needle-shaped aragonite, spherical vaterite) depends on the conditions of the precipitation process.

Many experimental work has been dedicated to finding the relationship between the conditions of a precipitation process and a morphology of obtained particles. It has been observed that in the case of the reaction taking place in the liquid phase (Nancollas and Reddy, 1971; Wray and Daniels, 1957), all three crystal polymorphic forms (calcite, vaterite, aragonite) are obtained, but in different proportions depending on the process temperature and solution supersaturation. Sohnel and Mullin (1982) confirmed the well-known fact that in supersaturated solutions vaterite crystals turn into calcite particles.

Hostomsky and Jones (1991) observed that the morphology of precipitated calcium carbonate in continuous MSMPR reactor depended on pH of solution. They performed reaction (1) between equimolar solutions

of $Ca(NO_3)_2$ and Na_2CO_3 leading to obtaining of supersaturated solution of $CaCO_3$.

$$Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaOH \quad (1)$$

According to their investigations, formation of vaterite by the reaction of calcium nitrate and sodium carbonate takes place at pH > 9.5, while calcite is obtained at pH equal to ca. 8.5. Similar observations for this reaction were made by Tai et al. (Tai and Chen, 1995; Tai et al., 1993), who studied the dependence of the morphology of the obtained particles, nucleation and crystal growth on the concentration of substrates and the pH of the solution.

An additional factor which, during the precipitation process, may significantly affect nucleation, crystal growth and their morphology is the formation of reaction by-products (i.e. soluble salts obtained in the reaction $Ca(NO_3)_2$ and Na_2CO_3). In most studies, however, this influence is neglected due to the difficulty of considering its impact on the outcome of the experiment. It is assumed that only the main reaction product affects the result of the experiment ($CaCO_3$ – the specific form of the precipitated particles), though it really depends on both the main product and the by-products.

In the most popular reactors – stirred tank reactors (STR), usually we deal with the system gas (CO_2)–slurry ($Ca(OH)_2$) – liquid (H_2O) where the reactions occurring during the crystallization process can be described in the following way:

$$CO_{2(g)} \rightleftharpoons CO_{2(l)} \quad (2)$$

$$CO_{2(l)} + OH^- \rightleftharpoons HCO_3^- \quad (3)$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \quad (4)$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_{3(s)} \quad (5)$$

Depending on the construction and the process parameters of the reactor different form, shape and size of the $CaCO_3$ crystals can be obtain. In the tank contactor with flat-blade turbine stirrer and baffles (Kakaraniya et al., 2007) almost uniform 4 μm crystals are formed. Contrary, in the surface-aerated tank reactor with LSB agitator (Ding et al., 2018) high-purity calcite with multimodal (d = 24−110 nm) particles size distribution was obtained. The size of crystals was dependent on the speed of rotation (increased with decreasing of the speed rotation), initial concentration on $Ca(OH)_2$ (increased with increasing of the concentration) and temperature (increased with increasing of the temperature) (Ding et al., 2018). In tank reactor with turbine stirrer and baffles (Ukrainczyk et al., 2007) different shape (rhombohedral, scalenohedral, spheroidal or truncated prismatic) of 0.02−2 μm calcite particles were formed and no significant effect of the stirring rate on the size of the obtained crystals was noticed.

Interesting results were obtained by Bao and Zhang (2009). They investigated calcium carbonate formation in the high-pressure tank reactor and found out that in the process parameters needle-like aragonite (size between 5 and 15 μm) was formed and organized into microsphere superstructure.

The experiments of Chen et al. (1997), carried out in a crystallizer with a stirrer, where carbon dioxide is supplied to the interior of the solution through an appropriate two-pipe system, showed that the morphology of particles and their growth were strongly dependent on the pH of the solution.

Modelling even so simple reactor as a stirred tank with impellor (Rielly and Marquis, 2001) we have to remember that we deal with very inhomogeneous fluid mechanical environment. The turbulence quantities and the relevant mean-flow may vary by orders of magnitude throughout the vessel, especially around the impellor. Therefore, it is clear that the 'well-mixed' assumption will lead to significant errors on the rates of growth, nucleation and agglomeration, and consequently, on the crystal size distribution. In these cases, information of the solid concentration distribution, as well as local velocities, shear rates and energy dissipation rates would be needed for the proper design of the process.

