VORTEX FLOWS AND SALT TRANSFER IN WATER-SALT CRYSTALLIZERS

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An establishment of conditions for high-speed single crystal growth with an appropriate quality is a priority for the industrial production of crystalline materials. The potassium dihydrogen phosphate (KDP) crystals are the important optical materials, which are grown from a water-salt solutions. An increase of crystal growth rate and quality of such single crystals is of great practical importance.

The solution flow and salt transfer are numerically modeled within a framework of continuous medium, which is considered as a water solution of a special salt, potassium dihydrogen phosphate \([1]\). This salt dissolves in water to a saturation level at a high temperature. Then, such supersaturated solution is used for crystal growth at lower temperatures in static- and continuous-flow type crystallizers.

In static-type crystallizers, the salt-saturated solution is cooled with creating conditions for the precipitation (crystallization) of the salt on the seed crystal. In continues-flow crystallizers the solution is continuously pumped at a given temperature and at an appropriate level of supersaturation. One of the variants of an axisymmetric continuous-flow crystallizer is shown in Fig. 1a. This crystallizer is characterized by axial inflow and outflow of solution in the directions indicated by arrows.

The working temperature for KDP solution in such crystallizer is supported at \(T = 32^\circ C\), and the solution saturation by a salt is made at a higher temperature \((69^\circ C)\) to a concentration: \(C_0 = 1.59503 \times 10^{21}\) molecules per \(1 \text{ cm}^3\) solution. With taking into an account that at the working temperature the equilibrium salt concentration is \(C_e = 9.98578 \times 10^{20}\) molecules per \(1 \text{ cm}^3\) of solution, it is possible to estimate the supersaturation value of the solution with salt by the following formula:

\[
\sigma = \ln \left( \frac{C_0}{C_e} \right),
\] (1)
According to a theory of mass transfer, a salt precipitation may be occurred as a volumetric process on the single micro particles (centers) or as surface process on solid facets of growing single crystal. The presence of crystalline centers and facets in saturated salt solution causes the volumetric crystalline growth with according to thermodynamic laws, which may be considered in conjugation with the above-mentioned model of a fluid continuous medium.

On the crystal facets (the crystallization front) the "motionless" condition for the solution flow velocity and the "mass flux" condition for the salt flux on crystalline facets at the rate $R$ are set. The rate $R$ is calculated from the thermodynamic relation, which takes into account the saturation level of salt solution $\sigma$ at a given temperature $T$ and also the parameters corresponding to a growth of the crystalline facet: $\beta$ – kinetic coefficient of a step, $w$ – volume of a particle in a crystal, $h$ – height of an elementary step, $\alpha$ – specific surface energy of a step; $k$ is the Boltzmann constant. This relation is written as the
following formula:
\[ R = \beta \sigma^{\frac{5}{6}} \exp \left( -\frac{\pi w \alpha^2 h}{2k^2 T^2 \sigma} \right), \] (2)

The mathematical model is considered in a conjugate formulation with taking into account of salt transfer in the "solution-crystal" system. Table gives the parameters for calculating the crystallization rate of a facet \( R \). As a result of the conjugate calculation, the local features of hydrodynamics and salt transfer in a solution near the surface of a growing crystal are determining. They may affect on the local (for a particular place and direction) rate of facet growth and on the defect formation. These data help to justify the design of the crystallizers for the "right" hydrodynamics in the solution. As a result of the conjugate calculation, the local features of hydrodynamics and salt transfer in a solution near the surface of a growing crystal are determining. They may affect on the local (for a particular place and direction) rate of facet growth and on the defect formation. These data serve as a confirmation of the requirements on crystallizer work for the providing the "proper" hydrodynamics in the solution.

Table 1. Parameters for calculating the rate of the facet crystallization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>( w ) – volume of a molecule, cm(^3)</td>
<td>9.68×10(^{-23})</td>
</tr>
<tr>
<td>( k ) – Boltzmann constant, erg/K</td>
<td>1.38×10(^{-16})</td>
</tr>
<tr>
<td>( \beta ) – kinetic coefficient, cm/s (32(^{\circ})C)</td>
<td>0.00955</td>
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<tr>
<td>( \alpha ) – specific energy of the step for the face (100), erg/cm(^2)</td>
<td>19.5</td>
</tr>
<tr>
<td>( h ) – step height (100), cm</td>
<td>7×10(^{-8})</td>
</tr>
<tr>
<td>( D ) – salt diffusion coefficient, cm(^2)/s (32(^{\circ})C)</td>
<td>7.5×10(^{-6})</td>
</tr>
<tr>
<td>( \eta = \nu \times \rho ) – dynamic viscosity of solution, P (32 (^{\circ})C)</td>
<td>1.5×10(^{-2})</td>
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We consider the features of the flow of a solution in various designs of crystallizers. In contrast to the complicated three-dimensional flows [2] for innovative designs in this work attention has been paid to the simpler – axisymmetric flow crystallizers, the effect of which is analyzed for various vortex structures arising in a crystallizer with a given crystal shape. The dependence of the crystallization rate \( R \) was determined by the formula (2), taking into account the concrete vortex flow around a crystal.

The scheme of the axial top inlet flow of the solution and its bottom outlet flow through the lower hole is shown in Fig. 1a. In this case, a lateral vortex
flow around the conical part of the crystal forms in the crystallizer and also a smaller vortex at the junction of the conical and cylindrical parts of it (Fig. 1b). The cause of this small vortex, as well as the vortex under the crystal, is the presence of ledges in its geometry. We note that these vortices create stagnant flow zones in which the conditions for convective salt transfer in the solution to the crystal surface differ substantially from the conditions on the rest of its surface. In this work, the dependences of the crystallization rate $R$ on the saturation level of the salt solution $\sigma$, the rate of flow of solution into the crystallizer and the rotation speed of the crystal were obtained.

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References
