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New method for the determination of precipitation kinetics using a laminar jet reactor

Mousa Al-Tarazi*, A. Bert M. Heesink, Geert F. Versteeg

Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract

In this paper a new experimental method for determining the kinetics of fast precipitation reactions is introduced. Use is made of a laminar jet reactor, which is also frequently applied to determine the kinetics of homogeneous gas–liquid reactions. The liquid containing one or more of the precipitating reactants passes a gas-filled reactor as a stagnant jet in which no mixing occurs. The remaining reactant needed for precipitation is supplied in gaseous form and causes the precipitation reaction to occur while it is diffusing into the jet. Hydrodynamics as well as transport phenomena are precisely known for this system, whereas agglomeration can be minimized by adjustment of the concentration of the solute supplied by the gas. The kinetics of the different crystallization steps can be determined by analyzing the size distribution of the produced particles. This new method is experimentally demonstrated for the precipitation of CuS using H_2S gas. The obtained data were successfully used to simulate a packed bed absorber in which H_2S is absorbed by a $CuSO_4$ solution.

Keywords: Absorption; Mass transfer; Multiphase reactor; Precipitation kinetics; Gas–liquid; Laminar jet

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1. Introduction

In a precipitation process, two or more reactants form a solid product (Mersmann et al., 1994). In many cases, the solubility of this product is very low. So when the reactants are brought together, a high degree of supersaturation occurs, which leads to the nucleation of new crystals and subsequent crystal growth. These processes proceed simultaneously in a given system. Secondary processes such as agglomeration and Ostwald ripening may also occur. All processes together determine ultimate product quality such as particle size distribution.

In almost all industrial cases, precipitation is followed by a separation process that prefers coarse over fine particles. In most crystallizers, it is therefore desired to produce coarse particles of narrow size distribution. Although precipitation is a common operation in the chemical industry, it remains very difficult to predict the size distribution of the produced particles. Particle size is a complex function of nucleation rate, crystal growth and agglomeration of the crystals (Mersmann, 1993). Knowledge of intrinsic precipitation kinetics is of crucial importance for the design and control of a precipitator. Such kinetic data have been measured for better soluble solids such as calcium carbonate, silver nitrate and calcium oxalate using the conventional mixed suspension mixed product removal (MSMPR) method, using a more or less ideally stirred vessel. For determining the crystallization kinetics of very fast precipitating solids, the MSMPR method is less suited since (local) precipitation rates may be much faster than (local) mixing rates. The precise hydrodynamics inside the crystallizer should be known then, but this is hardly the case with the MSMPR method. Nevertheless, because of the lack of alternative methods, many researchers have applied the MSMPR method to measure the precipitation kinetics of sparingly soluble solids (e.g. Rodgers and Bertherton, 1998; Palosaari et al., 1996; Graber et al., 1996; Al-Tarazi et al., 2004b; Narayan et al., 1992).

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* Corresponding author.
E-mail address: m.y.m.al-tarazi@utwente.nl (M. Al-Tarazi).

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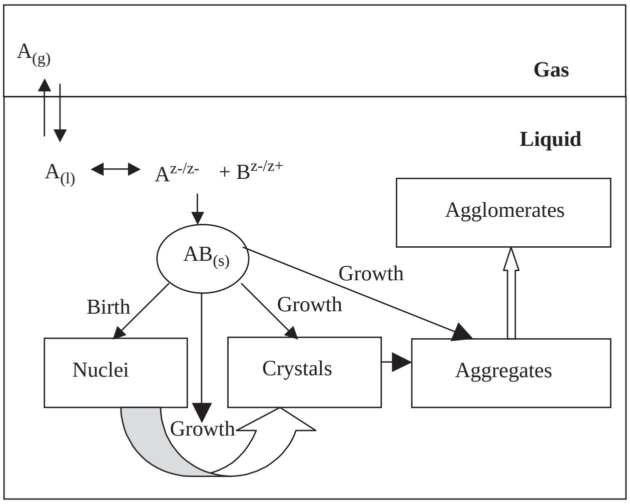

Fig. 1. Process of gas–liquid precipitation.