Good description of crystallization process in the new, segmented tubular reactor was given by Vacassy et al. (2000). This reactor was characterized by a reproducible particle distribution, independent of the flow rate, which indicated the maintenance of homogeneous precipitation conditions throughout the reactor. They tested several methods of conducted precipitation both in the liquid phase and in the gas-liquid system performing a series of experiments enabling statistical processing of the obtained results. They showed that the precipitation of either vaterite or calcite is strongly dependent on even small changes in the process conditions. The direct effects of the influence of such parameters as: temperature, pH, concentration of reagents, the use of doping substances, as well as the method and speed of mixing on the size and morphology of obtaining in the reactor calcium carbonate were measured. Very interesting relations between these parameters were found, showing the complex and complicated nature of the calcium carbonate crystallization process.

Depending on the above mentioned process conditions, a wide spectrum of precipitated crystals was obtained – from almost pure calcite, through mixtures of calcite and vaterite, with various ratios of these polymorphs, to almost pure vaterite. There were also differences in the precipitation processes of pure calcite, leading to the formation of agglomerates with different crystal morphologies and pure vaterite, forming spherical crystals and spherical agglomerates.

Every model describing crystallization in a continuous rector has to take into account the fluid dynamics, the fluid flow through the reactor and crystallization processes acting simultaneously. The simplest model describing crystallization from solution with specified feed concentration, in a wall cooled tube of defined length and radius, where the supersaturation is generated by cooling of the solution by means of an energy withdrawal at the wall, can be derived making the following assumptions (Kulikov et al., 2005):

- the system is considered to be quasi-homogeneous – it is assumed that the flow through the tube causes very well mixing of the fluid and solid (very small crystals) phases. So, instead of writing separate transport equations for the fluid and the solid phases, a single equation for the whole suspension is formulated. This results in assuming no slip and no particle drag which also implies no segregation of the particles,
- mixture properties (density, molecular viscosity, specific heat capacity, thermal conductivity) are assumed to be constant,
- no heat of crystallization is released,
- agglomeration and particle breakage are not considered. The fluid dynamics of the homogeneous mixture can be described by the Reynolds averaged Navier–Stokes equations consisting of the equations for mass and momentum conservation.

The population balance equation used in this model can be taken from (Marchisio et al., 2003). It contains (Kulikov et al., 2005) the accumulation term, the particle growth term, the convective transport term, terms describing molecular and turbulent diffusion of particles with the molecular diffusion coefficient and the turbulent diffusion coefficient, respectively, as well as particle birth and death terms.

The model is a multidimensional dynamic problem containing partial differential equations formulated in spatial coordinates, internal particle size distribution coordinate and the time coordinate. Moreover, the locally distributed velocities, temperatures, and particle size distribution are the unknown variables which cannot be calculated analytically and have to be obtained by a numerical simulation.

As it was mentioned before the numerical simulation can be done using two approaches. The first aims at the reduction of the complexity of the population balance discretization by selection a small number of variables characterizing the particle size distribution. It causes some loss of accuracy in the solution of the population balance, which is reformulated in terms of these variables. Transport equations are also reformulated for these variables and solved along with the CFD problem on the proper spatial grid. Usually, these variables are the moments of the distribution function i.e. the Quadrature Method of

Moments (Marchisio et al., 2003). A main disadvantage of this approach is the inaccurate reconstruction of the particle size distribution when no a-priori information about its shape is available.

The second approach which is based on the reduction of the spatial resolution for the population balance only. Most crystallization phenomena like growth, agglomeration, etc. do not change significantly on the resolution of the CFD grid and can be considered to act on larger scales. This allows for the representation of the population balance by collecting a set of CFD cells in an 'ideally-mixed' compartment. The population balance equations can then be solved in this compartment by a highly accurate discretization scheme. Set of such ideally mixed compartments represents different regions of the crystallizer. This approach has been well described in the literature (Kramer et al., 2000).

It is difficult to claim the superiority of one of these approaches over the other. The proper selection of the approach very much depends on the application to which it is addressed. The compartmental approach better describes the major crystallization phenomena in a cooled crystallizer with complex breakage and aggregation behavior while the reduced population balance approach better describes a high spatial fluctuation of supersaturation e.g., in reactive crystallization.

