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The influence of the crystallizer geometric characteristics on the crystal granulometric properties

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In order to determine the influence of the crystallizer geometric characteristics and the cooling profile on the obtained crystals geometric properties (shape, size and crystal size distribution), batch cooling crystallization of potassium chloride from the water solution have been performed. The measurements were undertaken on the laboratory scale in three geometrically similar crystallizers (flat bottom) and one round bottom crystallizer under stirring intervals from 300 to 600 min^{-1}. A stirrer was supplied with pitched (at a 45°) 4-blade propeller. Hydrodynamic conditions in the crystallizer, size and geometric characteristics of the equipment had major influence on the properties of the crystals. Under higher stirring rate and with bigger equipment the crystals assumed more regular shape and their size distribution showed finer fractions. Actually, these conditions reduced the amount of agglomerates in the finished product. In addition, more favourable hydrodynamic conditions for heat and mass transfer were achieved, whereas the secondary nucleation (contact) was minor. Two cooling profiles were used: linear and combined profile (linear followed with natural cooling). Crystals of higher quality (less agglomerates and more uniform CSD) were obtained in the round bottom crystallizer for linear cooling rate. Better hydrodynamics conditions were achieved, so nucleation starts at lower supersaturation levels (higher temperatures). More agglomerates were formed with the combined cooling rate (longer retention time).

1. Introduction

The most important characteristics of the crystals obtained by crystallization are the crystal granulometric properties such as crystal shape, size and CSD (Abbas et al., 2007). System geometry (vessel size and shape, impeller type) and process conditions (cooling profile and mixing intensity) has major impact on the crystal quality. Crystallization is a very complex separation process that involves simultaneous momentum, heat and mass transfer, and phase change (Mersmann, 1988). During crystallization the state of the system changes from the solution to the suspension. This requires great care when selecting hydrodynamic conditions in order to achieve an appropriate solid suspension scale-value (Holland et al., 1966).

1.1 Vessel design and impeller type

It is very important to properly select the vessel geometry (aspect ratio, bottom shape and baffles) and the impeller type for the given mixing process (Holland et al., 1966).

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Vessel bottom shape can have a significant effect on the hydrodynamic conditions within the mixing vessel and hence the ability to achieve homogenous solid suspension which is desirable for crystallization. At lower mixing intensity, crystals tend to settle at the bottom of the vessel in the regions where flow pattern is stagnant (Mersmann, 1988, Sharma et al., 2003)). This happens more often in the flat-bottom vessel, so the crystallizer with the round-bottom shape is better option. An appropriate impeller must be selected according to particular mixing operation and material system. Pitched blade turbines belong to the group of high speed impellers, which accelerates the liquid in the axial directions. These types of impellers are the best choice for homogenization and solids suspension (Holland et al., 1966).

1.2 Mixing

Crystallization is accomplished either by cooling a saturated solution, or by heating a solution to drive off the solvent. Mixing intensity must be high enough to ensure good flow of the solution past the heat transfer surfaces and satisfactory handling of the crystals being formed (Mersmann, 1988). In other words, all the surface of the particles has to be available for heat and mass transfer. On the other hand, at high agitation rates breakage or attrition of crystals happens more often (Genck, 2003).

1.3 Scale-up

Crystallization kinetics can be divided into two separated processes, nucleation and crystal growth. Both processes strongly depend on heat and mass transfer rates on a molecular scale, and are responsible for the quality of the obtained crystals. Nucleation, crystal growth, attrition and breakage of crystals, and solid phase distribution are functions of mixing conditions. All mentioned factors make crystallization very difficult to scale-up and highly irreproducible in batch processing (Angst et al., 2006). The most reliable scale-up is obtained by performing experiments in vessels of several sizes for a wide range of mixing intensity (Brodkey et al., 1989). From these results, scale-up trends can be obtained and then extrapolated to the final vessel size according to equation:

