Crystallizing Size Distribution Models

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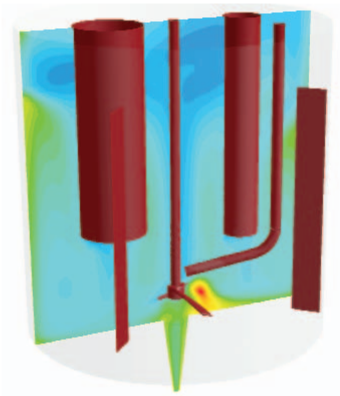
One of the main challenges in industrial crystallizers is to control the crystal size distribution (CSD). CSD control is important to ensure product quality and purity and the successful operation of the crystallizer. It often affects downstream processing such as filtration, centrifugation, and milling. In spite of its importance, CSD is not well understood. Part of the difficulty is that the size distribution varies in space and time in a crystallizer due to non-ideal flow patterns and heat transfer. Solution thermodynamics and crystallization phenomena also play a role.

One way to understand crystallization behavior is through numerical modeling. In the past, simple models were used that were based on the assumption of a well-mixed crystallizer with negligible hydrodynamic effects. Such models led to conservative designs that were not optimized for yield. Recently, CFD models for crystallizers have been developed that incorporate population balance methods. These models account for the coupled effects of fluid mechanics and crystallization phenomena. Through population balance, fluid flow occurs in conjunction with evolutionary processes of the crystalline phase. Particles of a specific state can form, migrate to another state, or disappear from the system as a result of nucleation, growth, dissolution, aggregation and breakage.

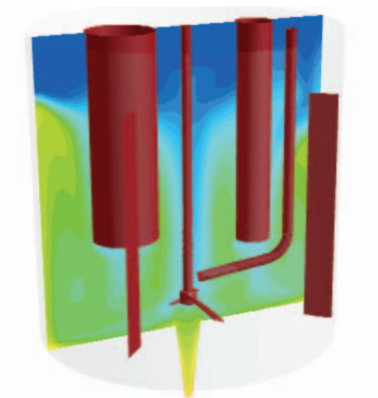
Fluent, Dow Chemical, and the University of Utah have been working together to model a crystallizer that is in operation on a pilot scale at Dow's Ludington facility. This effort was part of a funded project from the Department of Energy (DOE) that concluded in June of this year. The physical process is to enrich and purify a stream that is rich in calcium chloride ($CaCl_2$) and potassium chloride (KCl) by crystallization of sodium chloride (NaCl) and KCl, which are considered impurities. The inlet stream is a mixture of 45% $CaCl_2$, 1.28% KCl, and 4.22% NaCl. It contains 3.8% (by weight) NaCl particles with a Sauter mean diameter, a surface-area weighted average commonly used in multiphase applications, of 122 microns. The objective was to reduce the NaCl in the solution further to about 0.42%. The jacketed reactor is cooled to 300 K with the inlet stream at approximately 325 K. The solubility curve of NaCl, which is linear with temperature in this range, was obtained using StreamAnalyzer from OLI Systems.

The Eulerian granular multiphase model in FLUENT was used with the population balance solver on a 3D mesh of 400,000 cells. The rotation of the impeller was simulated using the multiple reference frames (MRF) approach. The constituents NaCl, $CaCl_2$, and KCl in water were each modeled as a species in the primary phase. The vessel has a curved feed tube, baffles on the walls, and two dip filter cartridges where clarified liquor is removed by collecting crystals on their surfaces.

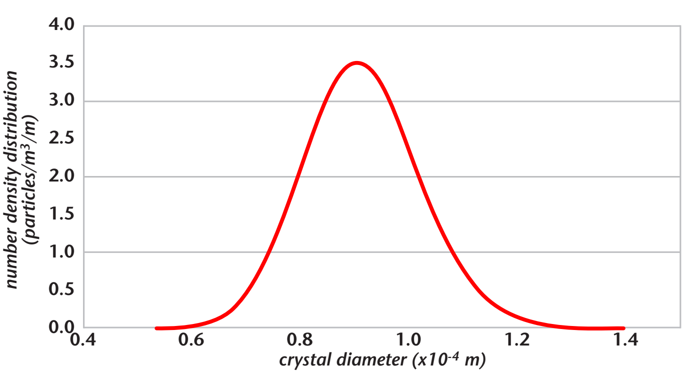
Results show that as the NaCl solute enters the (cooler) reactor, it is quickly consumed to form crystals. At the outlet, the mass fraction of NaCl in solution is 0.37%, compared to 0.44% at the inlet, indicating a purification of the solution. The solids volume fraction shows some settling and collection at the outlet filter. At the bottom of the crystallizer, the amount of solids is 3% and the Sauter mean particle size is 133.8 microns, almost 10% larger that the size at the inlet. Results for the total number density of solids shows that the maximum is close to the inlet where there is ample supply of solute and a high supersaturation ratio. The crystal size distribution at the outlet is in good qualitative agreement with observations. Further study is underway for quantitative comparisons. ■



Supersaturation profile on a vertical cross-section; the supersaturation ratio is higher near the inlet where there is ample supply of the solute



NaCl (solids) volume fraction contours on a vertical cross-section; the solids show some settling



Crystal size distribution at the outlet in the vessel bottom