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Effect of precipitation conditions on the morphology of strontium molybdate agglomerates

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ABSTRACT

Preliminary experimental results about precipitation of strontium molybdate particles show that they have morphology as hierarchical agglomerates [A. Cameirão, R. David, F. Espitalier, F. Gruy, Multiple agglomeration in strontium molybdate precipitation, 16th ISIC, 2005, pp. 355–360]. The precipitation of strontium molybdate was studied and monitored in a batch reactor. The precipitation parameters, i.e. initial concentration of strontium molybdate, temperature and stirring rate, have an effect on the particles and agglomerates morphology. The shapes of the crystals were observed by SEM, and the PSD was measured at the end of precipitation by laser diffraction. The powders were also analysed by XRD, surface area (BET) and porosity measurements. Finally, a model of agglomeration was designed in order to predict the morphology of the observed agglomerates.

1. Introduction

Many industrial compounds obtained by precipitation, namely catalysts and pigments, present a structure of agglomerated crystals bonded by crystalline solid bridges. The common structure consists of crystallites with sizes between a few nm and 1 μm, which generate agglomerates of about 10 μm (first degree of agglomeration), which in turn agglomerate to the final agglomerate sizes of about 100 μm or sometimes up to 1 mm (second degree of agglomeration) (Fig. 1).

Strontium molybdate particles seem to have such morphology. Söhnel and Mullin [1] have observed that $SrMoO_4$ precipitates are well-defined very compact crystals with neither formation of complexes in solution nor amorphous phase formation. The forming crystals quickly agglomerate during the entire crystallisation process.

The induction time of precipitation is determined visually and it increases between 2 and 400 s at 25 °C for decreasing concentrations of both reactants after mixing between 70 and 15 mol m^{-3}. At the end of the induction time crystals are spherical. After 1 min, they show an ellipsoidal shape of 8 μm size and are all agglomerated after 30 min [1].

Söhnel and Mullin have concluded that increasing concentration increases the final size of particles; increasing stirring rate diminishes the size and induction time. Spheres seem to continue to grow after agglomeration. The final PSDs show sizes between 10 and 100 μm [1].

This work presents the experimental results in order to understand and to model the dynamics of its precipitation. We have enlarged the work made by Söhnel and Mullin to a larger extent of concentrations and stirring rates, and we have introduced the study of the effect of temperature on the strontium molybdate precipitation. We have monitored the concentration during all precipitations in a way to model growth and nucleation and have characterised the most likely particles size distributions to understand and model the agglomeration process.

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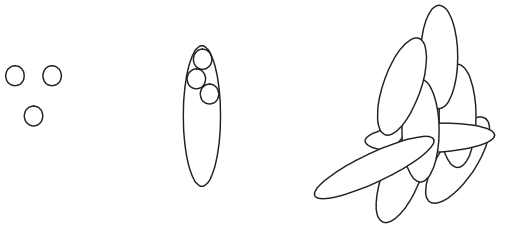

Fig. 1. Agglomeration degrees.

2. Experimental procedure

2.1. Materials

In order to obtain $SrMoO_4$, solutions of Na_2MoO_4 and $SrCl_2$ (Sigma-Aldrich®) were used. The precipitation obeys the chemical reaction

$$SrCl_{2(aq)} + Na_2MoO_{4(aq)} \rightarrow SrMoO_{4(s)}\downarrow + NaCl_{(aq)}$$

The solutions were prepared by dissolving the required amount of the analytical-grade chemicals, $SrCl_2$ and Na_2MoO_4, in 1 L of deionised water. The precipitation was considered as completed 2 h after addition of reactants.

2.2. Experimental apparatus

The mixing of equimolar solutions of Na_2MoO_4 and $SrCl_2$ was achieved in a 2 L glass crystalliser diameter (15 cm) with double jacket equipped with a three-bladed paddle stirrer [2] and four baffles, at a controlled temperature ranging between 10 and 80 °C. Initial concentration of strontium molybdate was varied between 4 and 100 mol m^{-3}.