MSMPR reactor as well as batch (or semi-batch) reactor is one of the most popular reactors widely used in chemical and pharmaceutical industry. The crystallization processes leading in these reactors, although widely investigated, are still not well understood because the process is strongly influenced by fluid mixing, particle aggregation and particle breakage. For those crystallizers where we deal with nucleation, aggregation, breakage and growth processes (Wan and Ring, 2006) the population balance can be calculated according to Randolph and Larson (1988), where for aggregation, the birth and death rate terms can be given by Hulburt and Katz (1964) and for breakage, these terms can be described by Prasher (1987).

The population balance equations can be solved by the use of the standard method of moments (SMOM) and the quadrature method of moments (QMOM) (Wan and Ring, 2006). Using these methods the population balance can be simplified into a series of a few discrete moment equations (some of them as number of particles, volume of particles, etc. have physical significance) defined, for k-th volume-dependent moment.

The both SMOM and QMOM models has been tested (Wan and Ring, 2006) using numerical cases with nucleation, growth, aggregation and breakage and the obtained results have been compared with the analytical measurements. For all cases the OMOM model gave the very good (the accuracy <1 %) description of the particle size distribution in the batch reactor.

The particle size distribution in a batch crystallizer can be also simulated in different way. As an example can be given a process of obtaining of calcium carbonate (Kangwook et al., 2002) when we deal with the overall precipitation reaction (1), where the feeds are a solution of sodium carbonate and a solution of calcium hydroxide at certain, defined concentrations, and the main product is calcium carbonate. The main variable which is to be estimated is particle size distribution of precipitated $CaCO_3$.

The precipitation occurs, when the calcium ions and carbonate ions are present at supersaturated concentration levels. Supersaturation implies that the ionized species are present in the solution where the solubility of the species is exceeded. If we assume that the ionization reactions are fast compared to the precipitation i.e. the ionization reactions reach equilibrium instantaneously and that the perfect mixing in the reactor is obtained, we can write properly the mass balance of the precipitation reactor (Kangwook et al., 2002) which should be solved together with the population balance equation.

Next important required equation is an equation describing nucleation rate. Typically, nucleation and growth rates of precipitation and crystallization processes are represented by semi-empirical power laws. A proper, nucleation model has to take into account the both primary nucleation induced by supersaturation

without particles and secondary nucleation related to the existing particles in the reactor. Growth rate is a function of supersaturation and particle size and can be calculated from the equations by Eek et al. (1995).

The kinetic equations are strongly nonlinear due to the power terms what combined with the mass balance equation makes the problem difficult. However, the computationally demanding part of the precipitation reactor model is the population balance equation. In general, the population balance equation can be converted into a set of ordinary differential equations. Many, various forms of the finite element method and the finite difference method can be applied for this purpose. The details on the solution techniques can be found in a book (Ramkrishna, 2000).

The population balance equation can be simplified in the case when we deal with a linear or an independent function of the density number. In this case a closed-form of the solution can be obtained using the method of characteristics (Varma and Morbidelli, 1997). Further simplification of the model equation is possible when we assume that the aggregation and breakage are negligible and the growth rate takes a separable from them form. In the case of size dependent growth, there are no general theoretical kinetics and the separable form is the exclusively used empirical form.

In order to simulate the precipitation reactor, the mass balance and the population balance equation should be solved together. They can be solved by explicit integration method in which the algebraic equations are solved just once at the beginning of each integration step and held constant or finite element method (Kangwook et al., 2002).

The usefulness of this model for the calcium carbonate precipitation (both an explicit integration and finite element method gave almost the same results) has been checked successfully by Kangwook et al. (2002) but is necessary to remember, that the assumption of negligible agglomeration and breakage (limits of the model) can be applied only for the reactor where the particle density is maintained on the low level (Kataki and Tsuge, 1990).

For the calcium carbonate precipitation in the continuous reactor, breakage can be treated as a negligible phenomenon but the agglomeration is usually significant according to the high particle density in the reactor (Collier and Hounslow, 1999). So, if we want to avoid the aggregation and breakage phenomena in this reactor we have to operate the process in a special way maintaining the low particle density.

4. BUBBLE COLUMN REACTOR

Bubble column reactor is an apparatus in which simplicity of design gives rise to extraordinary complexity in the physical and chemical phenomena. Many papers (Collier and Hounslow, 1999; Grimes et al., 2020; Rigopoulos and Jones, 2001; Rigopoulos and Jones, 2003a; Rigopoulos and Jones, 2003b; Tai and Chen, 1995; Wachi and Jones, 1991; Wen et al., 2003) have been dedicated to production of calcium carbonate in bubble column reactors. They explored the mechanisms of the formation and growing of precipitated calcium carbonate particles in the column. It is necessary to point out that calcium carbonate can appear, during the precipitation process, in three different polymorphs where the most prevailing polymorph appears to be calcite.