$$(P/V)_2=(P/V)_1\cdot(D_2/D_1)^s=(P/V)_1\cdot R^s. \quad (1)$$

2. Experimental

Three geometrically similar, flat-bottomed and one with round bottom Rushton type crystallizers were used for batch cooling crystallization of potassium chloride from aqueous solution (Table 1.). Each crystallizer is equipped with four baffles and a pitched (at a 45°) 4-blade impeller. Two cooling profiles were used: linear and combined profile (linear followed with natural cooling). Experiments have been performed for the agitation rates from 300 to 600 rpm. Initial solution concentration was 0.36 kg/kg and the solution temperature changes from 27 to 10 °C. The power inputs for all crystallizer (in the range of mixing intensity from 100 to 700 rpm) were measured with the Power analyzer DW-6090. Crystal size distribution was determined by the sieve analysis with the standard series of screens (from 90 to 1400 μm). Crystal shape was analyzed by the light microscope *MOTIC BA200* connected to the computer (Softwer *MOTIC PLUS*).

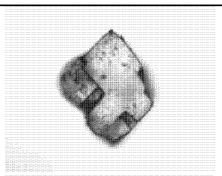
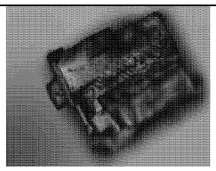
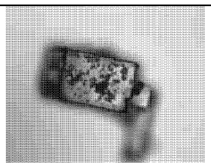
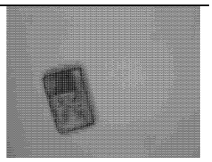
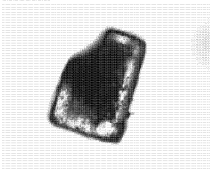
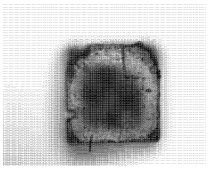
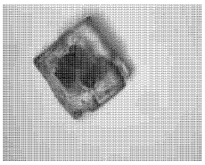
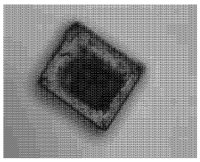
Table 1 Crystallizers geometric characteristic

Shape of the bottom	*Crystallizer diameter, D*, m	Impeller diameter, d_m, m	Scale-up factor, R
Flat	0.055	0.018	1.00
Flat	0.097	0.032	1.76
Flat	0.150	0.050	2.73
Round	0.150	0.050	2.73

3. Results and discussion

In order to compare the granulometric characteristics of the crystals obtained in the flat and round bottom crystallizer the shape of the obtained crystals and the crystal size distributions were determined for all experimental conditions. During all experiments concentration of the solution was changed within the metastable zone width, so the primary nucleation was suppressed. Mixing intensity, size and geometry of the equipment had major influence on the properties of the crystals. Under higher mixing intensity, with bigger equipment and round-bottomed crystallizer, the crystals assumed more regular shape (Table 2) and their size distribution showed finer fractions.

Table 2 The influence of the mixing intensity and crystallizer size and bottom shape on the crystal shape

Impeller speed, rpm	Crystallizer diameter, *D*, m			
	0,055	0,097	0,150	0,150
	Flat bottom	Flat bottom	Flat bottom	Round bottom
300				
600				

The influence of the mixing intensity on the CSD is illustrated in Figure 1. The mean crystal size decreases with an increase in the agitation rate, because at higher mixing rates the amount of agglomerates is reduced. In addition, more favourable hydrodynamic conditions for heat and mass transfer were achieved, whereas the secondary nucleation (contact) was minor. In smaller vessels with low slurry densities, most secondary nuclei are generated by crystal contact with the impeller and walls. In order to minimize the secondary nucleation crystal-impeller contacts agitation rate must be reduced. At lower mixing intensities (300-400 rpm) more agglomerates (presence of stagnant flow patterns) and irregular shape crystals (breakage and attrition) were

formed. Bigger vessels have longer crystal flow-paths in both the axial and radial directions than smaller equipment.

