Bernoulli offers a solid basis for crystallization

Introduction

The state of knowledge about crystallization is associated with the names Mersmann and Mullin, who showed 40 years ago that the average crystal size in stirred crystallizers is < 1 mm.
The theory that leads to this result is based on practice (MSMPR- **m**ixed **s**uspension **m**ixed **p**roduct **r**emoval)) and a coupling of mass and population balances.

Crystallization and crystal solvation are opposing physical processes in the tiny cosmos of nanoparticles. They occur in the boundary layer on the crystal surface. The reaction enthalpy that is implemented in these processes is 3890 J / mol for NaCl

Related to a NaCl molecule these are:

$$RE_{NaCL} = 40{,}31 \times 10^{-3} \text{ eV}$$

$$1 \text{ Mol} = 6.022 \ 10^{23} \text{ Particle}$$
$$1 \text{ J} = 0{,}624 \times 10^{19} \text{ eV}$$

While the NaCl molecules inside the crystal are held together by an enthalpy of 411 kJ/mol, the molecules in the crystal surface wetted by the solvent may be liquified in turbulent flow.

What is the impact of the kinetic energy that is permanently fed into the process in order to disperse the suspension sufficiently? It is converted into kinetic energy that flows partly into the degrees of freedom of the floating crystals. Especially the collision of rotating crystals produces a large number of hydrated ions and increases local supersaturation.

This locally increasing supersaturation with hydrated ions is neither visible nor measurable. However, the effect is convincing. A large number of very small crystal nuclei form while releasing energy. Waste heat resulting from this process increases the suspension temperature a little. But the formation of these small crystal nuclei is extremely undesirable and requires fine grain dissolution in order to be able to operate crystallization economically.

The thermodynamics of crystallization.

Crystallization is a thermodynamic process that is made possible by a state of equilibrium in the surface of a crystal. The thermodynamic equilibrium is defined as the state to which the system left to itself strives and in which it finally comes to rest.

A crystal in a supersaturated suspension combined with a positive but hydrated ion and a negative but hydrated ion forms a system which dissipates the heat of crystallization to the suspension when the two different ions are embedded in the crystal lattice. This equilibrium state, which is formed briefly by the release of heat, stabilizes the crystalline structure of the surface.

The supersaturation in the liquid is of crucial importance for crystallization processes.
It is brought about by:
a) Solvent removal
b) Cooling the suspension
c) Reduction of the solute by a displacement agent.
d) Energy supply: The saturation / supersaturation increases in the suspension consisting of solid and solvent when kinetic energy is added to it.

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The kinematics of the particles

The following participants in a saturated suspension come into contact with each other.

- Large crystals > 100 µm
- Small crystals < 100 µm
- Very small crystals
- Hydrated ions

The relative speed of these substances is very different. For large crystals in a laminar flow it is the sink rate. For small crystals, the sink rate is actually zero. A change in the crystal size therefore takes a relatively long time because a change in saturation near the crystal surface takes place only via diffusion. On the other hand, very small crystals quickly dissolve according to the Gibbs-Thomson effect. This increases the saturation or supersaturation locally.

Hydrated ions follow the Brownian movement. Their individual speed changes constantly.
The slow hydrated ions develop an affinity for the crystal surface and form the so-called diffusion boundary layer. This is up to now an accepted model. It regulates the chronological sequence of the crystallization process postulated by Mullin of diffusion and integration of the hydrated ions into the crystal surface. This idea implies a relatively slow transport of the hydrated ions to the surface.

In this calm zone an orderly mass transfer becomes possible. A zone that appears to be absolutely necessary for crystallization processes.

The kinetics of crystallization

The low reaction enthalpy decides between solid and solution. A negatively charged ion and a positively charged ion meet at the crystal lattice during the crystallization process and release the enthalpy of reaction.

In the laminar flow range, Mullin, Mersmann and many others have described and investigated these processes in detail. These investigations form the knowledge for the existing crystallization plants. But what do turbulent flow conditions to crystallization processes. Turbulent flow takes place on the rotor and a second time when the rotating suspension is broken. The rotating suspension must be slowed down so that the suspension can be sufficiently dispersed.

What happens to the Mullin diffusion boundary layer? It is probably washed away under the influence of turbulent currents.