It was found out (Grimes et al., 2020) that particles precipitate both at the liquid-gas interface as well as in the bulk of the solution. However, due to the size of the bubble and the formation time of the particles they deposit at the base of the bubble. It is important to notice that secondary particles cannot be produced by the bubble template method because of the large difference in size between the particle and the bubble produced and agglomeration of the particles takes place mostly in the bubble wake as the bubble rises providing a site for occurring of the secondary nucleation.

Very important is also the final solution pH (Grimes et al., 2020) which has a great influence on the formed particle structure. At large pH (around 8.5) a vaterite particles (porous shell with a solid core) are formed. When the pH drops from 8.6 to 6.6, the dissolving surface of particles causes their size reduction while the internal structure begins to hollow out. The further pH drop causes the start of particle shell thickening and an increase in the number of particles produced (hollow particles have a much lower density than solid ones).

The particle structure can also be changed by increasing the aging time in solution (Grimes et al., 2020) because it allows for the transformation of vaterite into the more stable calcite particles.

It is interesting to know (Grimes et al., 2020) that the mean size of precipitated particles is independent of the membrane pore size used for CO_2 bubble production. However, the use of a smaller pore sized membrane did alter the particle characteristics (e.g., surface porosity).

The comprehensive study concerning the influence of many process parameters on the calcium carbonate crystallization in bubble column reactor was done by Wen et al. (2003). They determined the influence of initial $Ca(OH)_2$ concentration, CO_2 concentration and temperature on the morphology of obtained $CaCO_3$ crystals. It was found out that independently of the reagents concentration and temperature of the process the only polymorphic form obtained in the reactor was calcite. It had a form of spatial plates with one dimension much smaller than the other two. However, its morphology strongly depended on the initial $Ca(OH)_2$ concentration. The most homogeneous $CaCO_3$ crystals were obtained for very low (< 0.1%) concentration of calcium hydroxide. Increase of the CO_2 concentration as well as its flow rate caused formation of higher but also regular calcium carbonate crystals, while the temperature increase (from 20 °C to 40 °C) had an opposite effect and caused precipitation of smaller and thinner $CaCO_3$ crystals.

The obtained size of calcium carbonate particles in bubble columns strongly depends on the design of the reactor. In bubble column with internal loop airlift reactor (Konopacka-Łyskawa et al., 2009) without mechanical mixing the size of particles oscillates around 2.5 μm while with mechanical agitation around 2 μm. However, it is seen that increasing in the reactive mixture circulation results in decreasing of the obtained particle size.

In the case of the use of bubble columns with external circulation (Popescu et al., 2014) the size of particles varied from 1 to 10 μm and two different polymorphic forms: calcite and vaterite were obtained. This type of column provides a good mixing of a liquid-solid suspension formed during precipitation and enables the formation of microbubbles that ensure a large gas-liquid contact surface (Popescu et al., 2014). Bubble column with single bubble generator (Tsutsumi et al., 1991) produces $CaCO_3$ particles with dimension about 2 μm but in the form of different shape agglomerates (cubic/multiwalled and spindle units) with size of 6 to 40 μm.

Tamura and Tsuge (2006) proposed a multistage column crystallizer (a standard bubble column divided into several sections by perforated plates) which allows for formation of calcium carbonate particles of different size dependently on the initial $Ca(OH)_2$ concentration and cross-sectional area of G-C contact between sections. The size of obtained particle varied from 4 to 15 μm and decreased with increase of initial $Ca(OH)_2$ concentration. In opposite, the size of particles increased with increase of cross-sectional area of G-C contact between sections.

Complexity of the processes led in the bubble column reactor causes that a modeling of the precipitation process in this reactor needs an integration of reaction kinetics, population balance and hydrodynamic principles. Such successful modeling of the bubble column reactor applied for the precipitation of calcium carbonate by carbon dioxide absorption into lime has been done by Rigopoulos and Jones (2003a). They used their own finite element method (Rigopoulos and Jones, 2003b) for solving the time-dependent population balance equation with combined nucleation, growth, agglomeration, and breakage. The previous

studies of gas-liquid precipitation (Rigopoulos and Jones, 2001) which used the method of moments, took into account only a nucleation growth and did not agreed with both gas-liquid (Wachi and Jones, 1991) and liquid-liquid (Collier and Hounslow, 1999; Tai and Chen, 1995) experiments of precipitation of $CaCO_3$ where the presence of agglomeration and its importance in determining of the product crystal size distribution was evident.