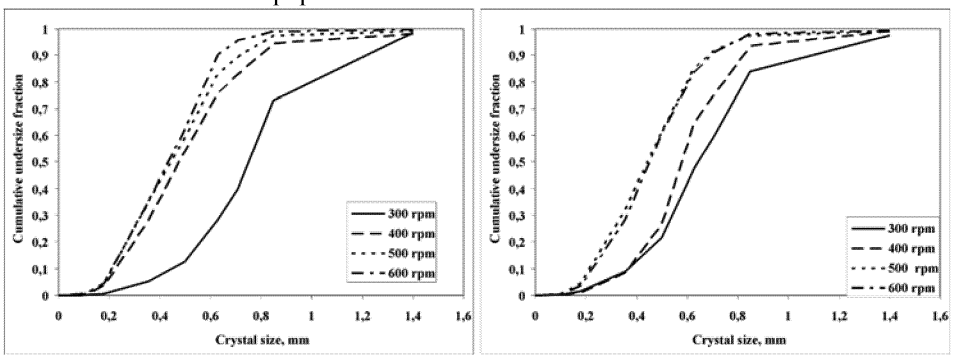


Figure 1. The influence of the mixing intensity on the CSD: a) flat bottom; D=0.150 m, b) round bottom, D=0.150 m

As the vessel size increases, there are relatively more crystal-crystal collisions. Those collisions are of lower intensity than crystal-impeller collision so the obtained crystals were of more regular shape (cube) (Table 2.).

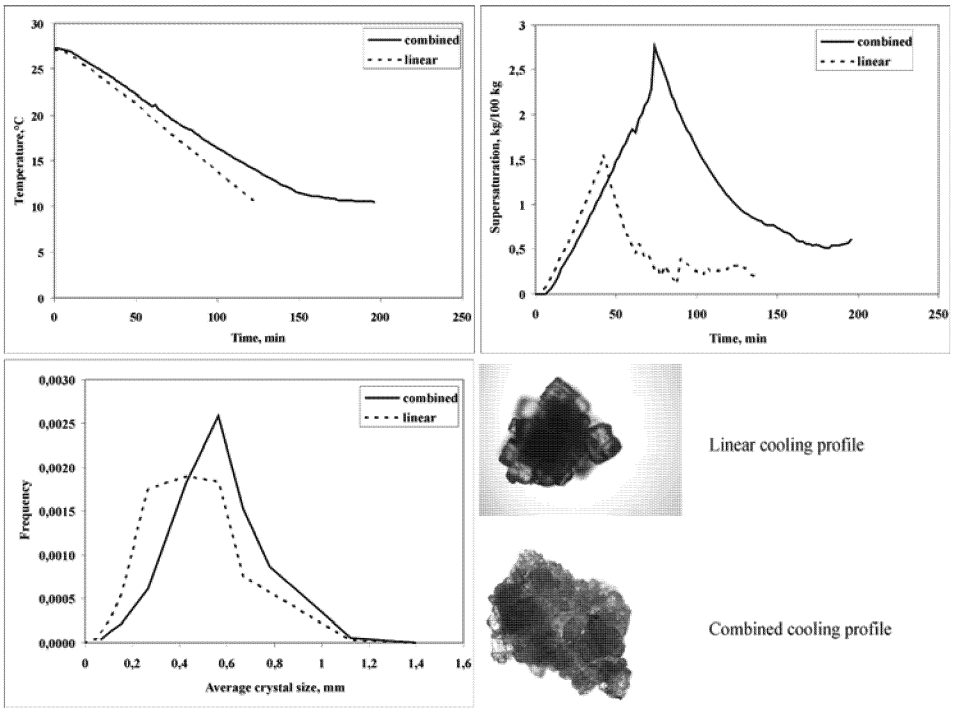


Figure 2. The influence of the cooling profile on the granulometric properties of crystals:a) cooling profile; b) supersaturation; c) CSD; d)agglomerates