A turbulent flow is characterized by the fact that larger crystals, due to their inertia, only undergo any change in direction with a delay. It happens that larger crystals are bombarded continuously by a lot of smaller crystals in the suspension.

If a 1µm large crystal moves at a relative speed of 1 m / sec on a collision course with another crystal, its kinetic energy is:

$$E_{kin} = 6{,}74 \text{ k eV}$$

Sufficient energy to release many NaCl molecules from the crystal lattices of the colliding crystals. 100 µm big crystals achieve a 10^6 times greater effect when colliding with a 500 µm big crystal. The effect of large rotating crystals must also be noted.

Fracture particle increase the number of crystals, which in turn collide with other crystals. This collision cascade in a turbulent environment ultimately leads to the dissolution of crystal mass, which then forms hydrated ions. As a result, the supersaturation increases in the turbulent area of the crystallizer, spontaneous nucleation will be triggered. A very large part of the drive power to disperse suspension is available for this process of crystal dissolution and energy dissipation.

This is a very fast and physically verifiable process of energy dissipation. If there are no solids in the suspension, the energy dissipation is only caused by viscosity and requires a relatively long time. Depending on the crystal content in the suspension, the energy dissipation takes place much faster.

Mersmann mentions a crystal volume fraction of 10 – 15 % in large crystallizers. Assuming the crystals are 1 mm in size, the average distance between the crystals is less than 1 mm.. In turbulent flow, the collision probability is very high.

The Physic offer other options!

A homogeneous suspension in a laminar flow offers much better crystallization conditions. It is not necessary to keep crystals in suspension. A sinking crystal should not be stopped and its growth should not be disturbed by unnecessary energy input. When the crystal is down, it can be transported back to the place where supersaturation is generated.
The inner and outer circulation is intended for this purpose. In this crystallizer, all crystals have an individual sink rate according to their size. This gentle treatment causes very little abrasion and allows the formation of larger crystals.

Bernoulli describes the lossless energy conversion along a current thread from pressure energy into potential energy into kinetic energy.

$$p \; + \; gh \quad + \; \tfrac{1}{2}\, \rho\, w^2 = \quad constant$$

In a Bernoulli crystallizer, only the low energy losses in the external circuit need to be compensated.

The inner cycle

The flow through the heat exchanger is driven by density differences in the suspension. The average density of the suspension in the evaporation vessel ($\rho1$) is greater than that of the suspension in the riser ($\rho2$).

The suspension is heated in the heat exchanger. If the local pressure in the riser pipe decreases with increasing height, the boiling point of the suspension can be reached. The sudden formation of gas bubbles reduces the average density $\rho2$ and causes additional thrust.

Both effects cause drive pressure (δp).

$$\delta p = H \; g \; (\rho1 - \rho2)$$

H = height of the liquid level
g = 9.81 m / sec2

The outer cycle

Only the energetic flow losses have to be compensated to ensure sufficient flow (w = 0,6 m / s) to collect coarse crystals with a rotary valve.

With this crystal size (2 - 4 mm), a curved screen is sufficient to remove the solvent. The surface moisture is then separated off in a fluid bed dryer.

The energy input for the whole process is correspondingly low and protects the crystal surface from destruction.

Summary

This process design based on the Bernoulli principle has been practiced for generations.
Gravity heating, driven by differences in density, transports heat from bottom to top.
These density differences are caused by the different water temperature between the flow and return. In the Bernoulli Crystallizer, the liquid transports crystals from bottom to top - back to the evaporation bubble, where new super saturation is formed.

So far, supersaturation has been continually reduced in the laminar region by crystallization, and at the same time crystal mass in the turbulent region has been broken off and dissolved.

Physics offers the possibility of transporting the crystals with little energy instead of dispersing the suspension with plenty energy. Low flow velocities (v = 0,6 m / sec) are sufficient for crystal transport, whereas relatively high flow velocities of up to v_{tip} = 18 m / sec are used locally for dispersing the suspension.

A process design that is not based on practice (MSMPR) but on Bernnoulli should enable the following population statistic.

d	<	0 – 1 mm	less than	2 %
d	=	1 – 2 mm	about	8 %
d	>	2 mm	about	90 %