In the most cases of the bubble column modelling the precipitation phenomena at the interface can be neglected because of the very short contact time between the reagents compared to the bulk. Moreover, the non-ideal mixing should be considered in the column but only for the relatively short its height and in the bulk an intense recirculation and full mixing can be assumed. Initial conditions can be calculated from the mixing of bulk and interface at the end of the previous contact time. The solution of the interface equations can be obtained numerically with an implicit iterative scheme, while the bulk equations can be calculated according to Adams method (Hindmarsh, 1983).

The first step (2) is a CO_2 absorption in water at the gas-liquid equilibrium. The equilibrium can be described by Henry's law, taking into account that we deal with an ionic species. The kinetics of carbon dioxide absorption into alkali solutions are determined by the conversion of $CO_{2(aq)}$ into HCO^{3-} (3) which proceeds at a great, but finite rate. This reaction is followed by an instantaneous ionic reaction (4) and the precipitation reaction (5). The rate of $CaCO_{3(s)}$ production is determined by a crystallization mechanism but always volumetric crystal growth is size-dependent even when the linear growth is size-independent (McCabe's law). To obtain the rate of change for the whole crystal mass it is necessary to integrate the volumetric growth function over the whole range of crystal volumes.

To estimate the rate of crystal mass production, which is coupled with the population balance, a complete kinetic model of precipitation taking into account the whole information concerning the crystal formation i.e. nucleation, crystal growth as well as agglomeration and breakage is required. The growth rate kinetics is usually described by the linear growth rate (the increase in nucleation process can have a variety of mechanisms (homogeneous, heterogeneous, secondary, etc.)).

In the bubble column it can be assumed (Rigopoulos and Jones, 2003b) that in the beginning of the process high supersaturation levels induce primary nucleation, but later, secondary nucleation causes the rise of crystal growth. So, the overall nucleation model consists of the sum of the two models: primary and secondary. The primary nucleation which depends mainly on supersaturation is usually described by a power law and the secondary nucleation is induced by the existing crystals (Garside and Davey, 1980) and is a function of the crystal mass.

As it was mentioned, calcium carbonate can appear, during the precipitation in the bubble column reactor, in three different polymorphs. That is why, a kinetic model should account for their simultaneous presence in the solution (Chakraborty and Bhatia, 1996) but usually, because of the complexity and difficulty of such calculations, the considerations are limited only to calcite.

Agglomeration of crystals is a very complex and system-dependent process. Usually, in modelling, it can be simplified and treated as a two-step process. The first step of agglomeration, i.e. the formation of flocculates through collisions and inter-particle attraction, is similar to the phenomena occurring in colloids and aerosols. The second step is the growth of crystalline material between the clusters at so-called cementing sites (Hounslow et al., 2001). In the case of the bubble column (Rigopoulos and Jones, 2003b) the agglomeration can be assumed to be roughly proportional to crystals growth (Hounslow et al., 2001) and described by the second-order dependence on supersaturation.

Hydrodynamics of the gas-liquid precipitation strongly depends on the gas holdup which determines the rates of the chemical phenomena. The Eulerian-Eulerian multiphase CFD model (Rigopoulos and Jones, 2001), where the turbulence in the liquid phase is calculated with k-ε model (Schwarz and Turner,

1988), can be used for its description. This model can be successfully used for modelling large-scale equipment because it gives sufficiently accurate results with respect to averaged properties. However, it is less successful in reproducing fine details i.e. the radial phase distribution.

The above model described very well (good agreement with the experiment) the precipitation of $CaCO_3$ by CO_2 absorption into lime, in the bubble column. The conjunction of penetration theory and CFD predictions of the gas holdup seems to yield an adequate description of the reactor performance. Such an integration of the population balance, reaction kinetics and hydrodynamic principles allowed for proper formulation of modeling approach for the gas-liquid precipitation process and the model may be used as a tool for the analysis and scale-up of industrial-class equipment.