The influence of the cooling profile is shown on Figure 2. Linear cooling profile was achieved with internally controlled cooling (the temperature of solution was controlled), and combined cooling profile with externally controlled cooling (the temperature of the cooling water was controlled). At the early stages of the crystallization, the nucleation is dominating mechanism, since the crystallization is unseeded. For combined cooling rate higher supersaturation level was achieved. This results with high nucleation rate, birth of large numbers of nuclei and production of smaller crystals. Small particles in liquid suspension have a tendency to cluster together. Given the very large number of particles, there is a high probability of their mutual collisions. Since the particles were very small, interparticle collision resulted in permanent attachment. Consequently larger quantities of agglomerates were formed, which consists of multiple structural units. Due to large amounts of agglomerate crystal size distribution is moved towards the coarser fractions. Linear cooling rate (lower supersaturation level, lower nucleation rate, fewer nuclei formed) results with better granulometric properties.

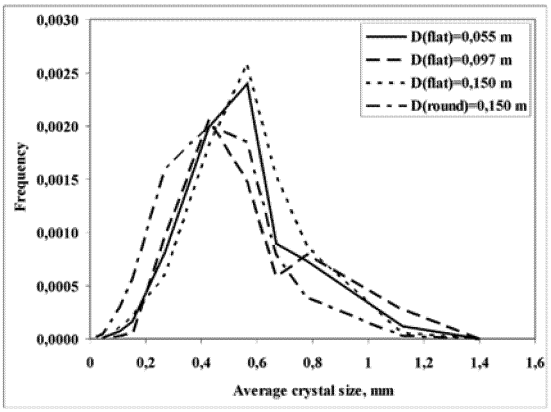


Figure 3. The influence of the crystallizer geometric properties (size and bottom geometry) on the CSD

The comparison between the obtained crystal size distributions in all investigated laboratory crystallizers showed that the mixing rate of 500 rpm yielded satisfactory results (Figure 3). They were further used to define the scale-up criterion for the batch crystallizer. Based on the scale-up methodology, when the measurements can be undertaken in three or more pieces of equipment (Brodkey, 1989), the scale-up criterion, for the batch crystallizer for cooling crystallization of potassium chloride from the aqueous solution, is defined (s=-3 in equation 1.). The methodology proposed for the studied crystallizer gives a relatively low mixing intensity (237 min^{-1}), which corresponds to the solution homogeneity 1 at minimal settling velocity (Table 3.). Given that crystallization required the suspension homogeneity between 6 and 9 (Chemineer ChemScale) (Gates, 1976), implying that the suspension homogeneity was 95-98% of the liquid height, mixing intensity for these conditions were determined as well (Gates et al., 1976; Hick et al., 1976). The obtained values were within the range of the used mixing intensity.

Table 3 Scaled-up crystallizer conditions (D=0.777 m, d_m=0.259 m, R=14.12)

Shaft speed, n, rpm	Solid suspension scale-value	Effective pumping capacity, V, $m^3\ s^{-1}$	Terminal settling velocity, v_d, $m\ s^{-1}$
237	1	0.053	0.111
414	6	0.092	0.195
578	9	0.129	0.272

4. Conclusions

Granulometric properties of crystals obtained by cooling crystallization are strongly influenced by cooling rate, mixing intensity and crystallizer geometry. Crystals of more regular shape were produced at higher mixing rates and linear cooling rate, in bigger vessel and in the crystallizer with round bottom. Better hydrodynamics conditions were achieved and consequently narrower crystal size distributions, shifted towards the finer fractions. For the same reason smaller amounts of the agglomerates were formed. Based on the scale-up procedures for turbulent flow with three or more test volumes, the scale-up rule for batch crystallization of potassium chloride is determined.

5. Symbols

P – power, W
s - scale-up exponent (equation 1)
V – volume, m^3

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