In gas–liquid precipitation reactions, a gaseous reactant A is contacted with a liquid solution of reactant B. Gas A is absorbed, dissociates and reacts instantaneously with B ions to produce AB clusters. When the concentration of the produced clusters exceeds the solubility concentration, supersaturation occurs and nuclei are formed, which start to grow to form bigger crystals. When the concentration of the crystals increases, the chances of forming agglomerates or aggregates become higher. When two or more crystals meet, they may aggregate and grow further as one crystal or agglomerate. These steps are illustrated by Fig. 1.

2. Previous work

Narayan et al. (1992) studied the agglomeration of copper sulfate pentahydrate, nickel ammonium sulfate, potassium sulfate and soy protein in a continuous MSMPR crystallizer. They determined the rates of nucleation, growth and agglomeration for these precipitates.

Jones et al. (1996) developed a model describing particle formation during an agglomerative precipitation process. In their work, processes that determine the formation of both primary particles and crystal agglomerates respectively are briefly reviewed together with simulation techniques that predict primary and secondary particle size distributions.

Zuoliang et al. (1997) developed a model to determine the rates of nucleation and crystal growth from the particle size distribution obtained in a non-ideal MSMPR crystallizer. Their model takes effects of mixing intensity and product removal location into account.

Hounslow et al. (1997) investigated the role of solution composition in aggregation during precipitation. In their work, experimental data of calcium oxalate monohydrate precipitation was used to show how the aggregation rate depends on solution composition. A discretized population balance method was used to extract growth and aggregation rates from experimental particle size distributions collected at regular time intervals. They found the measured growth rate to be second order in the relative supersaturation, regardless of the solution composition, that is the calcium to oxalate ion ratio. Further, they demonstrated that the rate of aggregation exhibits a more complex dependency on solution composition than the growth rate. In their work they presented a new model based on the diffusion of solute ions to a cementing site, which, despite a number of simplifying assumptions, was able to explain the experimentally observed aggregation rate.

Leubner (1998) has developed a new crystal nucleation theory for the continuous precipitation of silver halides. His model was based on a dynamic balance between growth and nucleation. The model is applicable for non-seeded systems with homogeneous nucleation and diffusion-controlled growth. It can predict the particle size distribution on the basis of average crystal size, residence time, solubility, feed concentrations and temperature. Also the model can predict the maximum growth rate, the ratio of nucleation rate to growth rate, the ratio of average to critical crystal size and the size of nascent nuclei. The experimental results show good agreement with model predictions.

Jones and Zauner (2000) studied the precipitation kinetics of calcium oxalate using the MSMPR method. They operated their reactor at 37 °C at various residence times, feed concentrations, stirrer speeds and feed points. A procedure to determine the kinetic parameters for nucleation, growth, agglomeration and disruption from the size distribution of the produced particles was introduced by them. They concluded that crystal growth occurs through a surface-integration-controlled mechanism with a second-order dependency of the growth rate on the absolute supersaturation. The nucleation rate was found to depend on power input and feed point position, and therefore was controlled by the rate of mixing. Agglomeration rates exhibited a maximum with increasing power input through the stirrer.

Jones et al. (2001) developed a model of agglomerative precipitation based on Monte Carlo simulation techniques. The processes of nucleation, crystal growth and agglomeration are first simulated to obtain the particle size distribution (PSD) obtained in a continuous MSMPR unit. An extension is then introduced to account for particle disruption by considering two size reduction mechanisms—one of particle splitting into two parts of equal volume, and the other taking micro-attrition into account. A comparison was made with experimental data for both calcium oxalate and calcium carbonate precipitation, showing reasonable agreement.

The determination of precipitation kinetics using the MSMPR method can be risky, especially with sparingly soluble material due to the extremely high degrees of supersaturation existing in such systems. In such cases, local mixing may become the rate-determining step rather than the intrinsic kinetics. A more precise method is therefore