5. THIN FILM REACTOR

The use of spinning disc reactors (SDRs) in several chemical processes very often results in an increase of the reaction and transport rates, as well as improved selectivity and yield. SDRs can be successfully applied for calcium carbonate production (Burns and Jachuck, 2005; Trippa et al., 2002). The process leading in those reactors bases on high centrifugal acceleration which generates thin films providing rapid heat and mass transfer. Trippa et al. (2002) and Burns and Jachuck (2005) demonstrated the use of a spinning disc reactor for the production of calcium carbonate particles from dissolved CO_2 (reactions 2–5). They show the possibility of obtaining a wide range of particle sizes and morphologies by proper controlling of the operating conditions (mainly the disc rotational speed). However, they could not present a good model describing the whole process taking place in the reactor.

The main problem concerning the modelling was connected with proper evaluation of gas–liquid mass-transfer coefficients. Many studies have been performed (Auone and Ramshaw, 1999; Boodhoo and Jachuck, 2000; Lim, 1980; Moore, 1986) to solve this problem but they do not give the clear answer. In 2005 Burns and Jachuck (2005) decided to use a noninvasive method of directly monitoring calcium carbonate production on the disc surface in SDR to obtain more direct mass-transfer data and elaborate the mass-transfer model of the precipitation process on the SDR.

The model proposed (Burns and Jachuck, 2005) based on diffusive mass transfer into a thin rotating film and is correlated with Fourier and Reynolds numbers. It was found out that the process was strongly linked to diffusive mass transfer and suggested that the transport mechanism was driven strongly by molecular diffusion with some enhancement arising from axial convection, probably caused by the action of surface waves (Sisoev et al., 2003; Sisoev et al., 2006).

In the model the Fourier number was defined for the case of film flow over the rotating disc surface and therefore was governed the effectiveness of diffusive transport axially through the film. The obtained results showed a good correlation between Fourier number and conversion. The additional axial convective transport processes appeared to be most noticeably influenced by the liquid flow rate over the disc and less influenced by the rotational speed. Moreover, the conversion of $Ca(OH)_2$ to $CaCO_3$ was compared with residence time, based on the Nusselt flow model and the results showed no clear correlation between conversion and residence time.

The final analysis showed that the model of conversion depends on the three operating variables: radius, rotational speed, and liquid flow rate. It was found out that a residual non-diffusive transport was a strong function of liquid flow and radius and a weaker function of rotational speed. This residual influence was to be the result of an axial convective transport process and was linked to Reynolds number. The combination of the influence of Fourier and Reynolds numbers could be used to characterize the observed production rate of $CaCO_3$ within the thin film flow over the rotating disc.

It is worth to point out that the results of this work show also that dissolution rates, formation of $CaCO_3$ at the surface of calcium hydroxide particles, and gas-side mass-transfer resistance may reduce the ability of an SDR process to achieve complete conversion over a single pass.

Jung et al. (2004; 2005) studied the $CaCO_3$ production in the Couette−Taylor reactor. They investigated the effect of stoichiometric reaction conditions on the morphology and crystal size of calcium carbonate crystals. The calcium carbonate was crystallized by the reaction between aqueous H_2CO_3 and $Ca(OH)_2$ solutions in the reactor where the H_2CO_3 solution was prepared by absorbing CO_2 gas (99%) into deionized water. It was found that the morphology and mean size of individual crystals significantly varied with the reactant conditions. Under the stoichiometric reaction conditions the largest rhombohedral crystals were obtained. An excess of Ca^{2+} ions caused that the individual crystal size was rapidly reduced and the morphology gradually changed from a rhombohedral shape to a spindle or to a needle shape. The individual crystal size was reduced also when we dealt with an excess of the CO_3^{2-} species but in this case the crystal morphology was not significantly modified. The excess of reactants also influenced on the molecular growth of the crystals by preferential adsorption on the crystal faces. Moreover, the agglomeration of crystals was increased with an increasing of the excess species concentration and the mean agglomerate size was approximately proportional to the ionic strength of the solution.

Morphology and size of obtained $CaCO_3$ crystals in the Couette–Taylora reactor, during the precipitation in three phase system gas-liquid-solid (reactions 2–5) was also investigated by Jung (Jung et al., 2005). They found that such process parameters as initial concentration of $Ca(OH)_2$, flow rate of CO_2 and rate of fluids mixing are crucial for the size and morphology of the obtained $CaCO_3$ particles. Additionally, it was stated that if the reaction is leading in non-stoichiometric conditions the produced particles are of a different size and morphology compared to those obtained in the stoichiometric conditions.

