

Industrial Crystallization Fundamentals

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During this tutorial we will present the theoretical background on Industrial Crystallization Fundamentals. In an industrial crystallization process a suspension of crystalline particles in the solution is formed which after filtration and drying leads to the desired particulate product. Crystalline form, crystal size distribution, crystal shape and purity are the important crystalline product quality aspects which are strongly determined by crystal nucleation & crystal growth as well as crystallization process type (evaporative, cooling, anti-solvent crystallization, precipitation).

Crystal primary nucleation is the start of a phase transition towards the crystalline solid phase. Classical Nucleation Theory (CNT) describes this process through an energy barrier for nucleus formation, the nucleation work, and the rate for the crossing of this energy barrier, the primary crystal nucleation rate. This nucleation rate is a strongly non-linear function of supersaturation and interfacial energy and therefore is strongly influenced by for instance mixing phenomena and the presence of heterogeneous particles. Secondary nucleation, the process of formation of new crystals due to the presence of larger parent crystals, is another important process with which new crystals can appear.

Once a crystal is nucleated, the growth phase can follow different paths and involve various mechanisms, depending on the growth conditions and roughness of the surface. Growth may involve 2D nucleation in the birth-and-spread mechanism, but in many cases proceeds through spiral growth originating from screw dislocations. The different mechanisms lead to different growth rates, and thus to different crystal morphologies. Both thermal and kinetic roughening can dramatically alter the growth behaviour. Additives (or impurities if they are unintentional) also modify the growth behaviour, typically through their interaction with steps. The elementary growth mechanisms take place on an atomic scale and from the basis of the often more macroscopic modelling that is normally used for industrial applications.

The design of industrial crystallization operations requires not only an understanding of the mechanisms and kinetics of crystal nucleation and growth but also the models and design techniques required to develop equipment and processes to achieve high quality products. Many current products potentially occur in a range of solid forms; hydrates, solvates, salts and polymorphic forms, where the properties of the product are highly dependent on the solid form produced. It is particularly important not only to be able to accurately predict the solubility of the species produced but also to understand the phase diagram to be able to ensure the correct solid form is produced. In addition, the application of engineering models such as mass balances, energy balances, and population balance equations are vital to ensure that an efficient crystallizer design is achieved. Finally, we will discuss the benefits and drawbacks of different types of industrial crystallizer designs including batch and continuous crystallizers, precipitation units, antisolvent addition crystallizers, and melt crystallizers.