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Fundamental insights into barium sulfate precipitation by time-resolved *in situ* synchrotron radiation wide-angle X-ray scattering (WAXS)

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HIGHLIGHTS

- Precipitated in a Y-mixer, characterization of barium sulfate particles without agglomeration and aggregation.
- Monitoring the build-up of the crystalline mass at high supersaturation by time-resolved *in situ* synchrotron radiation WAXS.
- Simulation of the particle formation by a population balance equation coupled with component balance equations.

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ABSTRACT

The particle formation of barium sulfate is examined *in situ* for reaction times from tens of milliseconds up to several seconds. Precipitation of the crystalline solid is performed in a tubular reactor of adjustable length equipped with a free jet cell. The transient development of the mass concentration of precipitated solid is determined using synchrotron radiation wide-angle X-ray scattering (WAXS). Precipitated suspensions are stabilized by off-line experiments to measure particle sizes without agglomeration and aggregation. The experimental data are compared to the results of population balance simulation calculations. Nucleation and growth kinetics are derived by theoretical approaches from the literature. It is found that barium sulfate particles grow by aggregation of previously formed particles.

1. Introduction

As a result of the very low solubility of barium sulfate in water, the precipitation process can be performed at very high supersaturation. Due to this high supersaturation, primary processes, such as nucleation and crystal growth, proceed very fast in a time scale of micro- to milliseconds. Detailed knowledge of fundamental mechanisms of nucleation and crystal growth is of great importance for tailoring the product properties, and for scientific and industrial purposes. *In situ* information especially on phase transition and the buildup of crystalline mass during fast precipitation at high supersaturation are rarely available in open literature. A fast measuring method is required capable of measuring at very short time scales of a few milliseconds to observe a solid formation process of crystalline matter *in situ*.

Several *in situ* X-ray diffraction methods using synchrotron radiation have been applied to investigate fast precipitation processes of inorganic material in the recent past. Quayle et al. (2002) have shown that wide angle X-ray scattering (WAXS) is very well suited to study fast batch crystallization processes on-line using a stopped-flow technique. Bolze et al. (2002) have done small angle X-ray scattering (SAXS) for the on-line investigation of calcium carbonate precipitation and proved the existence of a metastable, amorphous precursor phase in real time. Haselhuhn et al. (2006) have studied the pseudo polymorphic behavior of precipitated calcium oxalate by using a fast Y-mixing device, coupled with a reaction tube of variable length. Kucher et al. (2008) have quantitatively determined the transient increase of the crystalline mass during barium sulfate precipitation and found that the nucleation rate does not depend on the initial free lattice ion ratio. In context with oil and gas processing, Jones et al. (2008), Mavredaki et al. (2011) and Webster et al. (2014) have investigated surface deposition

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and its prevention on stainless steel due to barium sulfate precipitation. In the free jet micro mixer SAXS study by Marmiroli et al. (2009, 2010), calcium carbonate particles are detected in the range of microseconds after mixing. Schmidt et al. (2010) precipitated zinc sulfide by a heterogeneous reaction and measured the particle formation in a free jet. All these studies utilized synchrotron radiation to provide the necessary high photon flux. This high flux is necessary because of absorption of X-ray radiation by the solvent.

The fundamental process parameters supersaturation ratio S_a (see Eq. (6)) and free lattice ion ratio R (see Eq. (7)) have been studied off-line in great detail by Judat and Kind (2004), Kucher et al. (2008, 2006), Nielsen (1961), and Schwarzer and Peukert (2004, 2005) at high supersaturation. These authors preferred impinging jet mixers in millimeter scale to investigate the influence of fundamental process parameters at the precipitation of barium sulfate. By using such mixing nozzles, the effect of mixing on the build-up of the supersaturation can be neglected, according to Kucher et al. (2006), and Schwarzer and Peukert (2002). Precipitation with barium excess leads to a stabilization effect due to electrostatic repulsion, see Kucher et al. (2006) and Schwarzer and Peukert (2004). They have also shown that the measurement of particle size distributions at barium sulfate precipitation without barium ion excess is strongly influenced by agglomeration.[1] In this study, a method for stabilizing those suspensions after precipitation can be found. Agglomeration is an unwanted process obscuring the existence of single particles and enlarging the particle size measured by light scattering methods. Suppressing this secondary process step simplifies the comparison between experimental data and the results of numerical modeling of the primary processes. In this study, a surfactant obstructs the agglomeration.

