Crystallization of Calcium Sulphate during Phosphoric Acid Production: Improving Filtration through Improvement in Particle Shape and Size Distribution

by

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Abstract

The production of phosphoric acid from phosphate mineral rock involves the addition of phosphate rock to a concentrated sulfuric acid solution. The induced reactive crystallization process produces a side product of calcium sulfate hydrates, which become the filter media in the subsequent acid separation process. For most industrial processes, the dihydrate form of calcium sulfate crystals (gypsum) precipitates and its shape and size distribution are key factors in determining the downstream filtration efficiency. Particularly, the metal ion impurities coming from raw phosphate rock play an important role as shape modifiers. The presence of impurities in the acid mixture has an impact both thermodynamically and kinetically, although most of the available literature focuses on their sole role as growth inhibitors and has neglected their potential impact on altering solution speciation.

Past studies on gypsum crystallization in phosphoric acid solutions usually involve the study of crystal growth and nucleation kinetics. However, most of these works did not use the correct definition of supersaturation when quantifying kinetic parameters. The high concentrations in this multicomponent electrolyte system implies that supersaturation, which be written in terms of the solubility product ratio, as governed by nonideal thermodynamics, requires the computation of activity coefficients as well as free ion concentrations. For this purpose, the mixed solvent electrolyte (MSE) model is utilized to capture the solution speciation in order to properly quantify supersaturation at any given condition. The MSE model is a first-principles model that determines solid-liquid equilibrium by calculating excess Gibbs energy from additive pairwise interactions. When impurities are present, additional binary interactions need to be included in the databank, which is carried out by regression analysis using solubility measurements.

Continuous reactive crystallization experiments are carried out with and without additives using a mixed-suspension, mixed-product removal (MSMPR) crystallizer. The crystal size distribution and supersaturation are measured once the pro-
cess reaches steady state. Different conditions are imposed to acquire both the temperature and supersaturation dependency of the crystallization kinetics. A two-dimensional growth model with dispersion is developed in order to capture the needle-like crystal morphology and the temperature dependence of the crystal aspect ratio, which is made possible by performing multi-scale image segmentation and edge detection using the Canny method. Experimental and numerical results are obtained for the base system and in the presence of single and combined impurity ions. Different growth inhibition models are verified and compared for numerical quantification of step advancement retardation in the presence of impurities.

This study goes beyond past studies by providing a full two-dimensional kinetic model for a highly concentrated ionic system that includes crystallization kinetics and a thermodynamically correct driving force accounting for non-ideality as well as the effects of impurities.

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