



Measuring Sparingly-Soluble, Aqueous Salt Crystallization Kinetics

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Mission Issue

Expanding water supplies by treating impaired water sources.

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Problem

It is well accepted that a major drawback to widespread adoption of reverse osmosis (RO) desalination for inland areas is the lack of economical and environmentally-satisfying solutions for handling the concentrate streams generated from desalination processes. Sparingly-soluble salts from ions such as calcium, barium, strontium, magnesium, and silica, if present, limit the amount of water that may be recovered due to their becoming supersaturated and depositing (scaling) on the membrane and other surfaces.

To address this drawback, we addressed the following technical questions: what are the least expensive and most efficient process designs for a crystallizer to bring supersaturated concentrate streams back to saturation thereby not allowing for scaling to occur on membranes and other surfaces?

In this work, we present a steady state, continuous stirred tank reactors (CSTRs)-in-series approach to study crystallization kinetics of a model solution mixture that is supersaturated in CaCO_3 .



Jar test set up for reactors in series.

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Sankaranarayanan A. Ravichandran

More Information

<https://www.usbr.gov/research/projects/detail.cfm?id=7120>

Solution

We have used pH, conductivity and turbidity changes in the system to monitor crystallization using six CSTRs with individual residence times of nominally 3, 5, and 11 min. This system operates in a steady state mode with total crystallization times from ~ 15-68 min. and was capable of handling up to ~0.59 L/min of hard water for the shortest residence time studied.

The supersaturation of sparingly-soluble salts were depleted ~25% and over 50% with total reactor system residence times of ~15 and 68 min, respectively, without any added chemicals. Using the metric of 5 NTU turbidity as being the point of discernible crystal formation, we examined how mixing energy dissipation affects the induction times for crystallization.

Application and Results

A reaction engineering approach to study crystallization of sparingly-soluble salts using CSTRs -in-series has been developed. Design scale-up factors using Kolmogorov mixing lengths as well as exposure times to surface area have been developed to quantify the apparent nucleation time and crystallization rate, as indicated by turbidity measurements. It was found that mixing affects CaCO₃ crystal nucleation very significantly and is strongly dependent on the surface area-to-volume ratio of the mixing regions as opposed to simply power dissipation.

Our experimental approach facilitates study of the nominal kinetic effects from perturbations in the process conditions and reaction environment around an initial steady-state. Such results can provide clearer directions for crystallization process improvements.

Future Plans

An improved and scalable metrology for obtaining nucleation and crystallization kinetics is needed to optimize the design of fluidized bed pellet softener reactors and other seeded (and unseeded) crystallizers. Currently, they are designed and piloted using very empirically-driven vs. more mechanistically-inspired design heuristics. Thus, optimizing these systems is very difficult with so many variables, such as flow rate, seed/pellet content, variable feed concentrations, as well as, choosing proper seed material and addition of other materials, which might increase efficiency and make their outputs more predictable.