Dependently on the process parameters the obtained calcium carbonate particles had different shape and size (from cubes to spindles) but always the only obtained polymorphic form was calcite. Moreover, it was found out that both the size and the morphology of the particles depend on the excess of reagents in the system. The largest and most regular (cube) particles were obtained for the stoichiometric conditions of the reaction. As the reaction stoichiometry was deviated from, smaller and more spindle-shaped $CaCO_3$ particles were obtained.

Kang et al. (2003) studied the production of $CaCO_3$ in Couette-Taylor and obtained the particles of the size 2-10 μm in the form of different agglomerates (multi-walled, spindle-shaped or needles). They found out that a bimodal particle size distribution increased with the rotating speed, which on the other hand, decreased of the particle size. The process variables were interrelated and difficult to control compared to reactions carried out in the liquid-liquid system. Therefore, synthesis of calcium carbonate with a defined characteristics required to control many parameters and among them hydrodynamic conditions.

One of interesting approaches to $CaCO_3$ production is the use of a continuous Taylor crystallizer (Kim, 2014). In this type of crystallizer, the Taylor vortex is created in the gap between two co-axially positioned cylinders based on the rotation of the inner cylinder which rotation speed controls the vortex intensity.

In the system we deal with reactions (2–5) where the Taylor vortex flow facilitates the mass transfer at the gas–liquid interface. It, due to the high shear rate, causes that the bubble size of the carbon dioxide is considerably reduced compared to the size in a random turbulent eddy flow what improves the mass transfer rate because of a significantly enhanced mass transfer coefficient at the interface.

The Taylor vortex has a significant influence on the crystallization processes including nucleation, growth, agglomeration and breakage of formed crystals. It facilitated the mass transfer at the gas–liquid interface what results in formation of small crystals with a uniform size and morphology.

According to modeling (Jung et al., 2000), the mass transfer coefficient increases with the Taylor vortex intensity and can be expressed in terms of the wall shear stress as well as the bubble diameter in a Taylor vortex is very small due to the turbulent shear of a vortex.

It is important to remember that the mass transfer rate of carbon dioxide has a direct influence on the crystal morphology of calcium carbonate (Kang et al., 2003). The increase of the concentration of calcium hydroxide causes the crystal morphology shifts to a spindle or needle due to excess calcium ions. On the other hand, the crystal shape is changed to a rhombohedron when increasing the rotation speed of the inner cylinder in a Taylor crystallizer. When the mass transfer rate of carbon dioxide exceeds the stoichiometric ratio for calcium hydroxide at a high carbon dioxide gas flow rate and high rotation speed, the crystal morphology also shifts to a spindle.

The reaction in a Taylor crystallizer based on the direct contact of the reactant feed streams, generating a high supersaturation at the inlet region of the Taylor crystallizer resulting in a high number of small-sized crystals produced. The hydrodynamic conditions in a Taylor crystallizer are very uniform throughout, as the fluid motion in the crystallizer is induced by the rotation of the inner cylinder. Also, the strong radial vortex motion promotes a homogenous hydrodynamic property in the radial direction. As a result, the crystal morphology produced by a Taylor crystallizer is uniform according to the stoichiometric conditions of the reactants (Jung et al., 2000).

The another approach (Kędra-Królik and Gierycz, 2010) to the precipitation of calcium carbonate in the thin film, can be presented on the example of the rotating disc precipitation reactor (Kędra-Królik and Gierycz, 2006; Kędra-Królik and Gierycz, 2009).

In this reactor the reaction in liquid phase goes in contact with continuously flowing gaseous carbon dioxide in the thin film formed on the surface of the rotating disc (Kędra-Królik and Gierycz, 2006; Kędra-Królik and Gierycz, 2009) (reactions 2–5). This creates a constant surface area of gas-liquid interface and the carbonation reaction of lime water involves gas, liquid and solid phase.

The results obtained show that in the used reactor the carbonation of dispersed calcium hydroxide in water with co-existence of gaseous CO_2 at the ambient condition leads to the precipitation of nanometric, monodispersed crystals of size in the range of 90 – 320 nm. The size of the crystals strongly depends both on the precipitation condition and initial concentration of the slurry.

These results allow for a general conclusion concerning formation of nanoparticle in the reactor with rotating discs dependently on process conditions. At high interface area the high supersaturation degree occurs in the liquid film on discs surface and small crystallites can be formed. When discs rotate with small interface area the supersaturation degree is not always achieved, what results in a slightly bigger crystallites.