The Mixel®TT stirrer has a diameter of 50 mm and generates axial flow; the paddles are located at 120° and inclined at 45°. It is powered by a motor Bioblock Scientific Digital 2000. The stirrer was placed at a clearance of $\frac{1}{3}$ of the height of the reactor from its bottom. A Rushton turbine was also used, which generates radial flow and higher turbulence in the discharge stream.

All experiments with changing concentration and temperature were made with the Mixel®TT. The calculated energy dissipation rate of the stirrer per unit mass ranged between 9×10^{-4} and 1.5 W kg^{-1} (60–700 rpm). The stirrer Reynolds number was between 10^3 and 10^6, indicating mainly turbulent mixing regime.

2.3. Procedures and methods

2.3.1. Characterisation of solution and particles

The particle size distributions were measured by laser diffraction with a Malvern Master Sizer 2000 at the end of precipitation. We have observed that these measurements were reproducible when direct sampling of reactor suspension was made. Agglomerates were observed by SEM with a JSM 6400—Scanning Microscope after filtration of the suspension and drying at 40 °C.

Measurements of conductivity were also achieved on-line by using a conductometer (Consort 831, Bioblock). We verified that if the volume fraction of solids in suspension is lower than 0.5% particles do not interfere with conductivity measurements. Concentration of strontium molybdate was calculated from conductivity values [5].

The crystallite size was estimated by X-ray diffraction in a Siemens diffractometer D5000 Kristalloflex; the Hg-porosity was achieved in a Micromeritics—Auto Pore IV and the surface area measured by BET analysis in a Micromeritics—ASAP 2000.

2.4. Preliminary studies

We have made a preliminary study to settle the experimental protocol. We started with determining the minimum stirrer rate to suspend the particles. We have calculated this value by Zwietering's correlation [4] with a constant power number Np equal to 6 for a Rushton and 0.7 for a Mixel TT with a variable particle diameter d_p and a volume fraction of solid ϕ_{vs}, g is the gravity; $\Delta\rho$ is the difference between the solid and the liquid density, v is cinematic viscosity of the solution [4]. The minimal stirring rate depends on particles' concentration and size. From each experiment we measure the maximum size of particles. Thus, we can calculate N_{ms} for each particle size by Zwietering [4] correlation.

We can deduce that the minimal stirring rate which fulfils the suspended solids condition is 350 rpm for the Mixel stirrer and 125 rpm for the Rushton.

Also, we have estimated the micromixing effects. Therefore, we have analysed the influence of the way of addition of the second reactive in the first one. We have concluded that there is negligible influence of micromixing in nucleation of strontium molybdate [2].

Each precipitation experiment was realised three times with the same operating conditions. The results for concentration against time and for final PSD were compared. The concentration values were equal within 15% error. The maximal error on volume percentage in each class of PSD is 1%.

2.5. Kolmogoroff and Batchelor microscales

The Kolmogoroff microscale defined as

$$l_K = \left(\frac{v^3}{\varepsilon}\right)^{1/4} \quad (1)$$

denotes the limit between laminar and turbulent regimes for fluid eddies.

The Batchelor microscale is the limit between the Brownian and laminar regimes for fluid eddies:

$$\lambda_B = \left(\frac{\upsilon D_{AB}^2}{\varepsilon}\right)^{1/4} \quad (2)$$

where D_{AB} is the diffusivity of a particle.

3. Results

3.1. Change of supersaturation during precipitation

The evolution of supersaturation ratio (C/C^*) during precipitation is shown in Fig. 2 for several initial concentrations of $SrMoO_4$ between 4 and 50 mol m^{-3}. The solubility of $SrMoO_4$ was measured by means of dissolution experiments at different temperatures and its expression was approximated by $C^* = 10^{-5}T^2 + 0.0015T + 0.0676$ [5].

The desupersaturation versus time is shown in Fig. 3 for temperatures between 25 and 50 °C.

The desupersaturation versus time is plotted in Fig. 4 for various stirring rates and stirrer geometries. Note that the desupersaturation curve is very different between the two types of stirrers, which generate, even at the same energy dissipation rates, different patterns of flow and shear stresses.