Aggregate sizes can be determined by measuring particle sizes without agglomeration. Hereby, the hypothesis of Judat and Kind (2004) and Melikhov and Vuković (1975) is pursued that barium sulfate grows by aggregation.[2] The morphologies of precipitated barium sulfate at various levels of supersaturation are shown in the experimental study of Kucher et al. (2006). The SEM images led to the assumption that growth by aggregation dominates in a range of $S_{a,0} \lesssim 750$. At supersaturation ratios above that, particles are formed exclusively by primary processes. In this study, the influence on the particle formation process is proved by adding the surfactant chosen to one of the reactant solutions. A possible aggregation step could be restrained by using the reaction-inert surfactant. Hints about this particle formation mechanism can be found in numerous studies about barium sulfate precipitation with additives, for example, from Benton et al. (1993), Qi et al. (2000, 2001), Yu et al. (2005), and Jones et al. (2006). These authors preferably performed at low supersaturation with induction times of some tens or hundreds of seconds. It is shown that even traces of additive can have an influence on the particle morphology of barium sulfate due to influencing the aggregation. Other substances are also investigated regarding aggregation during low supersaturation, see the overview by Penn and Soltis (2014).

The aim of this study is to review the hypothesis that growth by aggregation happens during the precipitation of barium sulfate at high supersaturation. Therefore, on-line and off-line experiments are performed at various levels of supersaturation to observe the transient development of the crystalline mass and to measure the resulting size of aggregates and their primary particles. The experimental data about the timing of the precipitation process and final particle sizes are compared to numerical calculations based on population balance modeling. From these findings, it is possible to draw specific conclusions about the particle formation of barium sulfate.

2. Material and methods

All precipitation experiments are performed at a constant temperature of 25 °C. Barium sulfate is precipitated from aqueous barium chloride and sodium sulfate solutions. The aqueous reactants are prepared with the salts barium chloride dihydrate (Roth, 4453.4, pro analysis) and sodium sulfate (Roth, 8560.2, pro analysis) dissolved in deionized water. The reactant solutions are continuously mixed in a Y-mixer (jet diameter of 0.5 mm, jet angle of 150°, 2 mm in the mixing zone, 7 mm length of mixing zone, see Kucher et al., 2008). Reaction tubes of varied lengths and diameters can be connected to the mixer. The reactant solutions are fed with equal volume flow into the mixing chamber. Specific flow rates are generated by two gear pumps (Ismatec, MCP-Z Standard, pump head Z-130), measured by magnetic-inductive flow meters (Krohne, IFC90) and controlled by PID controllers (Jumo, dTron 316). The whole experimental setup can be operated by remote control. Generally, mixing has an influence on the build-up of the supersaturation also on the resulting particle size distribution. However, it was shown that mixing does not affect the particle formation even at high supersaturation, if total flow rates greater than 250 ml/min (equal to $Re = 2971$ and $\varepsilon = 114$ kW/kg) are maintained, see Kügler et al. (2011). The Y-mixer used operates at total flow rates between 300 and 900 ml/min, thus, the influence of mixing on the particle formation is neglected.

2.1. Stabilization

Off-line experiments are carried out in the lab to quantify particle sizes at solid–liquid equilibrium (SLE) by preventing agglomeration with a surfactant. Dynamic light scattering is used to measure the particle sizes of suspensions immediately after precipitation at a constant temperature of 25 °C (Malvern Instruments, Zetasizer Nano ZS). Some samples are analyzed by scanning electron microscopy (Leo 1530 Gemini). The surfactant MelPers0045 (BASF SE) is added for stabilizing suspensions at stoichiometric precipitation conditions ($R = 1$). MelPers0045 is an aqueous solution of a polycarboxylate ether polymer (see Puppe, 2008; former name: MelPers0030; molecular weight: 20,000 g/mol). The polymer content in MelPers0045 is 45 weight percent. A third gear pump, flow meter and controller are used to add the surfactant solution at a concentration of 2 g/l in a second Y-mixing device one or two seconds after mixing, see Fig. 1a. The first Y-mixer operates with a total flow rate of 300 ml/min and the second Y-mixer at 600 ml/min. Hence, the surfactant concentration after mixing is always 1 g/l. The points of time for reaching

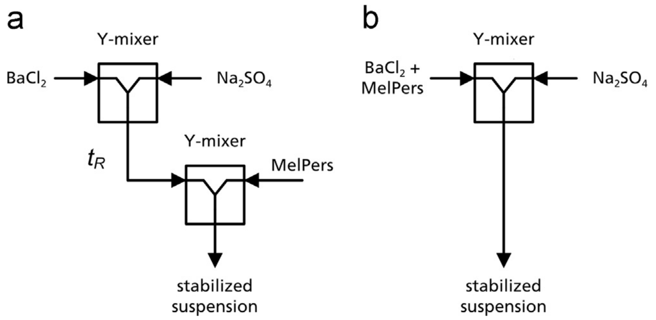

Fig. 1. Sketches of the setups for off-line experiments: (a) with quenching mixer and (b) without quenching mixer.

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[1] An agglomerate is a non-intergrown association of particles, whose total surface area is equal to the sum of individual surfaces, see DIN53206 (1972).

[2] An aggregate is an intergrown association of primary particles, whose surface is smaller than the sum of surfaces of primary particles, see DIN53206 (1972).