The precipitation processes taking place in the reactor (Kędra-Królik and Gierycz, 2006; Kędra-Królik and Gierycz, 2009), have been modelled (Kędra-Królik and Gierycz, 2010; Majerczak and Gierycz, 2016; Wszelaka-Rylik et al., 2015). The model takes into account not only kinetics of the multiphase reaction but also crystal growth rate and agglomeration of the obtained crystals (Kędra-Królik and Gierycz, 2010; Majerczak and Gierycz, 2016; Wszelaka-Rylik et al., 2015). In the case of the precipitation of $CaCO_3$ in the thin film the small crystals are obtained due to the very high nucleation rate compared to the crystal growth rate (Kędra-Królik and Gierycz, 2010). So, because of it the $Ca(OH)_2$ concentration decreases and higher supersaturation leads to smaller mean crystal size, since the nucleation rate is much more sensitive to the level of supersaturation than the growth rate and the high level of supersaturation is accumulated within the liquid film due to the large diffusion resistance. The model describes very well both the change of precipitation rate in the liquid film and the $CaCO_3$ crystals formation in the rotating disc reactor what is confirmed by the experiment (Kędra-Królik and Gierycz, 2006; Kędra-Królik and Gierycz,

2009). Therefore the model can be used and recommended for accurate calculation of the particle size and distribution obtained by gas-liquid precipitation in the reactor.

6. CONCLUSION

The aim of this paper was to present the different approaches to the proper and accurate production, modeling and simulation of $CaCO_3$ formation and growth in multiphase reaction. This very complex problem has been presented for most popular, different types of reactors, i.e. continuous, bubble column and thin film reactor.

Many different methods of calcium carbonate production have been presented in this paper. One of the most important feature, from the point of view of practical applications, is the morphology and size of the obtained in the crystallizer crystals as well as their agglomerates and size distribution. The size of the obtained, in the discussed precipitation processes, $CaCO_3$ particles and their agglomerates can vary from nanometers to micrometers. It depends on many factors. The most important are the conditions in which calcium carbonate is precipitated and then stored.

The experimental research was strongly aided by theoretical considerations on the correct description of the process of calcium carbonate precipitation. More than once, the correct modelling of a specific process contributed to the explanation of the phenomena observed during the experiment (i.e. formation of polyforms, intermediate products, etc.).

In the continues reactors batch (or semi-batch) precipitation process has been described by closed-form solution of population balance equation, which has not taken into account aggregation and breakage, what simplifies the simulation. However, the presented strategy is general and can be applied to batch or semi-batch processes described by more complex types of population balance equations.

In the case of tube reactor integration of simulation of crystallization and fluid dynamics was successfully applied by means of the Method of Moments. The used method allowed for reconstructing the solids fraction profiles on the fine CFD grid, while preserving the full information on particle size distribution on the coarser compartment scale. The technique is well established and has moderate computational costs.

The gas-liquid precipitation process in the bubble column was modeled by integration the population balance, reaction kinetics and hydrodynamic principles. The used model well described the precipitation of $CaCO_3$ by CO_2 absorption into lime and can be recommended the analysis and scale-up of industrial-class equipment. It gave also some explanations for the experimental results. It showed that the crystal mean size increase after the pH drop is due to the disappearance of the smaller crystals by dissolution, the secondary nucleation take place because a new wave of nucleation-growth is induced by the existing crystals and crystal agglomeration starts to take place at relatively high pH and proceeds to a considerable extent because the aggregates are less frequently disrupted than in stirred tanks.

The thin film reactor has been described by the model which takes into account both kinetics of the multiphase reaction and crystals growth rate. Results of calculation agreed very well with the experiment and the model described properly the change of precipitation rate from bulk liquid to the film region and showed that the higher supersaturation leads to smaller mean crystal size, since the nucleation rate is more sensitive to the level of supersaturation than the growth rate.

Moreover, a wide review of different methods and approaches to the accurate description of crystallization processes as well as main CFD problems has been presented in this paper. It can be used as a basic material

for formulation and implementation of new, accurate models describing not only multiphase crystallization processes but also any processes taking place in different chemical reactors.

Combined population balance and kinetic models, computational fluid dynamics and mixing theory enable for well prediction and scale-up of crystallization and precipitation systems but it is necessary to remember that each process (performed in the well-defined reactor) needs always its own modeling.

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Received 25 February 2021
Received in revised form 30 March 2021
Accepted 22 April 2021